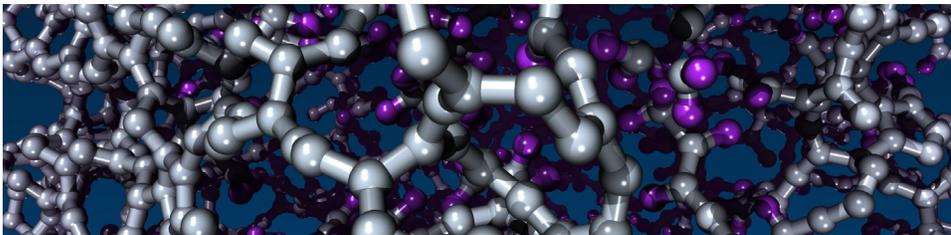
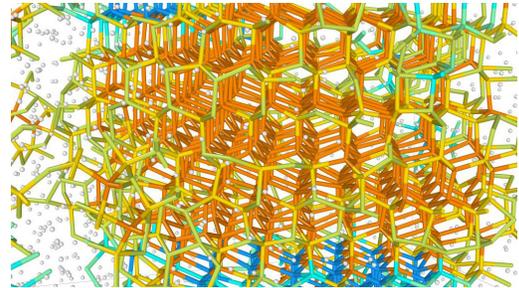


# LDRD ANNUAL REPORT 2016

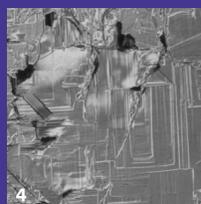
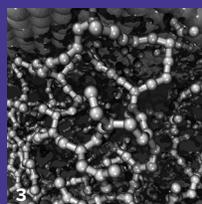
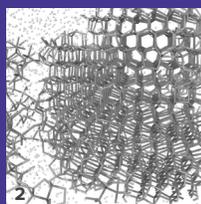


## Laboratory Directed Research and Development Program Activities

**Every day, scientists and engineers at Argonne National Laboratory make important discoveries that translate into a real difference in the world, working toward the Lab's mission to develop energy solutions, preserve the environment, protect the nation, and help the economy thrive.**

#### ON THE COVER

- 1 Single crystals of  $[K(\text{tmeda})_2]\text{perylene}$  (TMEDA = tetramethylethylenediamine). The blueish crystals are immersed in Paratone oil (appears grey) to protect the crystals from oxidation. The white dots are bubbles of nitrogen gas trapped in the oil. [See *New Paradigms for High  $T_c$  Superconductivity in Acene-Based Materials* (2014-025-R2, page 4).]
- 2 Snapshot from a microseconds-long molecular dynamics simulation showing the homogeneous nucleation of ice in supercooled water. The simulation is performed by using a new machine-learned coarse-grained water model developed by using a data-driven approach. Blue and orange colors represent cubic and hexagonal ice, respectively. [See *Bridging the Electronic and Atomistic Scales: Force Field Development for Reactive Interfaces from First Principles* (2014-161-R2, page 128).]
- 3 Snapshot from a reactive molecular dynamics simulation of a catalytic transformation of lubricating oil into a diamond-like carbon film. This process is possible only under the extreme conditions of temperature and pressure afforded by friction at a sliding interface. Carbon and hydrogen atoms are depicted as gray and purple spheres, respectively. [See *Bridging the Electronic and Atomistic Scales: Force Field Development for Reactive Interfaces from First Principles* (2014-161-R2, page 128).]
- 4 Optical micrograph of the surface of a relatively thick  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  (Bi-2212) superconducting film grown by liquid phase epitaxy on a  $\text{NdGaO}_3$ . The visible steps on the surface confirm that the same crystallographic orientation is maintained over the total film area. [See *Josephson Plasma Wave-Based Ultra-High-Frequency Electronics* (2015-078-R1, page 19).]



# DIRECTOR'S MESSAGE

Laboratory Directed Research and Development (LDRD) at Department of Energy (DOE) laboratories is a vital resource that creates new program opportunities for the Department and maintains and enhances the laboratories' ability to support the Department's several mission areas. The accompanying report on fiscal year 2016 LDRD program activities at Argonne National Laboratory exemplifies the value and productivity of LDRD and is submitted herewith for Department review. The overview of LDRD-supported research projects presented here reflects the creativity and innovative ideas of Argonne's technical staff and the world-class science and technology we pursue here at Argonne.

Reports on projects relevant to each of DOE's critical mission areas will be found in this compilation. In all cases, LDRD has proved to be a critical resource for identifying and establishing nascent research efforts that have the potential to grow into substantial science and engineering projects both at Argonne and within the DOE laboratory complex at large. Many, if not most, of our major program initiatives as well as many of our user facilities began as innovative concepts granted seed funding under LDRD, only to grow into the critical resources for the delivery of world-class research in the basic energy sciences and beyond that they are today.

We are always looking to the horizon for the next objective that will need to be met in order to secure our country's position at the forefront of science and energy technology development. LDRD allows us to rapidly address such challenges through new areas of scientific inquiry as we adapt to the evolving technological environment faced by our nation. Such agility and innovation allow Argonne to maximize its value to sponsors of our work and to the broader community.

In addition to providing initial support to those nascent research and development ideas, LDRD serves a second and equally important purpose for the Laboratory. We are committed to using LDRD to fund important research that not only holds the potential to make a difference in our scientific communities, but also attracts the best minds from across the world to join our teams of scientists and engineers. As you will see in this year's report, Argonne LDRD funds research in everything from advanced computing to sustainable transportation to the development of new materials and tools to ensure national security. Just as the exploratory research opportunities afforded by LDRD have led to such premier facilities and programs as the Advanced Photon Source or the Argonne Leadership Computing Facility or the Joint Center for Energy Storage Research, we believe that in these pages lie the beginnings of the next such major facilities and programs.

I attest that in managing the LDRD program, Argonne has adhered without exception to the requirements of DOE Order 413.2C and associated guidelines. Our program management operates with a strategy of continuous quality improvement—in addition to meeting all reporting requirements, throughout FY 2016, the LDRD Program Office continued to implement process enhancements that better serve all LDRD stakeholders, from our researchers and managers to our DOE Site Office colleagues.

I am pleased to have the opportunity to deliver this report on our LDRD FY 2016 activities, as it demonstrates Argonne's continuing innovative and energetic leadership in the fields of science and technology of greatest importance to DOE and the nation.



Paul Kearns  
Interim Laboratory Director



**Paul Kearns**  
Interim Laboratory Director  
Argonne National Laboratory

# LABORATORY OVERVIEW

Argonne National Laboratory, as a U.S. Department of Energy (DOE) national laboratory, is dedicated to advancing the energy frontier through science and technology. Argonne works to accelerate innovation in science and technology for its primary sponsor, the DOE Office of Science (SC), as well as for DOE's Office of Energy Efficiency and Renewable Energy (EERE), for its National Nuclear Security Administration (NNSA), and for a variety of other federal agencies.

As a national laboratory, Argonne concentrates on scientific and technological challenges that can be addressed only through a sustained, interdisciplinary focus at a national scale. Argonne's eleven major initiatives, as enumerated in its laboratory plan, are *Advanced Environmental Sensing, Alternative Computing Architectures, Energy Storage Futures, Exascale Codes and Data, Hard X-Ray Sciences, Molecules and Materials to Manufacturing, Optimized Mobility, Protein Function Discovery, Resilient Infrastructure, Safe and Secure Nuclear Energy, and Universe as Our Lab (ULab)*.

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# PROGRAM OVERVIEW

# PROGRAM OVERVIEW

Argonne's Laboratory Directed Research and Development (LDRD) program encourages the development of novel technical concepts, enhances the Laboratory's research and development (R&D) capabilities, and enables pursuit of strategic laboratory goals.

Argonne's LDRD projects are proposal based and peer reviewed, supporting ideas that require advanced exploration so they can be sufficiently developed to pursue support through normal programmatic channels. Among the aims of the projects supported by the LDRD program are the establishment of engineering proofs of principle, assessment of design feasibility for prospective facilities, development of instrumentation or computational methods or systems, and discoveries in fundamental science and exploratory development.

The projects supported by the LDRD program are distributed across the major mission areas at Argonne, as indicated in the Laboratory's LDRD Plan for fiscal year (FY) 2016. All LDRD projects have demonstrable ties to one or more of the science, energy, environment, and national security missions of the U.S. Department of Energy (DOE) and its National Nuclear Security Administration (NNSA), and many are also relevant to the missions of other federal agencies that sponsor work at Argonne. A natural consequence of the more "applied" type projects is their concurrent relevance to industry.

In addition to their relevance to strategic and programmatic activities, LDRD projects naturally fall under science and technology areas where Argonne's technical staff are trained and excel in supporting existing programs. The reports in this document illustrate the expertise that is often drawn from multiple technical areas to pursue the goals of each project. This multidisciplinary approach is one of Argonne's hallmarks, and reflects the synergistic manner in which both LDRD and programmatic work are pursued.

The FY 2016 DOE-approved funding cap for LDRD was \$38.0 million, or about 5.8% of Argonne's estimated FY 2016 operating plus capital budgets. Actual expenditure amounted to \$33.8 million, which includes an overhead levy of approximately 30%.

Individual brief project reports for FY 2016 make up the bulk of this document.

# LDRD MANAGEMENT PROCESS

Argonne's R&D activities are organized under four Associate Laboratory Directors (ALDs), who oversee the research conducted in some 16 programmatic divisions. Responsibility for management and oversight of LDRD during FY 2016 lay with the Deputy Laboratory Director for Operations (COO) and the Director for Strategy and Innovation (SIO). In FY 2017, the Deputy Laboratory Director for Science assumed the LDRD oversight role previously held by the COO. This senior management team makes final recommendations concerning the LDRD program investment and management to the Laboratory Director.

As described below, Argonne's LDRD program has consisted of the following components: LDRD Innovate, LDRD Named Fellows, LDRD Swift, LDRD Prime, and the Director's Grand Challenge. All LDRD projects under all components align with DOE mission areas and core competencies of the Laboratory. The LDRD Prime, Named Fellows, and Director's Grand Challenge projects are also explicitly aligned with initiatives within Argonne's Strategic Plan, whereas LDRD Innovate and Swift projects may pursue more wide-ranging exploratory research. Every year, the Laboratory Director determines the appropriate balance of funding among the various components. In addition, a Director-Designated Exceptional Opportunities fund (a portion of the total allowed expenditure held in reserve to handle mid-year opportunities, strategic hires for LDRD projects, and LDRD collaborative arrangements) may support projects within any of the LDRD components.

The Director's Grand Challenge component was comprised of a few "wrap-up" months of activity in FY 2016 and has not continued into FY 2017. All final decisions concerning Argonne's LDRD program reside with the Laboratory Director. Certain responsibilities regarding funding, oversight, proposal evaluation, and project direction are delegated.

The LDRD Program Office reviews all proposals to ensure their adherence to DOE Order 413.2C and associated guidelines, as well as to Laboratory administrative procedures.

The LDRD program is funded lab-wide through the Laboratory's indirect budget, which derives from a levy against all program operating and equipment budgets. Although two- or three-year durations are proposed for many projects, funding levels and project selection are determined annually and based on technical progress and the Laboratory's strategic goals and resources.

LDRD funds may be used in collaborative arrangements with third parties to enhance the application or scope of the research, with attendant beneficial interactions. To effect these arrangements, the Laboratory has in place DOE-approved procedures and instruments, such as Cooperative Research and Development Agreements (CRADAs), subcontracts, and site access Guest Agreements. These instruments and procedures enable the application of LDRD funds while ensuring that appropriate terms and conditions are applied thereto, including those related to intellectual property protection.

Line managers in Argonne's programmatic divisions are responsible for monitoring the progress and performance of LDRD research during execution. LDRD Prime Focus Area contacts, line managers, and subject matter experts confirm that mid-year progress reviews have occurred and indicate whether any remedial action or advice is needed. The responsibility for the actual conduct of all LDRD projects, including associated environmental safety and health requirements, resides with the ALDs and their line managers.

During FY 2016, all program management requirements were satisfied. Reports required by DOE, including the Annual Report for FY 2015, the LDRD Program Plan for FY 2017, and project data uploaded to the DOE CFO (Office of the Chief Financial Officer) database, were submitted completely and in a timely fashion.

Concurrence request forms (also referred to as "data sheets" in relevant guidance documents) were submitted electronically for each FY 2016 LDRD project to DOE's Argonne Site Office (ASO) to obtain the DOE Site Manager's concurrence before work on the project proceeded.

# FISCAL YEAR 2016 LDRD PROGRAM COMPONENTS

## LDRD INNOVATE

The LDRD Innovate component invests in a full spectrum of investigator-initiated proposals across the Laboratory in DOE-mission-related science and engineering areas. This component provides an avenue for R&D staff to propose highly innovative projects directly to the Laboratory Director. Proposals are subjected to peer review by the LDRD Innovate Advisory Board to assess their scientific and technical quality. The board is composed of non-managerial scientists and engineers selected by the Laboratory Director. The Committee is currently comprised of eight members who have substantial expertise in their technical fields, are familiar with the peer review process, and represent a broad cross section of the Laboratory.

The Advisory Board conducts a two-stage review process for all LDRD Innovate project proposals. An initial peer review of one-page pre-proposals results in a smaller number of proposals advancing for further review. The second stage consists of a more extensive peer review conducted by the Advisory Board. A rank-ordered list of proposals are then given to the Laboratory Director and brief critiques of proposals are sent to the proposing investigators.

The Advisory Board also solicits proposals for continuation of a project into a second or third year. Proposals for continuation are assessed according to progress made against previously proposed milestones.

The LDRD Innovate review process for new proposal submissions is supported by the Laboratory's research community, which serves as a source of volunteer subject matter experts to help the Advisory Board review proposals. Approximately 101 researchers volunteered, and their assistance made it possible for the Advisory Board to recommend the highest-quality proposals for funding in FY 2016.

## LDRD SWIFT

The LDRD Swift component provides an avenue for R&D staff to conduct short-term research with a targeted funding opportunity in mind, as well as a means for researchers to explore ideas before developing a full proposal. Projects funded through this component area have a maximum one-year duration. As with the LDRD Innovate component, the LDRD Swift component invests in a full spectrum of proposals across all mission-related science and engineering areas.

Proposals are evaluated based on the targeted funding opportunity, the potential return on investment, and the urgency of the funding request. The preliminary review is conducted by the LDRD Program Office. Those proposals meeting these minimum criteria are then subjected to peer review to assess their scientific and technical merit. An ordered list of proposals is then provided to the Laboratory Director for consideration for funding.

## LDRD NAMED FELLOWS

The LDRD Named Fellows component aims to support the scientific or engineering research of exceptional early career scientists and engineers. Working with an Argonne sponsor (a senior member of research staff), LDRD Named Fellows carry out work that is either at the forefront of new research areas or is synergistic with current research efforts.

There is a Named Fellows Review Committee in place to assess the scientific and technical merit of each proposal. The Committee is comprised of one member from each technical division. The outcome of this review process is a list of finalists provided to the Laboratory Director for final approval.

## LDRD PRIME

The largest component of Argonne's program is LDRD Prime, which emphasizes R&D explicitly aligned with Laboratory major initiatives as defined by senior management (the Laboratory Director, Deputy Laboratory Director for Science, and ALDs) in support of Argonne's strategic plan. Strategic goals are reevaluated periodically and revised as necessary.

The choice of Focus Areas under the LDRD Prime component for FY 2016 reflects the major initiatives; the state of development of relevant technical fields; the potential value of advancing those fields to DOE/NNSA and the nation; and the compatibility of the fields with existing facilities, capabilities, and staff expertise at Argonne.

For FY 2016, the individual ALD organizations issued a preliminary call to Laboratory staff for LDRD Prime concept papers in order to better define Focus Areas. Researchers seeking funding under this component of the program were encouraged to limit the duration of their proposed projects to 24 months, although exceptions could be made for a third year of funding if necessary.

Informed by reviews of the concept papers, a subsequent invitation for full proposal submission produced a well-defined portfolio of strategic research proposals. Each LDRD Prime proposal undergoes an extensive review process by committees impaneled for that purpose. Prioritized results are then assembled by the LDRD Program Office and provided to the Laboratory Director who makes final funding decisions.

The selected FY 2016 Focus Areas capture the Laboratory's capabilities and fundamental knowledge in areas of strategic importance and address the future mission needs of the Laboratory and DOE/NNSA. Our work in high-performance computing, x-ray science, and R&D on detectors and sensors exemplifies crosscutting capabilities that contribute to a broad spectrum of Focus Areas. In addition, integration of basic and applied approaches is often an important feature of the LDRD projects selected for support under this program component.

These Focus Areas are described below.

#### **APPLIED ENERGY AND SUSTAINABLE TRANSPORTATION**

Key topics include sustainable transportation, water-energy nexus, advanced manufacturing, and renewable energy.

#### **BIOLOGICAL AND ENVIRONMENTAL SCIENCE CAPABILITY DEVELOPMENT**

Key topics include expanding the technological options for acceleration the determination of protein/gene functions for a given sequence and the assignment of sequence to known functions with unknown sequence; addressing strategies and approaches to leverage the Southern Great Plains ARM site into a next-generation climate research facility; prototyping the Next Generation Ecosystem Experiment (NGEE) framework for an NGEE urban site; focusing on new methods of analysis and characterization of antimicrobial resistance mechanisms and target strategies for defeating these mechanisms; and focusing on development of novel uses of the Advanced Photo Source to characterize proteins.

#### **HARD X-RAY SCIENCES**

Key topics include research and development in support of the Advanced Photon Source Upgrade Project, science enablers, and future hard X-ray sources.

#### **MATERIALS AND MOLECULES TO MANUFACTURING**

Key areas include materials and molecules design and discovery (M2D2), computational chemistry and materials (CCM), and the integrated imaging initiative (I<sup>3</sup>).

#### **NATIONAL AND GLOBAL SECURITY**

Key topics include the science of secure and resilient infrastructure and infrastructure modeling and simulation.

#### **NEXT GENERATION COMPUTING**

Key topics include planning and early development of new applications codes targeted at exascale systems; new types of environmental sensors, sensor systems, and sensor related infrastructure; novel capabilities for integrating high-performance computing capabilities into real-time and near real-time data stream analysis; mathematical methods for analysis, modeling, and simulation of natural and man-made systems; and exploration of open questions related to the models of computing that exploit computing substrates and computing devices expected to emerge in the mid-2020s.

#### **NUCLEAR ENERGY AND SECURITY**

Key topics include increased understanding of nuclear energy phenomena and behaviors; development of advanced technologies and concepts; and nuclear energy system modeling and analysis.

#### **UNIVERSE AS A LAB (ULAB)**

Key topics include cosmic microwave background (CMB); and cosmology/particle theory, data analysis, and computation.

# RESEARCH REPORTS BY COMPONENT

## *LDRD Innovate*

2014-018-R2	Dynamics of Spin Ice.....	2
2014-019-R2	Exploring the Universe with Full-Sky Simulations of the Cosmic Microwave Background .....	3
2014-025-R2	New Paradigms for High $T_c$ Superconductivity in Acene-Based Materials.....	4
2014-046-R2	Plastic Artificial Leaves for Water Splitting.....	6
2014-051-R2	Carbon Nano-Network as Next Generation Support for Catalysis and Electrocatalysis.....	8
2014-054-R2	Thin Film Skyrmion Spin Textures.....	9
2014-077-R2	Directly Probing Nanoscale Dynamics in Shear-Thickening Complex Fluids.....	10
2014-081-R2	Pb-Assisted Corrosion/Cracking Mechanisms at the Interface between Pb-Containing Solution and Nickel Oxide Surface.....	12
2014-084-R2	Probing the Chemistry of Atmospheric Dust Particles Using X-ray Spectromicroscopy: Implications for Climate Science .....	13
2014-095-R2	Tuning the Transport Properties of Coupled Majorana.....	15
2014-108-R2	Single Cell Structural Genomics of Uncultured Sediment Archaea: On the Trail for Novel Proteases.....	17
2015-015-R1	Detection of Dark Matter Directionality by Means of Columnar Recombination .....	18
2015-078-R1	Josephson Plasma Wave-Based Ultra-High-Frequency Electronics.....	19
2015-091-R1	Next Generation Natural Gas Adsorbent through Rational Design and Modeling.....	21
2015-096-R1	Understanding Atomic-Scale Uranium Interactions under Severe Accident Conditions.....	23
2015-121-R1	Development of Advanced $VO_2$ Nano-Composite Thermochromic Materials for High-Performance Smart Windows.....	24
2016-001-N0	Structure and Dynamics of Chiral Molecules and Radicals.....	27
2016-010-N0	A Theory of Out-of-Equilibrium Phase Transitions .....	28
2016-020-N0	Nano-Mechanical Delivery of Biomolecules into Live Bacterial Cells .....	29
2016-023-N0	Real-Time Monitoring of Material Structure Evolution in Additive Manufacturing Processes.....	31
2016-027-N0	A Novel Gas-Filled Microchannel Plate (GF-MCP) X-ray Polarimetry Imager.....	32
2016-048-N0	A Missing Protein in the Bacterial Methylmercury Pathway.....	33
2016-054-N0	Perovskite Halide-Based Intermediate-Band Solar Cells .....	35
2016-063-N0	Efficient Droplet-Based Environmental Mechanical Energy Harvesting through Reverse Electrowetting.....	36
2016-069-N0	GO-IN-EM – Genetic algorithm Optimization of INterface structure from Electron Microscopy ...	37

\* Some projects typically associated with an LDRD Prime Focus Area, as well as other innovative projects, were reviewed and selected by the Laboratory Director outside the normal annual LDRD call for proposals and review cycle.

2016-082-N0	Top Down Fabrication of Large Area Monolayers of 2D Materials .....	38
2016-092-N0	Spin Vortex-Based Non-Volatile Superconducting Memory .....	41
2016-094-N0	Ordered Core-Shell Nanostructure for Transverse Thermoelectric Applications.....	42
2016-098-N0	Images from Inner Space: Exposing Quantum Mechanics within Nucleons and Nuclei.....	43
<i>LDRD Swift</i>		
2016-240-N0	Recovery of Critical Materials from Post-Consumer Electronics.....	46
<i>LDRD Named Fellows</i>		
2016-180-N0	<i>In situ</i> Polarized Spectroscopy of Optically Transparent TRGO-Polymer Solar Cells .....	49
2016-181-N0	The Search for Weyl Semimetals .....	50
2016-182-N0	Core-Shell Nanowire Magnetic/Ferroelectric Multiferroic Heterostructure for Voltage-Tunable RF Devices .....	51
2016-183-N0	Understanding and Controlling Charge, Spin, Pseudospins, and Lattice Degrees of Freedom in Layered Transition Metal Dichalcogenides.....	52
2016-184-N0	Investigation of Solid-Liquid Interfaces in Energy Materials: Interfacing Multi-Scale Modeling with Experimental Characterization .....	54
2016-185-N0	Charge Transport in Nanostructured Materials from <i>ab initio</i> Simulations .....	56
2016-186-N0	Ultrafast Spectroscopy of Nanometer-Scale Heterojunctions Fabricated by Self-Assembly.....	57
2016-187-N0	Coherent X-ray Investigations of Defect Dynamics in Next-Generation Nanostructured Materials.....	58
2016-188-N0	Understanding the Structure of Matter .....	59
<i>LDRD Prime – Applied Energy and Sustainable Transportation</i>		
2014-120-R2	Grid-Level Energy Storage for Integration of Renewable Energy .....	63
2014-169-R2	Magneto-Dielectric Composite Substrates Comprised of High Aspect-Ratio Magnetic Nanofibers for Smart Antennas Operating at Microwave Frequency.....	64
2015-151-R1	Chemical Vapor Processing for Additive Manufacturing .....	65
2015-157-R1	Sustainable Transportation: Novel Bio-Derived Fuel Additives for Improved Vehicle Efficiency .....	66
2015-159-R1	Large-Scale Modeling and Simulation for an Adaptive and Resilient Power Grid.....	68
2015-176-R1	Connected and Automated Vehicles .....	70
2016-126-N0	Advanced Control Algorithms for Improving Energy Consumption of Connected and Automated Vehicles .....	72
2016-152-N0	Integrated Water-Energy Systems Assessment Framework (IWESAF) for Water-Energy Sustainability and Resilience.....	73
2016-175-N0	VERIFI 2.0: Next Generation Engine/Fuel Simulation Codes .....	75

\* Some projects typically associated with an LDRD Prime Focus Area, as well as other innovative projects, were reviewed and selected by the Laboratory Director outside the normal annual LDRD call for proposals and review cycle.

*LDRD Prime – Biological and Environmental Science Capability Development*

2014-132-R2	Identifying Patterns and Associations among Hyperspectral Data and Meteorological and Biological Measurements for Investigating Near-Surface Atmosphere-Biosphere Interactions... 78	78
2014-141-R2	Minimizing Environmental Microbial Community Complexity at the Bench: Isolating and Characterizing Minimal Stable Communities (MSCs) Over Time .....80	80
2014-145-R2	Developing Remote Automated Sensors to Direct Sampling of Aerobic-Anaerobic Switching in Floodplain Ecosystems to Characterize the Response of Microbial Carbon Metabolism at High Temporal Resolution..... 81	81
2014-157-R2	Biology@Speed: D-Factory, A Novel Experimental Framework..... 82	82
2014-183-R2	Impact of Radiation and Surface Turbulent Fluxes on the Transition from Stratocumulus to Cumulus Cloud Regimes ..... 84	84
2015-170-R1*	Biomimetic Approaches for Water-Smart Landscapes..... 85	85
2015-171-R1*	Genome Engineering of Environmental <i>P. fluorescens</i> to Investigate Bacterial Interactions with Plant and Other Microbes ..... 86	86
2015-179-R1*	Illuminating Linkages between Microbial Diversity and Biogeochemical Cycling in a Redox Dynamic Environment..... 88	88
2015-180-R1*	Functional Analysis of Proteins from a Key Signaling Network Involved in Plant-Growth-Promoting Bacteria ..... 89	89
2016-139-N0	Models to Observations, a Digital Atmospheric Library (MODAL)..... 91	91
2016-164-N0	Resolving Land-Atmosphere Interactions at Kilometer Scales: Model and Measurement Needs for Next-Generation Earth System Models ..... 93	93
2016-165-N0	Establishing a Proof-of-Concept for Protein Function Discovery Initiative..... 93	93

*LDRD Prime – Hard X-ray Sciences*

2014-127-R2	Development of a Novel Analyzer System for Resonant Inelastic X-ray Scattering with Better Than 10-meV Resolution ..... 97	97
2014-134-R2	Three-Dimensional Coherent Diffraction Imaging Using Polychromatic Hard X-rays..... 98	98
2014-137-R2	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub> High-Temperature Superconducting Prototype Undulator..... 100	100
2014-175-R2	Automation of <i>in situ</i> Crystallization Plate Screening and Data Collection at Room Temperature ..... 101	101
2015-141-R1	Using Hard X-rays to Accelerate the Synthesis of Materials ..... 103	103
2015-147-R1	Development of a Compact 352-MHz/12-kW CW Solid State RF Power Amplifier System for Accelerators..... 104	104
2015-150-R1	Unraveling Mesoscale Spatial-Temporal Correlations in Materials Using Coherent X-ray Probes..... 105	105
2015-153-R1	The VelociProbe: Ultra-High-Resolution Ptychographic Hard X-ray Nanoprobe .....107	107
2015-161-R1	Ion Beam Figuring with <i>in situ</i> Metrology: Diffraction Limited X-ray Optics and Dynamic Aperture for Three-Dimensional Control of Thin-Film Deposition and Ion-Beam Erosion ..... 108	108

\* Some projects topically associated with an LDRD Prime Focus Area, as well as other innovative projects, were reviewed and selected by the Laboratory Director outside the normal annual LDRD call for proposals and review cycle.

2015-164-R1	Next Generation Mössbauer Spectroscopy.....	110
2015-173-R1*	Isotope Geochemistry via Sn Isotope Fractionation Using Inelastic X-ray Scattering of Synchrotron Radiation.....	110
2015-182-R1*	Developing New Schemes for Nuclear Resonant Scattering Measurements at an Upgraded APS.....	112
2015-183-R1*	Implementing New Microscopy Capabilities at the APS.....	113
2015-184-R1*	Development of Novel X-ray Tools for Understanding Extreme-Pressure Magnetism and Electronic Ordering at Fourth-Generation Synchrotron Storage Rings .....	114
2016-150-N0	A Conveyor Belt of Nanoliter to Picoliter Droplets for Hard X-ray Pump-Probe Experiments.....	115
2016-191-N0*	Exploring Next Generation Coherent X-ray Science .....	117
<i>LDRD Prime – Materials and Molecules to Manufacturing</i>		
2013-184-R3	Hierarchical Modeling of Self-Assembly in Nanostructured Soft Materials at Equilibrium and Far from Equilibrium .....	119
2013-216-R3*	Directed Assembly and Three-Dimensional Characterization of Block Copolymers in Semi-Thick Films .....	120
2013-219-R3*	Transition Edge Sensors for Fundamental Physics.....	122
2014-128-R2	Length-Scale-Bridging Computational Scheme for Structure and Transport.....	123
2014-129-R2	The Design and Synthesis of Novel Oxides: Coupling Materials Informatics with a Next Generation Deposition System Employing <i>in situ</i> X-ray Scattering and Photoemission Spectroscopy .....	125
2014-139-R2	Fast Electronic Structure Methods for Rapid Reaction Screening for Inorganic Materials Synthesis and Particle Formation.....	126
2014-151-R2	Developing Predictive Models of Wide Bandgap Semiconductor Synthesis and Processing.....	127
2014-161-R2	Bridging the Electronic and Atomistic Scales: Force Field Development for Reactive Interfaces from First Principles .....	128
2014-191-R2*	Defect-Localized Spins in Semiconductors for Quantum Optoelectronics .....	130
2014-192-R2*	Computational Spectroscopy of Heterogeneous Interfaces .....	132
2015-144-R1	Framework for Integrating Multi-Modal Imaging of Materials for Energy Storage.....	134
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\* Some projects typically associated with an LDRD Prime Focus Area, as well as other innovative projects, were reviewed and selected by the Laboratory Director outside the normal annual LDRD call for proposals and review cycle.



# LDRD INNOVATE

# Dynamics of Spin Ice

2014-018-R2

Axel Hoffmann and Olle Heinonen

## PROJECT DESCRIPTION

Magnetic systems have complex dynamics and are a fundamentally intriguing research topic, but they are also important for applications such as information processing. Toward this end, the nascent research field of magnonics aims at processing information with spin waves. The behavior of spin waves can be controlled by the magnetic state of the underlying magnetic elements. In that respect, we have recently shown theoretically that so-called artificial spin-ice systems exhibit specific oscillations tied to peculiar magnetic defects.

Frustrated magnets, such as spin ice, have long been of scientific interest because of their highly degenerate ground states, which result in complex magnetic ordering and collective behavior. These frustrated magnets can be realized in crystalline materials, but analogous physics can also be observed in artificial spin ice, which consists of patterned, magnetic, nanoscale elements with dipolar interactions. Compared to crystalline systems, the artificial spin-ice systems have the advantage that magnetic microscopy can directly access the magnetization state of each individual spin (that is, single-domain magnetic particle). Artificial spin ices exhibit large versions of elusive magnetic monopoles, originally predicted by Paul Dirac, and are connected by a chain of magnetic defects called a Dirac string.

Until now, experimental investigations of these systems focused exclusively on the statistics of the defects and their quasi-static evolution after field and thermal cycling. But the new theoretical predictions open new opportunities to characterize topological defects in crystalline and artificially frustrated magnetic systems, and to use these defect strings and monopoles in information storage and computing devices based on magnetic oscillations. The goals of our project are to experimentally investigate the localized dynamics due to topological defects in spin-ice systems, and to ultimately develop new approaches for their controlled manipulation. Toward this end, Brillouin light-scattering microscopy is an ideal tool, as it allows spatial imaging of the magnetization dynamics with high frequency and spatial resolution. Using this tool, we will test theoretical predictions at the microscopic level, which will be used to explore novel ways to control and manipulate the evolution of the topological defects.

## MISSION RELEVANCE

This project is relevant to DOE's energy and science missions, and will have both fundamental and applied impacts. The prospect that certain dynamic modes propagate only along defect Dirac strings opens up exciting possibilities for guided energy and information flow in magnonic systems. This means manipulating the topological defects in spin-ice systems in a controlled way may enable new ways of processing information with magnetization dynamics. The most direct impact of this work will be in obtaining a better fundamental understanding of how topological defects affect the dynamic behavior of frustrated magnetic systems. Typically, statistical information from the whole ensemble is the only information available in crystalline frustrated systems. Artificial spin-ice systems, however, are ideal models for this assessment, as they allow us to correlate statistical information from the whole ensemble with a detailed microscopic arrangement of the individual spins comprising the frustrated system.

## RESULTS AND ACCOMPLISHMENTS

In the first year of this project, we fabricated artificial spin-ice systems integrated with co-planar waveguides that allowed investigation of their dynamics and also allowed optical access for spatially-resolved, Brillouin light-scattering microscopy. We also refined the theoretical model for these systems. In FY 2015, we obtained, for the first time, clear, high-frequency spectra of the magnetization dynamics of artificial spin ices. As a function of magnetic field, we observed distinct changes in the absorption spectra, which directly correlate with different magnetization states. In fact, comparison of the experimental observations with numerical simulations and a newly developed analytical model provided good agreement. Particularly exciting is that differences in the magnetic field dependence of the dynamic spectra directly correlated with the presence or absence of specific topological defects.

Preliminary results with spatially resolved measurements using Brillouin light-scattering spectroscopy reveal that the magnetization dynamics of specific modes can be very inhomogeneous, suggesting that spatial distribution may directly reflect the locations of topological defects. However, at this point, we do not yet have a direct correlation between magnetization structure and local dynamic properties. Parallel to the optical investigations, we also developed an approach to directly detect, electrically, the magnetization dynamics by using spin Hall effects. This provides an excellent signal-to-noise ratio, suggesting that electrical approaches may also be well suited for obtaining local information on the magnetization

dynamics. Preparing such samples is the first step toward electrically manipulating the local magnetization structure and dynamics.

In FY 2016, we analyzed in detail the magnetization dynamics of an artificial square spin-ice lattice prepared with permalloy (Ni<sub>80</sub>Fe<sub>20</sub>). These investigations were performed with magnetic fields applied in the lattice plane using broadband ferromagnetic resonance spectroscopy. The experimentally-observed dispersion shows a rich spectrum of modes corresponding to different magnetization states. Exchange and dipolar interaction between individual islands determine these magnetization states. This assumption was confirmed by a semianalytical model. In the low field regime (below 400 Oe), the mode spectrum becomes hysteretic. Using micromagnetic simulations, we showed that the observed spectra originate from the initialization of different magnetization states of individual nanomagnets. This work was published in March 2016 in *Physical Review B*.

These results indicate that ferromagnetic resonance experiments may indeed distinguish between different magnetization states. So far, the preliminary measurements are still inconclusive. Parallel to the dipolar, coupled, artificial spin-ice structures above, we also started to investigate the dynamics in patterned, magnetic, antidote lattices. These structures differ from the previous ones by having connected islands instead of isolated islands. As a result, the coupling is mediated by exchange coupling, and different magnetization structures must be accommodated via domain walls. But the basic concept of frustration provides similar complexities in the dynamics. One profound advantage to having a connected system is that it makes direct, electrical, transport measurements possible. For this, we harnessed the possibility of detecting magnetization dynamics electrically by spin pumping and inverse spin Hall effects. We fabricated rectangular permalloy (Ni<sub>80</sub>Ni<sub>20</sub>)/Pt antidote lattices with different lattice parameters. We then investigated the spin dynamics driven by the Oersted field, by measuring DC voltage spectra and comparing them to micromagnetic simulations. When these systems are driven to resonance, we detect a DC voltage across the length of the sample that changes sign upon field reversal, which agrees with a rectification mechanism based on the inverse spin Hall effect.

We also show that the voltage output scales linearly with the applied microwave drive in the range of investigated microwave powers. This result was published in February 2016 in *Applied Physics Letters*. The result is important, because it can also allow direct, local, electrical detection, which should allow us to locally detect varying

magnetization dynamics and to correlate it directly to the magnetization configuration.

## Exploring the Universe with Full-Sky Simulations of the Cosmic Microwave Background

2014-019-R2

Katrin Heitmann, Hal Finkel, and Samuel Flender

### PROJECT DESCRIPTION

Our understanding of the Cosmic Microwave Background (CMB) is witnessing a paradigm shift through measurements of arc-minute scale anisotropies by a new generation of telescopes, such as the South Pole Telescope (SPT) and the Planck Satellite. By combining these CMB observations with large-scale structure surveys, it is possible to address and connect some of the most fundamental questions in physics about the nature of dark energy, dark matter, the sum of the neutrino masses, and the number of relativistic species. To realize the potential of these measurements, next-generation studies in theory, modeling, and simulation are needed. Accurately capturing the physics of the real universe is crucial for interpreting CMB experiments to answer fundamental science questions.

This project is based on a set of state-of-the-art simulations carried out on Mira at the Argonne Leadership Computing Facility (ALCF). Extracting exciting science from the simulations and furthering Argonne's theoretical CMB effort are the major aims of this project. We will generate a set of CMB maps spanning different cosmological models and astrophysical effects.

### MISSION RELEVANCE

This project addresses key areas in the DOE High Energy Physics (HEP) Cosmic Frontier focus area and touches upon related questions in the Intensity Frontier (such as the mass of the neutrino). It seeds a new effort regarding CMB theory, simulation, and analysis at Argonne, complementing the existing, successful experimental effort. It also builds upon Argonne's key strengths in high-performance computing. Our simulation capabilities position us to do the following:

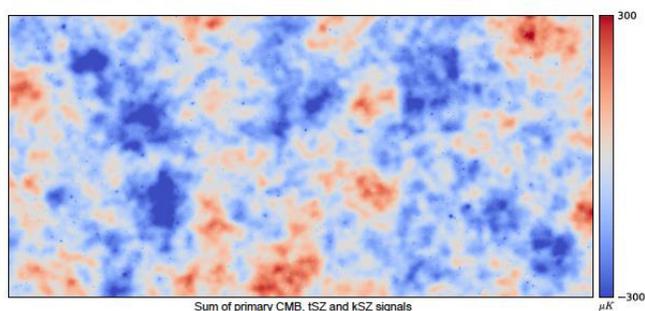
- Complete the CMB effort at Argonne by adding an analysis and theory component to take full advantage of the data that will be forthcoming.

- Provide the best simulated maps of the universe, which will be essential for extracting the science from surveys.

## RESULTS AND ACCOMPLISHMENTS

In FY 2014, we built a first set of CMB maps, including astrophysical effects, and scaled up our analysis pipeline to efficiently process our very large simulations. The first CMB map includes foreground sources using a semi-analytical approach. We identified dark matter halos and added the Sunyaev-Zel'dovich (SZ) effect by using a semi-analytic model for gas physics. We added infrared sources to the halos, using a semi-analytic approach calibrated to observations. We used the resulting synthetic maps, in different wavebands, to investigate the effects of different biases on the CMB lensing power spectrum; This work was published in the *Astrophysical Journal*.

In FY 2015, we finished work to efficiently construct light-cone outputs. First, we enhanced the Hardware/Hybrid Accelerated Cosmology Code (HACC) to produce *in situ* particle light-cones. Second, we wrote a new, parallel, stand-alone tool which efficiently extracts light-cones from output files. We integrated this light-cone capability with our SZ modeling pipeline, which was optimized to work within the HACC framework. Figure 1 shows an example of a kSZ map created from one of our light-cone halo catalogs. The pipeline was applied to a large simulation and used to investigate possible systematic effects that could degrade the SZ signal; This work was also published in the *Astrophysical Journal*.



**Figure 1.** A 4×8 square-degree cutout from a simulated map combining the primary cosmic microwave background, the kinetic and thermal Sunyaev-Zel'dovich (SZ) effect, and the noise map, including primary CMB, foregrounds, and detector noise. The map has been smoothed with a Gaussian beam of FWHM=1arcmin, which corresponds roughly to the SPT instrument beam. The dark circular spots in the map are due to the SZ effect and can be used to find clusters of galaxies. The color scale shows fluctuations with respect to the background temperature.

Finally, in FY 2016, the synthetic maps were used to aid in analyzing data from the South Pole Telescope and the Dark Energy Survey (DES), resulting in yet another publication.

This project is complete. The work performed under this project strengthened Argonne's position to take a lead role in the upcoming project CMB-S4.

## New Paradigms for High $T_c$ Superconductivity in Acene-Based Materials

2014-025-R2

Wai-Kwong Kwok, Scott M. Brombosz, Hsein-Hau Wang, and John Schlueter

### PROJECT DESCRIPTION

The recent discovery of a new class of organic superconductors, alkali-doped acenes, bolstered the search for high-temperature superconductors (HTSs). For many years, acenes themselves were explored for application in thin film transistor and organic photovoltaics, leading to a wealth of knowledge on their synthesis and electronic properties. Doped acenes, however, are only now coming under greater scrutiny for their unique properties. This juncture of a new application and an extensive base of knowledge leaves the field of superconducting doped acenes open for rapid exploration.

Until now, most efforts to produce the alkali-doped acenes relied on simple, solid-state reactions and high heat. We believe using solution-based methods provides an opportunity to precisely control the doping levels, and to more accurately characterize these environmentally-sensitive materials. In particular, growth of single crystals of these target materials will allow us to unambiguously assign not only the structure and doped state, but also the three-dimensional arrangement of the constituents.

### MISSION RELEVANCE

The DOE Basic Energy Sciences (BES) Advisory Committee highlighted the search for HTSs as critical for the energy security of the country. A superconducting electrical grid would provide efficient transport of power by reducing energy losses. Also, HTS would alleviate the need for cryogenics, such as strategically important helium, to cool the high-field magnets used in instruments like magnetic resonance imaging (MRI) scanners. The current early stage of research on alkali-doped acenes provides a foothold to accomplish groundbreaking research. While investing in a project at such an early stage has risks, the potential payoff for discovering an HTS would be substantial.

### RESULTS AND ACCOMPLISHMENTS

In FY 2014, we developed a solution-based method for producing alkali-doped acenes. This method quickly produced charged states under much milder

conditions than used in the literature reports of solid-state reactions of acenes with alkali metals at high temperatures. Using sonication allowed the reaction rate to increase substantially for less reactive acene-alkali metal combinations. From these solutions, doped acenes were isolated, or could be further processed to induce crystallization. We found that adding a supporting ligand was extremely important to producing high-quality single crystals of the acenes.

In FY 2015, we produced an array of samples by combining sodium, potassium, rubidium, or cesium with several acenes, including phenanthrene, pyrene, perylene, coronene, and dibenzopentacene. Figure 1 shows crystals of  $[K(\text{tmeda})_2]\text{perylen}$ , where TMEDA (tetramethylethylenediamine) has been used as a stabilizing ligand. From the ligand-supported samples, we were able to obtain crystal structures of many of the highly air-sensitive samples. For example, Figure 2 shows the rubidium coordination mode in  $[\text{Rb}(\text{tmeda})_2]\text{perylen}$ . The use of different alkali metals resulted in variation of the packing arrangement, which became more dramatic as the atomic radius of the dopant increased. Understanding how the packing evolves is important, as the superconductive states are highly dependent on the relative positions of adjacent molecules.



Figure 1. Single crystals of  $[K(\text{tmeda})_2]\text{perylen}$  (TMEDA = tetramethylethylenediamine). The blueish crystals are immersed in Paratone oil (appears grey) to protect the crystals from oxidation. The white dots are bubbles of nitrogen gas (from dry box) trapped in the oil.

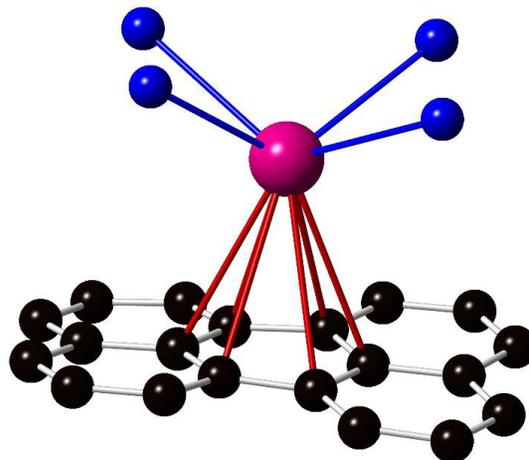


Figure 2. Rb coordination mode in  $[\text{Rb}(\text{tmeda})_2]\text{perylen}$ . The atoms are represented as colored spheres: carbon (black), rubidium (pink), and nitrogen (blue). For clarity, only the nitrogen atoms of tmeda are illustrated and the hydrogen atoms of perylene are removed. The red bonds illustrate the rubidium coordination to the central six carbon atoms of perylene.

The literature has only reported superconductivity in polycrystalline samples where the reduction state of the phenacene is believed to be -3. Much attention has been focused on the stoichiometry of the alkali metal dopant and the annealing conditions required for high-temperature, solid-state reactions. Typically, an incorrect stoichiometry or insufficient annealing time led to decreased superconducting transition temperatures or loss of superconductivity altogether. In our laboratory, high-quality single crystals have only been grown for samples containing alkali metals with stabilizing ligands and phenacene reduction states of -1 or -1.5. However, samples produced through use of non-coordinating solvents, such as toluene, rapidly produced high-purity samples of doped phenacnes as amorphous solids.

Based on Raman spectroscopic characterization in FY 2016, our method cleanly provided potassium-doped phenanthrene in the desired -3 state, by precipitation from solution. Most notably, this -3 product formed even when only one equivalent of potassium was added, indicating that the -1, -2, and -3 states are in an equilibrium, and only the highly-charged state is insoluble in the solvent system. This finding provides an excellent example of the advantages of producing alkali-doped acenes in solution and highlights the need to produce these materials under a more homogenous, controlled environment. Due to the highly air-sensitive nature of the -3 products, magnetic and transport measurements have not yet been able to confirm superconductivity in these materials.

FY 2016 was the last year of this project. Proposed further work would focus on advancing the solution-based chemistry to achieve materials in the superconducting -3 state. We would use physical measurements, including magnetization, to search for magnetic and superconducting states. We would continue to explore the electrochemical generation of the acenes as a secondary pathway to the highly-reduced states. Synergistic feedback from computational studies based on the elucidated crystal structures would further guide the discovery of new, promising, alkali-acene pairs.

## Plastic Artificial Leaves for Water Splitting

2014-046-R2

Lin X. Chen and Luping Yu

### PROJECT DESCRIPTION

Sunlight is intermittent. Therefore, efficiently harnessing and using photon energy necessarily involves developing a means of solar energy storage. One way to do this is to use sunlight to drive the combined processes of water oxidation and reduction. This approach ultimately stores the energy from sunlight in the form of energy-dense chemical bonds such as hydrogen (H<sub>2</sub>). This is artificial photosynthesis and solar fuels formation, which require developing highly robust and efficient photocatalysts capable of water oxidation and/or proton or water reduction. Photocatalysts could also use electrons derived from water oxidation to carry out the reduction of carbon dioxide (CO<sub>2</sub>) by generating CH<sub>3</sub>OH; this process delivers benefits both by generating solar fuels and by mitigating the greenhouse gas CO<sub>2</sub>. One main challenge in using sunlight as an energy source involves coupling single-photon absorption events with multiple electron/hole redox reactions for the overall splitting of water into hydrogen and oxygen (i.e., 2H<sub>2</sub>O → 2H<sub>2</sub> + O<sub>2</sub>). Therefore, special attention must be paid to light-harvesting and how it is coupled to catalysis.

In this project, we combine our knowledge of photo-induced electron transfer in artificial photosynthesis and the photophysics of conjugated polymers, which are used in organic photovoltaic devices. We will construct a platform for photocatalytic water splitting, particularly to generate hydrogen. We seek to integrate a single, organic, photovoltaic *p-n* junction and a water-splitting, catalytic, transition-metal center into a bilayer, organic, artificial leaf. An artificial leaf forms when water oxidation and reduction catalytic reactions proceed simultaneously with sunlight absorption. The scope of the project includes the following:

- Designing and synthesizing metallopolymers
- Physically characterizing excited state properties and structures
- Testing photo-induced hydrogen generation under various conditions, using different materials and test devices

### MISSION RELEVANCE

This project is relevant to DOE missions in energy, the environment, and basic science. The project especially relates to the Photosynthetic Systems, Photochemistry, and Catalysis programs in the Chemical Sciences, Geosciences, and Biosciences (CSGB) division of DOE's Office of Basic Energy Sciences (BES), and may also interest the Office of Energy Efficiency and Renewable Energy (EERE) and the Air Force Office of Scientific Research with respect to generating fuel from renewable and clean energy sources.

### RESULTS AND ACCOMPLISHMENTS

In FY 2014, we focused on designing, synthesizing, and characterizing novel photocatalytic architectures that simultaneously combine the light-harvesting properties of conjugated polymers and transition-metal catalysts. We initially focused on optimizing structures for the hydrogen evolution half-reaction. Figure 1 shows the two polymer structures synthesized initially. These polymers consist of an electron-donating benzodithiophene unit (PBDT-bpy in Polymer A) or electron-accepting perylene diimide unit (PPDI-bpy in Polymer B) copolymerized with a transition-metal binding site, bipyridine (bpy). We used cyclic voltammetry to experimentally define the energy levels of these polymers.

These data indicated, for both polymers, that the lowest unoccupied molecular orbitals (LUMOs) were above the formal H<sub>2</sub> evolution potential and the highest unoccupied molecular orbital (HOMO) of PPDI-bpy was sufficient for water oxidation. Ultraviolet-visible (UV-vis) absorption spectroscopy complemented these results, and also allowed us to monitor the polymer structure and the metal binding, demonstrating that both polymers bind Co(II) (and other metals) efficiently. Correlating electronic structure calculations to the experimental data allowed for a detailed understanding of the electronic structures of both polymers, with and without Co(II) chelation.

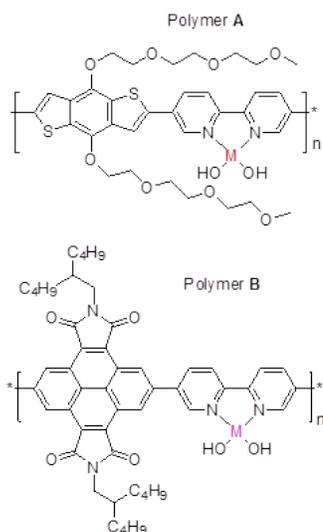


Figure 1. Polymer structures PBBDT-bpy (A, top) and PPDI-bpy (B, bottom).

In FY 2015, we demonstrated photocatalytic  $H_2$  production from  $H_2O$  and a sacrificial reductant using both PBBDT-bpy and PPDI-bpy polymers. These results represented the technical breakthrough for this project and demonstrated these metallopolymers are novel constructs for photocatalysis. To the best of our knowledge, this finding was the first report of photocatalytic  $H_2$  generation from this type of artificial photosynthetic system. With this result, we could systematically investigate specific contributions to photocatalytic  $H_2$  production. We showed that  $H_2$  generation depends strongly on Co(II) catalyst loading, with a maximum at  $\sim 10\%$  Co(II) loading for PBBDT-bpy and  $\sim 50\%$  Co(II) for PPDI-bpy. In addition, both polymer structures yielded different excitation wavelength dependencies for  $H_2$  production. We used electronic structure calculations to understand these differences in  $H_2$  production, and demonstrated that the different ground and excited state electronic structures of PBBDT- and PPDI-bpy effectively tune the efficiency of  $H_2$  production.

Goals in FY 2016 were two-fold:

1. Expand on the polymer structures for  $H_2$  production
2. Better understand the structure of the Co(II)-bpy active sites and the mechanisms for photocatalytic  $H_2$  production

For (1), our work in FY 2015 showed that these polymers are heterogeneous photocatalysts, which raised the issue of the ability of water (or protons) to access active sites. Poor substrate access could potentially decrease activity. We therefore developed porous, conjugated polymer structures that effectively increased the substrate access to active sites. This effort resulted in higher amounts of  $H_2$  production under similar conditions. For (2), we obtained X-ray absorption near edge structure (XANES)

and extended X-ray absorption fine structure (EXAFS) data for a series of Co(II)-loaded PBBDT- and PPDI-bpy thin films. Compared to Co(II)-bpy(x) standard samples, the data indicated that Co(II) can be less than six coordinated. This supports access to the active site through open coordination sites, where water can bind to Co centers. Further data analysis is in progress. In addition, transient optical absorption spectroscopy allowed for a better understanding of the photophysical properties of the neat and metal-loaded polymers. For example, Figure 2 provides transient absorption data for PPDI-bpy, which exhibits a strong spectral dependence on conditions and possibly indicates the detection of photochemically-generated intermediates.

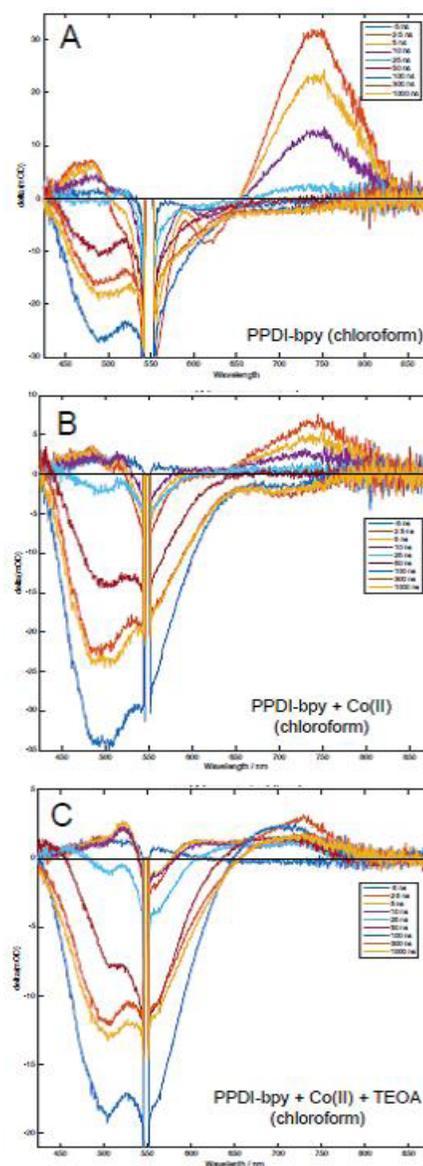


Figure 2. Transient absorption data for PPDI-bpy under several conditions, from -5 to 1000 ns. (A) neat PPDI-bpy in chloroform, (B) PPDI-bpy + Co(II) in chloroform, and (C) PPDI-bpy + Co(II) + triethanolamine (TEOA).

# Carbon Nano-Network as Next Generation Support for Catalysis and Electrocatalysis

2014-051-R2

Di-Jia Liu and Jeffery Miller

## PROJECT DESCRIPTION

This project focuses on developing a new type of catalytic substrate—a carbon nano-network—for catalytic and electrocatalytic applications. This substrate contains macropores and micropores almost exclusively, and is therefore fundamentally different from conventional carbon supports. It promises to overcome the shortcomings of traditional carbon supports by providing the following morphological advantages:

- A highly micropore-dominant surface area and a pore volume crucial for enhancing the rate of heterogeneous and electrocatalytic reactions
- Direct macropore-to-micropore connections that bypass the mesopores, thus lowering mass-transport resistances for reactants and/or products
- Catalytic active sites that are interconnected through a protective fibrous network and have better charge and/or thermal conductivities and chemical stability

We are preparing the carbon nano-network substrate through the electrospin method, which produces a finely dispersed metal-organic-framework (MOF) encapsulated inside nanofibers. Upon thermolysis, a new structure forms, featuring active-sites decorating catalytic carbon fibers which are connected by a network of strings and knots (see Figure 1). The goal of the project is to design and fabricate several nano-network catalysts with different morphological properties, and to demonstrate their improved performance in fuel cells and in biofuel catalysis.

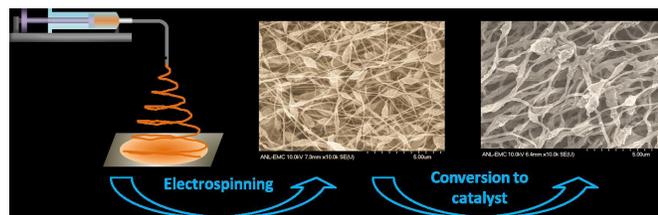


Figure 1. Schematic diagram of the synthesis, with micrographs, of Argonne's highly porous, nanofibrous catalyst.

## MISSION RELEVANCE

This project focuses on improving energy efficiency and producing renewable energy. The project is therefore

relevant to DOE's missions in energy supply and environmental quality. A pore-size-controlled carbon nano-network would not only have a strong impact on fundamental catalysis science, but also would have practical applications in next-generation catalysts and electrocatalysts. The new materials developed from this work could be applied directly to solve some of the most pressing problems in energy conversion and environmental protection.

## RESULTS AND ACCOMPLISHMENTS

During FY 2014, when the project started, we developed a one-pot synthesis method to prepare several MOF-based electrocatalysts with excellent catalytic activities toward oxygen reduction in an alkaline medium.

During FY 2015, we developed a highly porous catalyst for the carbon nano-network, with significantly improved catalytic activity for the oxygen reduction reaction without a precious metal such as platinum (Pt). We also developed a novel bimetallic catalyst, which demonstrated significantly improved activity and durability.

The FY 2016 objective of the project was to complete developing the material chemistry for an MOF-based, nano-network platinum group metal free (PGM-Free) catalyst and ultra-low Pt catalyst and demonstrate their performance in a fuel cell; and to explore other related catalytic applications. We had the following major accomplishments during FY 2016:

- Developed a highly efficient, MOF-based PGM-Free catalyst;
- Developed MOF-based, ultralow Pt, bimetallic catalysts; and
- Developed an MOF-based electrocatalyst for splitting water.

*Developed a Highly Efficient MOF-Based PGM-Free Catalyst.* We continued to investigate PGM-Free catalysts, using MOF as a precursor. One catalyst system we developed is a cobalt-doped composite. We incorporated a cobalt ion during the synthesis of the zinc zeolitic methylimidazolate framework,  $Zn(mIm)_2$ , to form the  $Co/Zn(mIm)_2$  precursor. The precursor was then subjected to high-temperature pyrolysis to carbonize and remove the Zn, forming a new composite catalyst,  $Co/N/C$ . We tested the new catalyst by the rotating disk electrode (RDE) method, in oxygen-saturated perchlorate acid, and it showed promising electrocatalytic activity. We then tested the catalyst in a proton exchange membrane fuel cell. The result indicated that the new  $Co/N/C$  composite has the best catalytic activity under the operating conditions

of the fuel cell, among known cobalt-based PGM-Free catalysts.

*Developed MOF-Based, Ultralow Pt, Bimetallic Catalysts.*

One of the concepts in the original proposal was to prepare MOF-based, bimetallic catalysts by combining the original MOF with a second metal precursor through the porous framework structure. We demonstrated such an approach by adding a platinum precursor over a cobalt zeolitic imidazolate framework (Co-ZIF, a subgroup of MOF), and prepared a Pt-Co bimetallic alloy catalyst through several steps of post-synthesis processing. The catalyst derived from Co-ZIF is known to be active in the electrocatalytic oxygen reduction, but generally lacked durability. By combining a low concentration of Pt with an MOF-based, bimetallic catalyst approach, the new catalyst demonstrated significantly enhanced durability. The preliminary test also suggests that the combined catalytic activity is higher than the sum of individual contributions from the Co-ZIF derived and Pt/carbon catalysts. The work led to an invention disclosure, "Low-Platinum Catalyst and Method of Preparation" (ANL-IN-15-143).

*Developed an MOF-Based Electrocatalyst for Splitting Water.* Splitting water by electrochemical reaction is a new direction for hydrogen production that uses excess electricity produced by renewable energy sources. A key step in water splitting involves oxygen evolution reaction (OER). Currently, the most effective catalysts for OER are materials based on costly iridium and ruthenium. Another major challenge is the durability of the catalyst. OERs are generally carried out at a potential higher than 1.5 V (reversible hydrogen electrode [RHE]). Under such high potential, electrochemical oxidation corrodes the amorphous carbon support, which impedes the OER. During FY 2016, we explored a new type of OER catalyst using an MOF-embedded, porous, nano-network catalyst prepared by electrospinning a polymer solution suspended with Co-ZIF nanocrystallites, followed by high-temperature pyrolysis. We tested the new catalyst in an alkaline solution and observed an OER onset potential as low as 1.3 V. This value is significantly better than the 1.5 V observed over RuO<sub>2</sub>/C, a benchmark OER catalyst. We prepared the nanofiber catalyst under inert gas at 1000°C. X-ray powder diffraction (XRD) showed that it is highly graphitized, containing cobalt nitride/carbide, active, and stable materials for OER.

This project is now complete. Pending follow-on support from programmatic sources, we will, however, continue to investigate and optimize the catalytic activity and durability of the bimetallic catalyst for the electrocatalytic oxygen reduction reaction (ORR) and the transition-metal nano-network catalyst for electrochemical OER.

We recently submitted a proposal to the DOE Office of Fuel Cell Technologies for continuous optimization of an ultralow-Pt, bimetallic catalyst in fuel cell applications.

## Thin Film Skyrmion Spin Textures

2014-054-R2

Suzanne G.E. te Velthuis and Axel Hoffmann

### PROJECT DESCRIPTION

A few years ago, it was discovered that certain magnetic materials lacking structural inversion symmetry could form complex magnetization patterns with magnetic spins, forming vortex-like structures. More surprisingly, one could manipulate this *skyrmion* structure of the magnetization with electric currents up to five orders of magnitude smaller than the currents needed for current-driven magnetization dynamics in ordinary ferromagnetic systems. This feature makes magnetic skyrmions promising candidates as information carriers in low-power, ultra-dense memory and logic devices. The goals of this project are to explore the possibility of creating and stabilizing room-temperature skyrmions in a variety of thin films and to then develop new approaches for skyrmion manipulation. We characterize the magnetic texture associated with skyrmions using optical imaging, neutron scattering, and electric transport measurements. We are investigating new strategies to form and manipulate individual skyrmions in patterned structures, and the results may directly affect information storage and computation.

### MISSION RELEVANCE

This project is relevant to DOE's mission in science. The main impacts from this work will be on low-power information storage and logic device concepts. The focus on the underlying fundamental science is of interest to DOE's Office of Basic Energy Sciences. Demonstrating the controlled manipulation of skyrmions in magnetic thin films will generate interest and opportunities for industry.

### RESULTS AND ACCOMPLISHMENTS

In FY 2014, we discovered how inhomogeneous electric current densities flowing through a heavy metal can transform chiral magnetic stripe domains into skyrmion bubbles in an adjacent ferromagnet [see Science 349, 283 (2015)]. These results were obtained in wires with a geometric constriction, formed from a film consisting of a thin layer of ferromagnetic metal, Co<sub>20</sub>Fe<sub>60</sub>B<sub>20</sub>, with

perpendicular magnetic anisotropy that was sandwiched between layers of nonmagnetic heavy metal tantalum (Ta) and insulating TaO<sub>x</sub> deposited on Si/SiO<sub>x</sub>, and most importantly, at room temperature, as was one of our goals.

In FY 2015, we extensively explored this novel behavior as a function of current density, pulse width, magnetic field, and size and geometry of the constriction. We found that the skyrmions move at a relatively high speed after de-pinning. The direction of the skyrmion's motion with current is consistent with them having Néel domain walls with a fixed chirality. We made a first test device for a skyrmion racetrack memory, based on the constricted wire but with an additional thin wire and current line attached orthogonally to the original. By sending pulsed currents through the constricted wire, skyrmions form in the lower half of the wire. Later, we found that a single skyrmion can be moved along the horizontal skyrmion bit line by applying a current pulse along that direction [see *AIP Advances* **6**, 055602 (2016)].

Working with coworkers in Argonne's Materials Science Division (MSD), we performed micromagnetic simulations using materials parameters matching our system. They showed that there are at least two mechanisms that can generate skyrmions from inhomogeneous currents. These depend on the magnitude of the current density [see *Phys. Rev. B* **93**, 094407 (2016)].

We directly observed the skyrmion Hall effect for the first time. Analogous to the ordinary Hall effect for electric charges, the topological charge of skyrmions was predicted to result in a transverse motion of skyrmions, also known as the skyrmion Hall effect. Using magneto-optical imaging, we observed in our Ta/CoFeB/TaO<sub>x</sub> heterostructures that skyrmions move at a well-defined angle with respect to a sufficiently large applied electric current. This skyrmion Hall angle increases monotonically with current density, when pinning hampers the motion, but saturates in the flow regime at values consistent with theoretical models that assume rigid skyrmion structures. We also demonstrated that the sign of the skyrmion Hall angle depends on the topological charge ( $\pm 1$ ) as controlled by the sign of the magnetic field [see *Nature Physics* (2016), doi: 10.1038/nphys3883].

Because nanometer-sized skyrmions are desired for potential device applications, we also explored other heterostructures. We interfaced thin ferromagnets between two different heavy metals, with stronger spin-orbit coupling than Ta. In addition, selecting two heavy metals (HMs) with opposite signs for the spin Hall angle creates complementary interfacial Dzyaloshinskii-Moriya interactions, which should stabilize smaller skyrmions

and boost their motion. Following this strategy, we grew [platinum/cobalt/HM2]<sub>x</sub>N multilayers. When HM2 is iridium, we observed skyrmions with a diameter of about 100 nanometers at room temperature and without magnetic fields. Lorentz transmission electron microscopy determined conclusively that these are Néel skyrmions.

## Directly Probing Nanoscale Dynamics in Shear-Thickening Complex Fluids

2014-077-R2

Suresh Narayanan, Jonghun Lee, Xiao-Min Lin, and Alec Sandy

### PROJECT DESCRIPTION

At high volume fractions, colloidal suspensions show non-Newtonian rheological behavior, in which the viscosity of the suspensions decreases (shear thinning) or increases (shear thickening) with increasing shear strength. Shear thickening is widely observed in many industrial applications such as in ceramics, bulletproof body armor, and chocolate. However, despite extensive studies over the decades, the underlying mechanism for this non-Newtonian behavior is still debated. The goal of this project is to understand the mechanism for shear thickening by examining the microstructure of the colloidal suspensions induced by shear. For this purpose, we have built the capability at beamline 8-ID-1 of the Advanced Photon Source to measure the rheology of suspensions with *in situ* small-angle X-ray scattering (SAXS). The microstructures at different shear regimes were measured using SAXS. In addition, stress relaxation in the shear-thickened state was studied using X-ray photon correlation spectroscopy (XPCS).

### MISSION RELEVANCE

This project is relevant to DOE's missions in science and energy. The scientific challenges addressed by this project involve connecting macroscopic rheological properties to nanoscale motion in shear-thickening complex fluids under shear flow. Using coherent X-ray scattering, non-equilibrium behavior at the nanoscale can be observed directly, without averaging over the many subsystems, as in macroscale measurements. The nature of such fluctuations is one metric for evaluating the existence of a non-equilibrium state. Understanding the shear-thickening and stress relaxation after shear-thickening is closely related to one of the missions of Basic Energy Sciences as stated in DOE's five Grand Challenges: non-equilibrium systems.

## RESULTS AND ACCOMPLISHMENTS

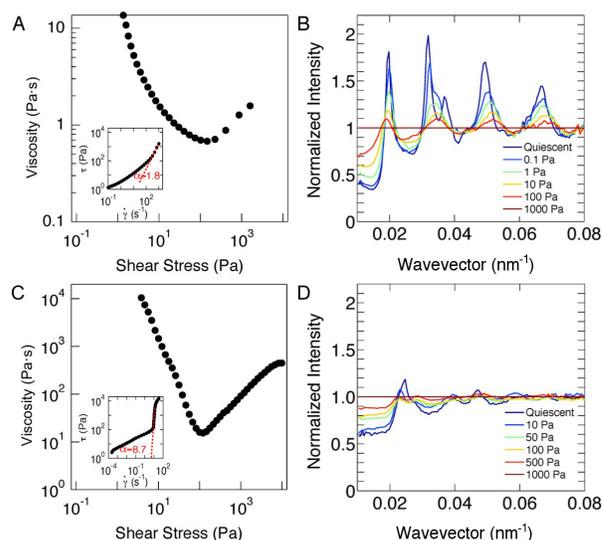
In the first two years of this LDRD project, the order-to-disorder transition (ODT) of shear-thickening fluids was the main object of study. Highly monodisperse silica nanoparticles were dispersed in polyethylene glycol with a volume fraction of 56%. When this colloidal suspension was sheared in an oscillatory manner, it showed the unprecedented rheology of two-step shear thinning/thickening behavior, in which, with increasing shear stress, its complex viscosity sharply decreased, increased slightly, and decreased and increased abruptly.

Small-angle X-ray scattering (SAXS) measurements during this oscillatory shear revealed that during the first decrease in viscosity, the colloids were rearranging themselves into a hexagonally close-packed structure, and at the first viscosity minimum, they formed the most ordered structure. The first slight viscosity increase was accompanied by the destruction of this structure. When this suspension was under steady shear, it shear-thickened at the stress of the second shear thickening under oscillatory shear, which indicates the second shear thickening is the typical shear-thickening behavior.

The ODT has long been proposed as a mechanism for shear thickening in many suspensions, as these two phenomena occur at indistinguishably similar stresses. In addition, other suspensions shear-thicken while not showing ODT; thus, the relationship between these two phenomena was not clear. In our study, we employed the highly monodisperse colloids that clearly separated these two phenomena by occurring at different shear stresses. The following studies were conducted this year to continue exploring shear thickening.

With increasing volume fraction of the colloids, the degree of shear thickening increases with increasing shear stress. Recent and accumulating experimental evidence shows that it is necessary to distinguish discontinuous shear thickening (DST) from continuous shear thickening (CST), where the distinction between them is the degree of increase in viscosity with increasing shear stress. The microstructures with increasing shear stress were measured on the suspension with a volume fraction of 56% showing CST and a suspension with a volume fraction of 62% showing DST (Figure 1). Both suspensions exhibit continuous microstructural change with increasing shear stress from the shear-thinning to the shear-thickening regime, which indicates that there is no sudden structural change associated with shear-thickening behavior. It has long been proposed that shear thickening occurs because of the formation of clusters resulting from the increased hydrodynamic force in the high-shear regime.

Our results contradict this proposed mechanism. Instead, the similarity in the SAXS patterns between CST and DST offers strong evidence that CST and DST might originate from the same mechanism, as several friction-based models have suggested.



**Figure 1.** Rheology of silica suspension of volume fractions of (A) 56% and (C) 62%. Insets are the plots of shear stress ( $\tau$ ) vs. shear rate ( $\dot{\gamma}$ ) from the same measurements, where red lines show what extent shear stress increases with increasing shear rate in shear-thickening regime with relationship of  $\tau \propto \dot{\gamma}^n$ . (B) and (D) are their respective azimuthally averaged SAXS intensities at different stresses normalized by that obtained at shear stress of 1000 Pa.

Stress relaxation in the shear-thickened state was measured using X-ray photon correlation spectroscopy (XPCS). When concentrated colloidal suspensions are shear-thickened, a strong force network percolates over the entire system, which transforms the suspensions from liquid to solid, the so-called shear-jammed state. We observed that during relaxation from a shear-jammed state, shear-jammed suspensions show an unusual dynamic response, which can be explained using the “heterodyne” mode of XPCS. In heterodyne XPCS, the sample consists of two components that move with different velocities, giving rise to interference in the speckle pattern from the two components. Using a concept similar to the Doppler effect, we were able to measure the velocity of the shear-thickened colloids in the suspension.

We have built a physical model based on the system in which part of the sample volume is shear jammed, whereas the other part of the volume is in an unjammed state. Figure 2 shows the velocity of the colloidal particles in the unjammed state as a function of time after the shearing is stopped in the shear-thickened state. The heterodyne mode of XPCS has been proposed as a promising method to study the dynamics of jammed

materials, and many model studies have been reported. Our XPCS study will represent a milestone in using this technique to study the dynamics of shear-thickened and jammed materials.

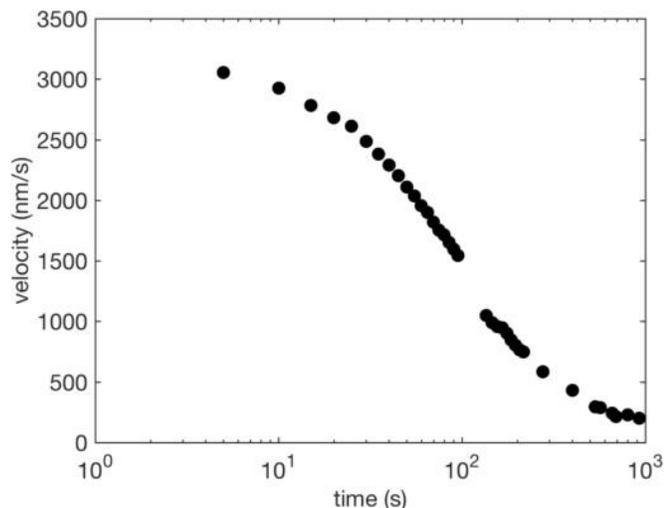


Figure 2. Velocity of the colloidal particles as a function of time after the shearing is stopped in the shear-thickened state.

This unique capability of combining small-angle X-ray scattering with *in situ* rheological measurements can be utilized for many complex fluids. In partnership with a paint company, we are currently carrying out studies on paint formulations and the drying process. An academic partnership has been formed to study the microstructure of 3-D printing inks at high shear rates.

## Pb-Assisted Corrosion/ Cracking Mechanisms at the Interface between Pb-Containing Solution and Nickel Oxide Surface

2014-081-R2

Seungbum Hong and Hawoong Hong

### PROJECT DESCRIPTION

The goal of this project is to study the fundamental mechanisms of lead (Pb) assisted corrosion/cracking by using both *in situ* X-ray reflectivity and advanced *in situ/ex situ* atomic force microscopy (AFM) imaging techniques. We performed *in situ* X-ray reflectivity imaging on pre-oxidized nickel [Ni(110)]–liquid interface or at a molecular beam epitaxy (MBE)-grown NiO–liquid interface while we varied Pb concentration and pH of the liquid. The surfaces or interfaces were characterized by AFM in air and in Pb-containing solution.

### MISSION RELEVANCE

This project is related to DOE's energy security initiative. The major benefits of the proposed work would be providing guidance for identifying the fundamental mechanisms of the Pb-assisted stress corrosion cracking in the short term and developing mitigation methods for this problem over the long term. Eventually, this mitigation effort will enhance the reliability and safety of nuclear power plants and help extend the plants' lives. The major beneficiaries/customers of the proposed work would be the nuclear power industry and DOE

### RESULTS AND ACCOMPLISHMENTS

We developed and manufactured a high-pressure, high-temperature water loop for hydrothermal experiments. The loop was equipped with a high-pressure pump, a backpressure regulator, and two cartridge heaters. A hydrothermal cell was designed to measure high-resolution X-ray reflectivity in high-temperature liquid environments. The equipment consists of a reaction chamber, high-pressure tubing, and a heater plate. The liquid volume exposed to X-rays is  $\sim 0.025$  ml. Using the MBE-grown nickel oxide on MgO(001), the high-resolution X-ray reflectivity was measured in water at 2500 psi, as we increased the temperature. The experiment was conducted at Argonne's Advanced Photon Source's (APS's) 6ID-B beamline. We were able to acquire X-ray reflectivity data up to 150°C. In order to measure the Pb's effect on the NiO layer, we used NiO/Ni(111), which is well known as the most stable nickel oxide. High-resolution X-ray reflectivity was measured in helium, water, and a 10-mM Pb-water solution with varying pH.

Figure 1a shows the combined X-ray reflectivity results of NiO/Ni(111) system in helium, water, and a 10-mM Pb-containing solution (pH 7). Because of the great oxide stability of NiO/Ni(111), we can measure all oscillatory features, even in water and Pb-containing solution. The reflectivity is sensitive to electron density changes due to the water and Pb molecules. The oscillatory features are different in Pb-containing solution between pH 7 and pH 11, as shown Figure 1b. The interface structure is affected by solution pH, even for the same 10-mM Pb concentration.

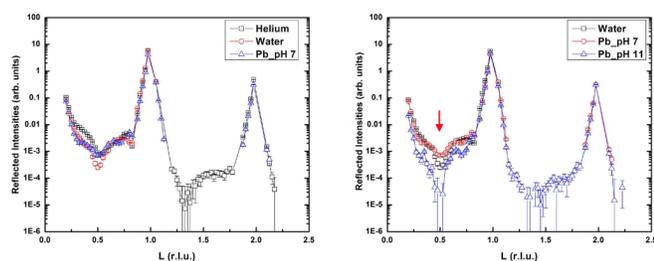


Figure 1. X-ray reflectivity results on NiO/Ni(111) system in (a) He, water, and 10-mM Pb-containing solution (pH 7); and (b) water and 10-mM Pb-containing solution (pH 11). Here, r.l.u. stands for reciprocal lattice units.

After flushing out each Pb-containing solution, we re-measured the X-ray reflectivity in re-injected water. Figure 2a shows the structure recovery by water re-injection for the pH 7 exposure case. This means that there are no chemical interactions between NiO and Pb. However, as shown Figure 2b, the interface structure does not recover after flushing out the Pb-containing solution (pH 11). We concluded that the NiO and Pb interacted and changed the interface structure at higher pH values.

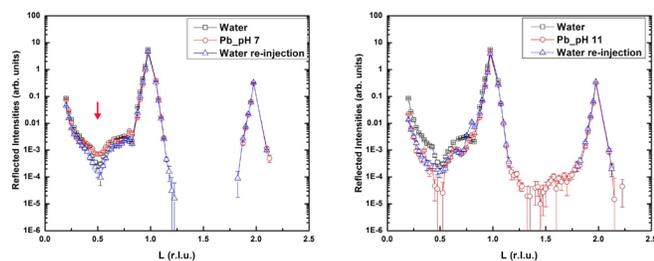


Figure 2. X-ray reflectivity results on NiO/Ni(111) system in (a) water and 10-mM Pb-containing solution (pH 7) and water re-injection after flushing out the Pb-containing solution; and (b) water and 10-mM Pb-containing solution (pH 11) and water re-injection after flushing out the Pb-containing solution.

The pH value of secondary water in nuclear power plants is close to 11. In that condition, the small amount of Pb in the secondary water in a nuclear power plant can react with the NiO of structural materials, thereby changing the oxide passivity; this can provide the nucleation site where cracks can begin and propagate.

We collaborated with Dr. Changyong Park at the High Pressure Collaborative Access Team (HPCAT) (APS Sector 16), Carnegie Institution of Washington for this project, especially for *in situ* hydrothermal cell development and high-resolution X-ray reflectivity applications.

The Electric Power Research Institute (EPRI) is currently funding experimental work related to the Pb induced corrosion and cracking; that work is mainly focused on traditional *ex situ* analysis. We, with an external collaborator, plan to request funding from EPRI related to our fundamental approach.

## Probing the Chemistry of Atmospheric Dust Particles Using X-ray Spectromicroscopy: Implications for Climate Science

2014-084-R2

Yan Feng, Rao Kotamarthi, Barry Lai, and Stefan Vogt

### PROJECT DESCRIPTION

Iron (Fe) is a key micronutrient that is vital for all organisms. In many ocean regions, its availability controls primary productivity, affecting marine biogenic emissions and carbon dioxide fluxes between the ocean and the atmosphere. About 95% of the global Fe supply to the open ocean is from atmospheric dust particles (aerosols), and most photosynthetic aquatic organisms can take up Fe only in the dissolved form. It is thus critical to understand the solubility and, in turn, the bioavailability of Fe in atmospheric dust aerosols. Because of a lack of fundamental understanding about dust chemistry, current Earth system models (ESMs) assume that the soluble Fe fraction of dust aerosols is constant globally, independent of dust mineralogy and chemical processing in the atmosphere. This simplification has been subject to an increasing scrutiny. In order to assess human influences on ocean ecosystems, ESMs need to distinguish between the influences of changes in both climate-driven dust emissions and anthropogenic pollutants on dust Fe chemistry so that global soluble Fe deposition to the ocean regions may be accurately predicted.

This project strives to improve understanding of the chemical transformation processes of Fe minerals in dust by using experimental studies combined with ESM simulations. X-ray fluorescence (XRF) microscopy at Argonne's Advanced Photon Source (APS) is used to probe the chemical composition of individual dust particles down to trace quantities. Furthermore, the microspectroscopic beamlines at the APS are used to determine the oxidation states of Fe(II) or Fe(III) in Fe-containing dust particles, which are linked to the solubility of Fe in dust aerosols. In this project, we will first map the chemical composition of dust particles collected from multiple locations (including the remote Southern Ocean, polluted urban regions, and near the dust-source regions), and then derive statistical relationships between the chemical components identified, depending on atmospheric conditions. We will use the derived datasets representative of different

regions to evaluate and improve the existing models for dust Fe dissolution and speciation, and incorporate them into the Community Atmospheric Model (CAM), which is part of the Community ESM (CESM). The CESM will be enhanced with the capability of capturing highly resolved temporal and spatial variabilities in the deposition of soluble or bioavailable Fe to the ocean, as well as long-term changes in soluble Fe fluxes perturbed by climate variability and human activities.

### MISSION RELEVANCE

The project is tied to DOE's mission in environmental science, and supports the Biological and Environmental Research (BER) program of the Office of Science regarding "understanding... the roles of Earth's biogeochemical systems (the atmosphere, land, oceans, sea ice, and subsurface) in determining climate." In particular, the success of this initiative will be important in developing DOE's next-generation ESMs focused on the feedback between ocean biogeochemical cycles and atmospheric aerosols. This topic has been projected as a major and transformational research area of climate science in the next decade by the DOE/BER Earth System Modeling Program, the National Science Foundation, and the U.S. Department of Agriculture.

### RESULTS AND ACCOMPLISHMENTS

In FY 2014, we primarily focused on developing a library of samples through data collection. Dust samples were gathered from six sites representing a wide range of dust aerosol characteristics including: the Southern Ocean, the Mediterranean, the Atlantic Ocean, Hawaii, Bermuda, and Patagonia. Both filter area-averaged (bulk) and individual-particle Fe oxidation states were characterized for these samples. Initial data analysis performed on the Mediterranean dataset suggested that some of the dust Fe particles consisted of about 60% goethite (an Fe(III) oxyhydroxide) and 40% heterosite (an Fe(III) phosphate). The finding of heterosite indicates the acid processing of dust particles in the atmosphere, because heterosite is not found in the original Saharan dust samples and is likely a product of chemical reactions with acids.

By FY 2015, we completed bulk and individual-particle beamline tests on more than one hundred dust samples including new samples from India. We extended the Mediterranean data analysis for the near-source Saharan dust to include Saharan dust transported over long distances to the Atlantic Ocean and Bermuda. Nearly half of the aerosol iron in the Bermuda samples was iron sulfates, which are a minor component in the original Saharan dust; the formation of these iron sulfates has

been shown to significantly enrich iron solubility. The data also present strong evidence of a reductive Fe transformation [from Fe(III) to Fe(II)] occurring as dust is transported over the long distance. Because Fe(III) is more soluble than Fe(II), the experimental study highlights the importance of both acidic and reductive pathways in Fe dissolution. On the modeling side, we set up the latest CAM version 5 (CAM5) on the Argonne Leadership Computing Facility (ALCF) Blue Gene/Q test and development platform, Vesta. Eight different dust minerals (illite, kaolinite, montmorillonite, hematite, quartz, calcite, feldspar, and gypsum), each with a unique set of physical and chemical properties, were added to CAM5 for improved dust mineralogical representation. We also implemented a new dust emission scheme into CAM5, which shows a substantial impact on the total Fe deposition flux to the ocean.

In FY 2016, we conducted additional ion chromatography analysis on the Saharan dust samples. Specifically, ion chromatography was used to measure major soluble ions for each aerosol sample. The obtained ion concentrations were then used as inputs to estimate the aerosol acidity (pH) of each sample with a thermodynamic model (ISORROPIA). The pH values were found to drop from circumneutral in the samples near the Saharan desert to less than four pH units in those samples that had been in the atmosphere for approximately 15 days. The decrease in pH corresponds to a marked increase in solubility. This result suggests that proton reactions are solubilizing the iron during atmospheric transport. This is consistent with our observations of iron sulfates and phosphates in the Bermuda samples from the XRF analysis conducted in FY 2015 and helps support the hypothesis that Fe(II) sulfates are formed as a result of acidic reactions in the atmosphere.

By combining synchrotron-based XRF techniques with wet chemical extractions, we have also quantified samples taken from India and the Southern Ocean. Aerosol Fe solubility was found generally to have an inverse relationship to total Fe content, when all sampling locations were taken together (Figure 1). But no single predominant factor, such as composition, pH, oxidation state, or distance traveled, could explain the variations in aerosol Fe solubility universally. The presence of secondary phases such as Fe phosphates and Fe sulfates combined with correlations between pH and Fe solubility at downwind sampling locations supports the view that acidic reactions influence aerosol Fe solubility generally. In contrast, correlations between the iron oxidation state and iron solubility found at some sampling locations but not others suggest that photoreduction may be a regionally important process for Fe dissolution.

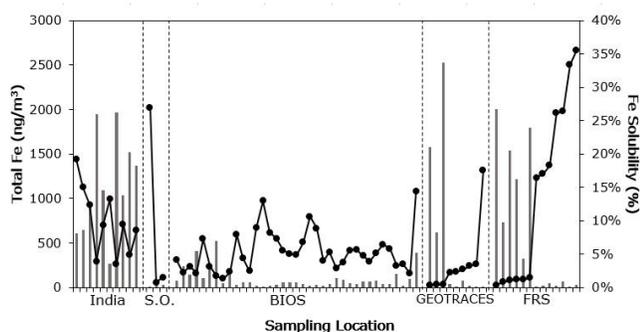


Figure 1. Total (gray bars) and soluble (black line) iron from global sample set. Note: "S.O." represents samples from the Southern Ocean, and "FRS" represents samples from the Finokalia Research Station.

The derived spatial variability in total and soluble Fe from observations was compared with simulations of six ESMs, all of which include fixed dust Fe solubility. Three of them including the CESM/CAM predict the largest soluble Fe deposition in the subtropical Northeast Atlantic and the Arabian Sea, while more Fe was predicted by the other three models to deposit to the mid-latitude North Pacific and the Mediterranean Sea due to differences in dust simulations. Furthermore, sensitivity studies suggest that inclusion of proton and photoreduction dust-Fe dissolution schemes as well as combustion soluble Fe sources modifies the predicted soluble Fe deposition in both magnitude and spatial distribution, agreeing better with observations than the assumption of fixed dust Fe solubility. The uncertainty from the Fe dissolution chemistry is comparable to the uncertainties in dust simulations. Finally, the inter-model differences in the predicted sea-surface dissolved Fe are less than those in the soluble Fe deposition fluxes. This finding implies that the response of sea-surface dissolved Fe distributions to anthropogenic influences (i.e., from dust-Fe dissolution) depends not only on the soluble Fe deposition from the atmosphere, but also is modulated by the Fe cycle in the ocean. Future research is needed to constrain the Fe budget and processes in the ocean biogeochemical model.

## Tuning the Transport Properties of Coupled Majorana

2014-095-R2

Konstantin Matveev, Wade DeGottardi, Lei Fang, and Wai-Kwong Kwok

### PROJECT DESCRIPTION

Hailed as one of the top scientific discoveries of 2012 by *Science* magazine, an experiment offering evidence of Majorana fermions in a superconducting wire by the Kouwenhoven group at Delft, The Netherlands, has set off a firestorm of interest in further exploring Majorana physics. This excitement is driven by the promise that these particles hold for applications to quantum computing. Like any computer, the operation of a quantum computer is based on the ability to store and manipulate information. In a quantum computer, the units of storage are microscopic degrees of freedom subject to the laws of quantum mechanics. Remarkably, quantum computers can perform operations "exponentially" faster than ordinary computers, and this feature has led to a great deal of research activity. One of the biggest challenges in quantum computing is minimizing the loss of information resulting from environmental noise.

Majorana fermions are very promising because the information they store is expected to be immune to many of the forms of noise that plague other implementations. In this project, we are fabricating a device that can probe thermal and electrical transport through a system of coupled Majoranas (Figure 1). The architecture consists of a topological insulator on a substrate that has a thin superconducting strip. The role of the topological insulator is to render the electronic degrees of freedom spinless—a crucial condition for isolating Majorana fermions. We are also fabricating devices made from bismuth selenide (BiSe) in which we have detected signatures of superconducting order. These two ingredients—spin-polarized electrons and superconductivity—are sufficient to generate Majorana fermions in the cores of vortices.

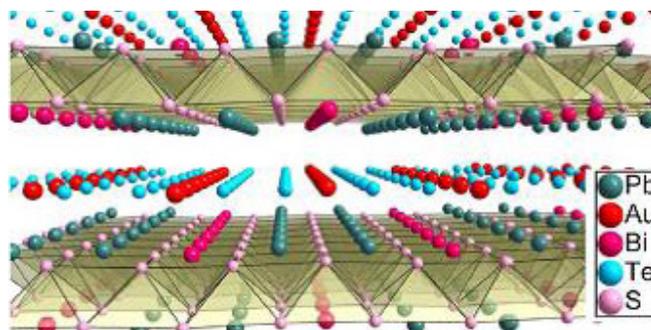


Figure 1. The intergrowth structure  $[\text{PbBiSe}][\text{AuTe}_2]$ .

## MISSION RELEVANCE

This project supports DOE's science mission. Majorana fermions represent an exciting new aspect of superconducting order. The quantum information encoded by these exotic quasiparticles is expected to enjoy unprecedentedly long decoherence times. Applications to quantum computing arising from this project would strongly support the DOE mission of leading innovation in computer technology.

## RESULTS AND ACCOMPLISHMENTS

Topological superconductors have the potential to host Majorana fermions. Experimental work in FY 2014 and FY 2015 focused on the synthesis and characterization of the topological insulator bismuth selenide ( $\text{Bi}_2\text{Se}_3$ ). A challenge in working with this material is that bulk  $\text{Bi}_2\text{Se}_3$  always exhibits semimetallic behavior owing to the large number of crystal defects, a common characteristic of chalcogenide materials. The isolation and detection of Majorana fermions requires the existence of a bulk gap. To this end, we fabricated samples and characterized the effects of doping on  $\text{Bi}_2\text{Te}_2\text{Se}_x$  ( $x=0.95\sim 1.05$ ). Challenges in establishing a clean gap led us to consider the naturally occurring heterostructure  $[\text{PbBiSe}][\text{AuTe}_2]$ . Theoretical work in FY 2014 and FY 2015 focused on the study of topological insulating phases of the Majorana fermions themselves. These studies led us to propose a technique for carrying out topological quantum computational protocols that do *not* require the large-scale motion of individual Majoranas.

In FY 2016, our experiments focused on the transport characterization of novel topological superconductors that exhibit strong spin-orbit coupling. We have shown that copper (Cu)-doped topological insulating nanowires of  $\text{Bi}_2\text{Se}_3$  are good candidates for realizing topological superconductivity. A challenge that we have encountered is that these nanowires are chemically active and tend to degrade when exposed to reagents during nanofabrication processing.

We continued our work on the heterostructure  $[\text{PbBiSe}][\text{AuTe}_2]$ , a naturally occurring intergrowth of conductive gold telluride sandwiched between two insulating lead bismuth selenide sheets (this structure is shown in Figure 1). This material exhibits nontrivial topological protection at heterostructure interfaces. Our data shows clear evidence of strong spin-orbit coupling in this material, as revealed by magnetoresistance measurements [see Figure 2(a)]. The behavior shown in Figure 2(a) is characteristic of weak antilocalization, a quantum interference phenomenon present in disordered two-dimensional systems. Our quantitative analysis shows

that the spin-orbit coupling strength in  $[\text{PbBiSe}][\text{AuTe}_2]$  is comparable to that of topological insulators. Moreover, our theoretical calculations predict a rich helical spin texture. As shown in Figure 2(b), the spin vector in the hole pocket flips as the spin vector moves from  $k$  to  $-k$  along the Fermi surface. The helical spin texture produces a Berry's phase of  $\pi$  that is associated with topological protection. Our experiments and theoretical calculations suggest that the heterostructure  $[\text{PbBiSe}][\text{AuTe}_2]$  is a promising new quantum system that is a suitable host for topological superconductivity.

Tuning chemical compositions in the heterostructure may lead to superconductivity. Figure 2(c) shows evidence of the superconducting behavior observed in this material. Given the strong spin-orbit coupling and nontrivial topological protection in this system, unconventional spinless superconductivity may be realizable in this material. We hope to be able to perform future experiments that will focus on characterizing the pairing symmetry of this superconductor and that of other emergent topological superconductors.

Theoretical work has turned to the role of nontopological edge states. As one moves from inside to outside of a topological insulator, there is a point at which the gap closes. At these points, "topologically" protected zero energy Jackiw-Rebbi edge states arise (Figure 3). An important feature of this system which has not been explored is that for a generic mass texture, there are also other edge modes which do not possess topological protection. Such modes have been studied in different contexts (e.g., bound states of solitons). However, these states have not been explored in the context of topological insulators. Given that they have a large spatial overlap with the protected edge states, we anticipate that they could play an important role in the transport properties of the system.

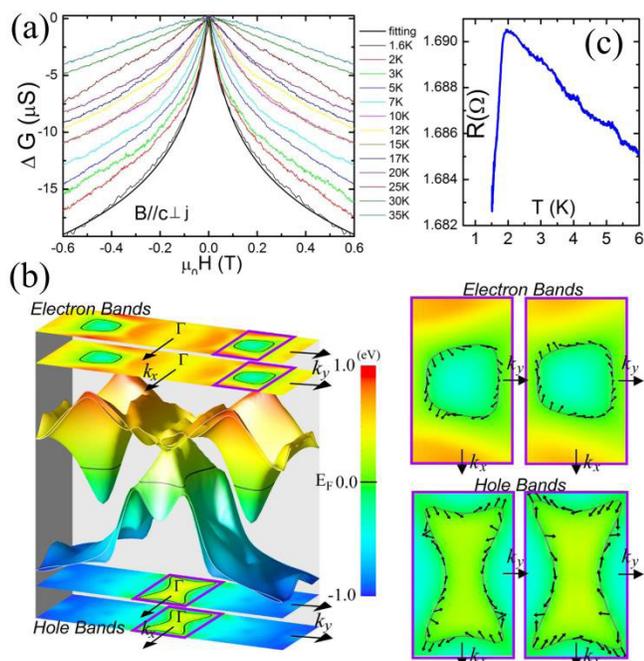


Figure 2. (a) Change in conductance as a function of magnetic field strength in a heterostructure of  $[\text{PbBiSe}][\text{AuTe}_2]$  showing a clear signature of weak anti-localization; (b) *left*, electron and hole bands showing the position of the Fermi level, and *right*, non-trivial spin texture for the electron and hole bands; (c) temperature-dependent resistance of Cu-doped  $[\text{PbBiSe}][\text{AuTe}_2]$  showing evidence of a superconducting transition near 1 K.

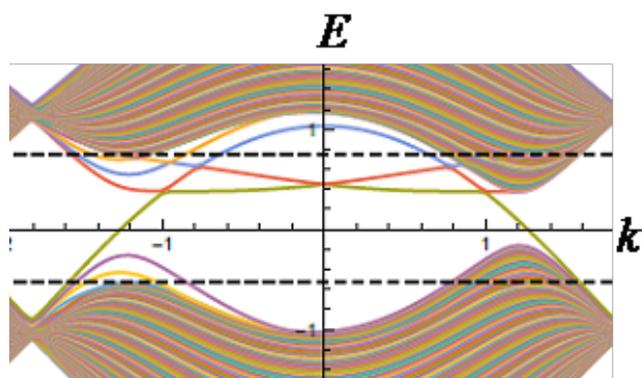


Figure 3. Band structure and edge modes for the Haldane model on a honeycomb lattice. Massless edge modes (green curve) arise as the result of topologically protected edge modes near the two Dirac points (where the green curves pass through zero energy). For the Dirac point on the left hand side of the graph ( $k \sim -1.2$ ), additional (gapped) edge modes arise due to the mass texture at the edge of the system.

## Single Cell Structural Genomics of Uncultured Sediment Archaea: On the Trail for Novel Proteases

2014-108-R2

Karolina Michalska, Gyorgy Babnigg, Robert Jedrzejczak, Andrzej Joachimiak, and Joseph Mootz

### PROJECT DESCRIPTION

Marine sediments are the ultimate sink for organic carbon. At the same time, this cold ecosystem represents one of the richest microbial niches on Earth, predominantly inhabited by archaea and estimated to constitute about one-tenth of the total planet biomass. These microorganisms actively participate in sulfur, nitrogen, and carbon cycling. The latter process occurs predominantly through methanogenesis—a process converting simple organic molecules and  $\text{CO}_2$  into  $\text{CH}_4$  – and reverse methanogenesis—an anaerobic methane oxidation. A recent study identifying novel archaea through single-cell genomic sequencing reports that these organisms encode putative extra- and intracellular protein-degrading enzymes (proteases) to utilize detrital proteins as a source of basic nutrients. Thus, these newly discovered microorganisms might be key players in deep-sea biogeochemistry. However, their physiology and molecular adaptations to this unique environment are poorly understood. In particular, the predicted proteases have not been studied. Therefore, the purpose of this project is to investigate the properties of these uncharacterized enzymes, which may reveal unknown functional and/or structural features.

### MISSION RELEVANCE

This project is relevant to DOE's mission in science and the environment. DOE is committed to the characterization of ecosystems pertinent to carbon sequestration. Moreover, the DOE funds several large-scale projects for the characterization of highly specific classes of proteins. No such work is being performed to study proteases, which are indispensable for the turnover of biomass-derived proteinaceous material. Characterization of archaeal enzymes will help to understand how these microorganisms contribute to global carbon cycling via protein remineralization in marine sediments.

## RESULTS AND ACCOMPLISHMENTS

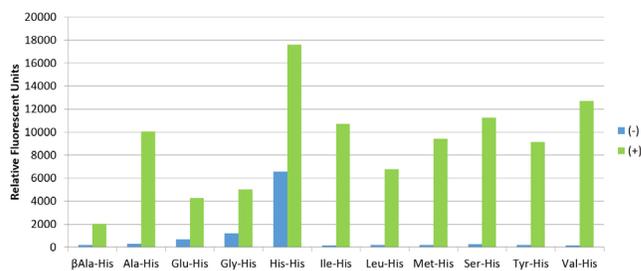
To characterize archaeal proteases we used recombinant DNA techniques to produce selected proteins in the laboratory, enzymatic assays to test their activity and X-ray crystallography to determine 3D structures to obtain molecular insights into the enzymatic mechanism.

We previously analyzed genomes of four novel archaea (*Thermoplasmatales archaeon* SCGC AB-539-C06, *T. archaeon* SCGC AB-540-F20, *Thaumarchaeota archaeon* SCGC AB-539-E09, and *T. archaeon* SCGC AB-539-N05) derived from marine sediment. Fifty-five genes encoding putative proteolytic enzymes were cloned for recombinant expression. To date, we purified 16 proteins; five of these crystallized and two of them provided structural information. In addition, functional screening performed on six proteins resulted in the characterization of three representatives: a bathyaminopeptidase (BAP) and a TAE1 aminopeptidase from *T. archaeon* E09, and an M20 dipeptidase from *T. archaeon* N05.

**BAP.** BAP is an intracellular aminopeptidase with preference for dipeptides with L-cysteine (L-Cys) ( $K_m^{L-Cys-AMC} = 80 \pm 17 \mu M$ ) or a hydrophobic/aromatic residue at the N-terminus. Even though it functions in a cold ecosystem (2°C), its optimal temperature is ~30°C, suggesting that its activity may increase with the rising temperature of the sediment. The enzyme is a hollow sphere tetramer with four active sites localized inside the assembly, which poses significant restrictions on the size of substrates. Our findings were published in *FASEB Journal*.

**TAE1.** TAE1 is an intracellular aminopeptidase representing the M42 family of proteases. It displays activity toward aromatic and aliphatic amino acids, with the highest affinity for tyrosine at the N-terminus of the hydrolyzed peptide. Furthermore, this enzyme exhibits N-terminal deblocking activity, as it is able to hydrolyze acylated N-terminal residues. TAE1 requires divalent cations for catalysis, and cation preference is pH-dependent, with the cobalt ion ( $Co^{2+}$ ) being the most preferred at pH 6.5 and the zinc ion ( $Zn^{2+}$ ) at pH 7.5. The optimum temperature for TAE1 activity is ~45°C, much higher than the temperature on which the enzyme naturally functions. Analogous to BAP, TAE1 is an oligomeric sphere with the active sites located inside, with several openings into which substrates can diffuse. The dimensions of the gates limit the size of the peptides that can access the active sites. The crystal structure was obtained under optimal conditions for enzymatic activity—in the presence of cobalt ions and at a pH near 6.5. Therefore, our structure represents the active state of TAE1, with two cobalt ions participating in the catalytic reaction. A manuscript describing TAE1 is in preparation.

**Xaa-His dipeptidase.** Intracellular Xaa-His dipeptidase from the M20 family of proteases shows broad substrate specificity. Among other substrates, it cleaves an unusual dipeptide – carnosine –  $\beta$ -Ala-His (Figure 1). The enzyme requires either  $Co^{2+}$  or manganese ( $Mn^{2+}$ ) ions for activity. In agreement with that finding, its activity is inhibited by EDTA (ethylenediaminetetraacetic acid) and, to a lesser extent, by 1,10-phenanthroline.



**Figure 1. Enzymatic activity of Xaa-His dipeptidase from M20 metalloprotease family toward various dipeptides. Green bars represent samples containing the enzyme, blue bars are controls with no enzyme added.**

**Gingipains.** Recently, we focused on three extracellular proteases from the gingipain family. These proteins are produced as zymogens that do not show any proteolytic activity prior to maturation. We are currently optimizing initial crystallization hits to yield diffraction quality crystals and are developing protocols for enzyme activation. This work is currently supported by the NIH grant R24GM115586.

## Detection of Dark Matter Directionality by Means of Columnar Recombination

2015-015-R1

Richard Talaga, Marcellinus Demarteau, and Stephen Magill

### PROJECT DESCRIPTION

This project was undertaken to study a new idea proposed for direct detection of both the directionality and energy of weakly interacting massive particle (WIMP) dark matter in the same experiment. Current direct-detection dark matter experiments having enough target material to possibly detect dark matter cannot reveal its directionality. Detectors capable of reconstructing a recoil track from a WIMP dark matter collision with a nucleus have far too few targets for any possibility of an interaction. It is the purpose of this effort to investigate the suitability of a Penning gas mixture of xenon (Xe) and trimethylamine (TMA) in a static electric field to display the directionality of recoil ions and electrons using the correlation of light from recombination

and the total collected charge. The ultimate goal of this project is to determine if the selected gas mixture of Xe with a small percentage of TMA can produce enhanced signals via the Penning effect, and then to determine the optimal TMA concentration to use for further testing of recoil tracks.

### MISSION RELEVANCE

This project is relevant to DOE's mission in science specifically in High Energy Physics (HEP) Cosmic Frontier Program. If successful, this method could lead to the first dark matter experiment capable of detecting both the energy and direction of WIMP dark matter in the same detector. The detector could be scaled to contain more targets for WIMP-nucleus interactions than current non-directional detectors, with the added benefit of simultaneous directionality determinations having reduced backgrounds relative to other direct-detection experiments. A positive signal from a detector with this capability would be strong evidence for the discovery of WIMP dark matter.

### RESULTS AND ACCOMPLISHMENTS

In FY 2015, we designed and built a flexible detector capable of safely testing gas mixtures of poisonous and/or flammable gases in an ionization chamber. We also designed and built diagnostics for ionization chamber experiments, including ultraviolet light detection in wavelengths ranging from 160 nm to visible light, a gas analyzer that samples the gas in the chamber, and a field cage with charge readout and external control of voltage and electric field direction.

In FY 2016, we fully-tested our gas mixing system and gas analyzer with a mixture of argon and carbon dioxide gas in the same concentrations and pressures as planned for the Xe/TMA mixture. We created a database of light and charge measurements from Xe/TMA mixtures at pressures ranging from 1 to 4 atmospheres, at TMA concentrations from 0 to 5% of the gas mixture, and in electric fields ranging from 0 to 3000 volts. We analyzed light and charge measurements as a function of gas composition, electric field, and pressure (see Figure 1).

### PROPOSED FUTURE WORK

If our method is successful and funding allows, we will use the optimal gas mixture composition in an electron or pion beam or with an alpha radiation source to produce ionized recoils in the test chamber. By varying the direction of the electric field, we can then confirm the correlation of light and charge with the field direction. By tagging the incoming and outgoing particle beams, we can make an

accurate determination of the direction of the recoil in order to further understand the correlation of the light and charge measurements with the field direction. If no signal enhancement is seen with this gas mixture, there are several other mixtures we could test in our system in the future that might also prove that columnar recombination can be used to determine WIMP directionality.

Our plan is to compare the light and charge results for the mixed gases to the results for pure Xe. If enhancement of the signal is seen at a particular gas composition, we will propose additional tests with atomic recoils.

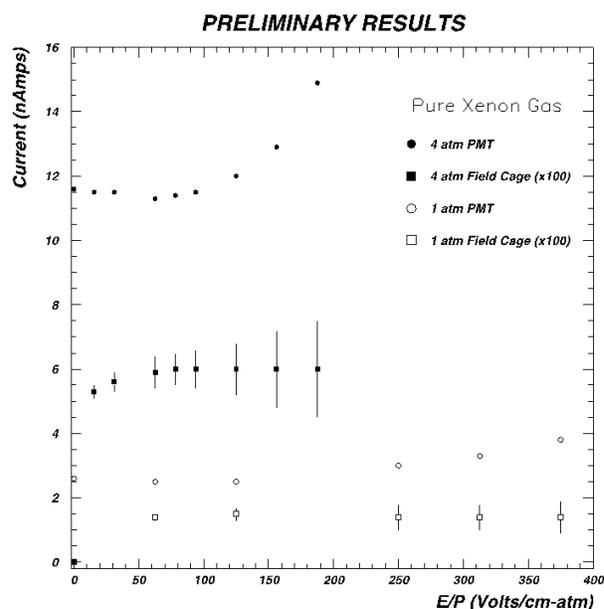


Figure 1. Preliminary results of ionization chamber measurements of light using a photomultiplier tube (PMT) and charge (field cage) for pure Xe gas at two pressures with a Cs-137 gamma ray source. The data shown here represent one-twelfth of the total data taken.

## Josephson Plasma Wave-Based Ultra-High-Frequency Electronics

2015-078-R1

Alexei Koshelev, Timothy Benseman, Yilmaz Simsek, and Vitalii Vlasko-Vlasov

### PROJECT DESCRIPTION

Operation at frequencies of 100 GHz and above is beyond the reach of conventional electronics, making this frequency range the next frontier for high-bandwidth communications and high-speed signal processing. Certain devices built from high-temperature superconductors promise to be naturally suited for operation at these frequencies. Extremely anisotropic

high-temperature superconductors such as  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  (Bi-2212) and  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  contain copper-oxygen ( $\text{CuO}_2$ ) planes alternating with insulating barrier layers. These naturally formed Josephson junctions can be used for DC-to-AC conversion at terahertz frequencies, allowing them to act as very compact sources and detectors of electromagnetic radiation in the “terahertz gap” range, spanning approximately 0.3 to 1.3 THz. These periodic structures are also predicted to act as nonlinear waveguides, allowing the propagation of so-called Josephson plasma waves (JPWs) with switchable transmission characteristics at frequencies of 100 GHz and above. These various properties can thus be exploited for novel optoelectronic integrated circuits, incorporating components such as interferometers, ridge waveguides, and mixers for which the unique properties of layered superconductors can be fully exploited. Such systems would be of particular value for ultra-high-bandwidth telecommunications. In the course of this project, we propose to demonstrate proof-of-concept for such devices, by testing, mixing, and controlling JPWs in the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  devices we will build. We also plan to test a new technique for growing high-quality thin films of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ , with a view to enabling wafer-scale fabrication of JPW devices.

### MISSION RELEVANCE

This project is relevant to DOE’s missions in national security, environmental quality, and science. The rapidly emerging field of THz science and technology holds immense promise for diverse areas, including high-speed electronics, high-bandwidth communications, environmental monitoring, and security. Directly related to DOE’s missions in basic science are the development of new materials platforms for high-speed electronics and the generation of electromagnetic nonlinearities in an energy-efficient way.

### RESULTS AND ACCOMPLISHMENTS

In FY 2015, we investigated propagation of the JPWs through the layered superconductor Bi-2212. We used the THz radiation generated by a Bi-2212 mesa at 0.75 THz to study angle-dependent transmission through a 5- $\mu\text{m}$ -thick Bi-2212 crystal. The incident radiation was coupled through a 125- $\mu\text{m}$  Au grating into JPWs. The measured transmission has peaks at positive and negative angles, which are consistent with the anticipated excitation of JPWs traveling along the  $\text{CuO}_2$  planes. To develop better understanding, we performed a theoretical calculation of the electromagnetic wave transmission through a Bi-2212 crystal with the periodic metallic grating on the top and bottom surfaces. The calculation took into

account grating-induced conversion of the incident electromagnetic wave into the JPW inside the crystal and multiple reflections from the top and bottom surfaces. The transmission experiment demonstrated that the JPWs indeed can be used to transport electromagnetic energy and that these waves can be effectively coupled with free-space electromagnetic radiation.

Our major effort in FY 2016 was on fabrication of epitaxial Bi-2212 films. Most previous experiments (published by us and by other groups) on the THz radiation were implemented using mesas prepared by laser lithography and ion milling on the surface of the Bi-2212 single crystals. Generation and detection of the THz waves have been reliably demonstrated in such mesa devices. However, the practical implementation and upscaling of the superconducting THz technology will be strongly facilitated by the availability of high-quality, large-area Bi-2212 films, which can be used for manufacturing the integrated circuits of coherently coupled arrays of THz resonators and waveguides. In FY 2016, we assembled a setup and searched for optimum parameters for growing thick Bi-2212 films by liquid phase epitaxy (LPE). LPE, based on high-temperature crystallization from a solution, is a promising way for manufacturing single-crystalline high-quality films, but is demanding because of the precise growth conditions it requires. Choice of the matching substrate, composition of the solution, substrate temperature, temperature gradients, and speed of substrate rotation all must be precisely adjusted. The following components have been used for the growth solution: bismuth(III) oxide ( $\text{Bi}_2\text{O}_3$ ), strontium carbonate ( $\text{SrCO}_3$ ), copper(II) carbonate ( $\text{CuCO}_3$ ), and copper(II) oxide ( $\text{CuO}$ ). Potassium chloride (KCl) was used as a solvent, allowing us to reduce the crystallization temperature. The substrate ( $\text{NdGaO}_3$ ,  $\text{SrTiO}_3$ , or  $\text{MgO}$ ) on a specially built platinum holder was slowly immersed in the melted solution. The superconducting properties of the resulting films were tested by SQUID. The structure and composition of the films were controlled by X-ray powder diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX) measurements.

The films of 2- to 3- $\mu\text{m}$  thickness and of correct crystallographic structure and composition [Figure 1 (a, b)] had well-aligned structures with large single-crystalline regions [Figure 1 (c)]. The best films showed high superconducting onset temperatures around 80 K but broad transitions [Figure 1 (d)]. We associate the width of the transition with poor oxygenation of the as-grown films and are working on establishing proper annealing procedures for uniform oxygenation. At this stage, we are confident that we will soon be able to grow high-quality films that will be suitable for device fabrication.

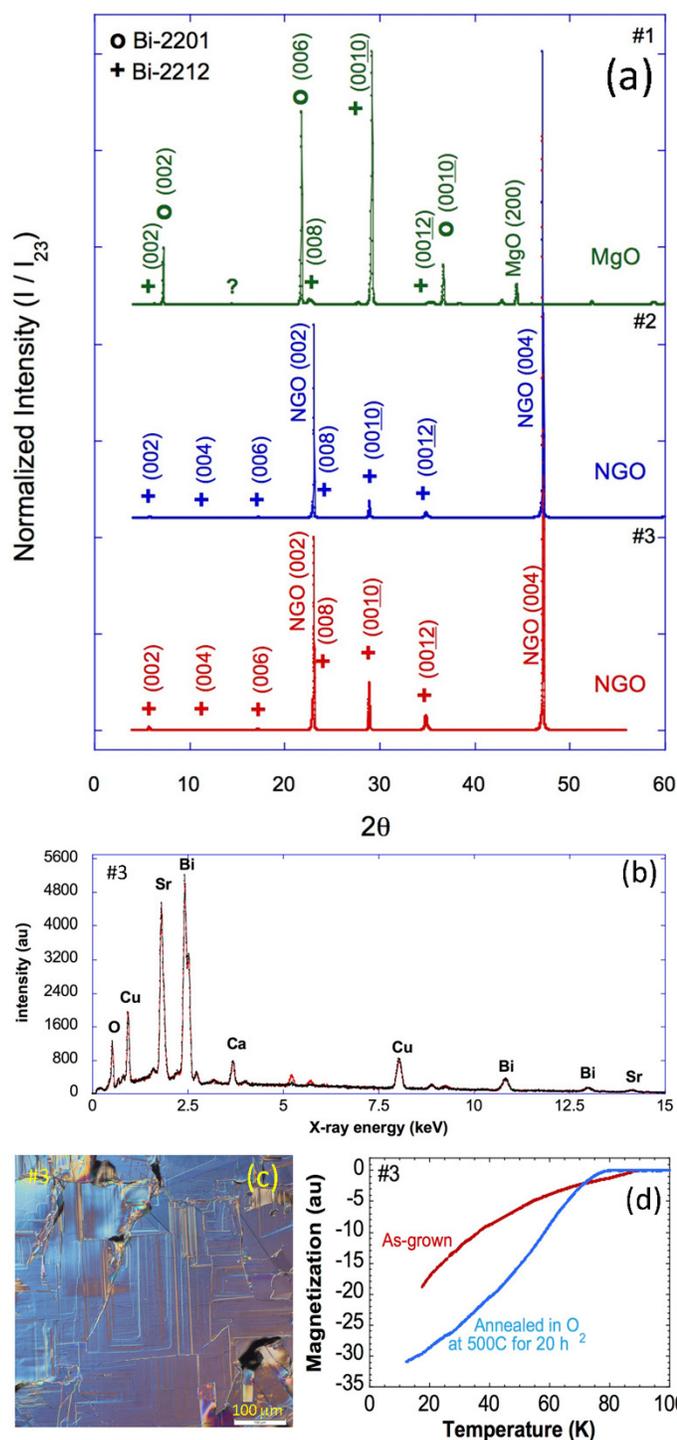


Figure 1. (a) X-ray  $2\theta$  diffraction data (XRD) for three superconducting Bi-2212 thin films grown on different substrates at  $870^\circ\text{C}$ . Indices near the peaks show crystallographic reflection planes and labels “o” and “+” correspond to Bi-2201 and Bi-2212 phases. The height of the peaks shows relative content of the phases. (b) EDX spectra of the superconducting film (#3) grown on NGO for two different locations. (c) Optical picture of the film #3 surface. The steps indicate that the same orientation is maintained over the total film area. (d) The superconducting transition curves for film #3 measured by SQUID before and after oxygenation.

## PROPOSED FUTURE WORK

In FY 2017, we will further improve the fabrication process to achieve high-quality epitaxial Bi-2212 films. One caveat so far involves the unexpected erosion of the PtRh crucible and the appearance of a small amount of Rh in the final films. In FY 2017, we intend to replace the crucible with one that is purely Pt, which could improve the film properties. We will continue optimization of the conditions for homogeneous flat Bi-2212 inconsistencies film growth and for film oxygenation.

When high-quality films become available, we plan to fabricate mesa arrays generating THz radiation. We will pattern gratings on the films to study generation and propagation of the JPWs. We also will build ridge guides and interferometers for plasma waves onto these films, investigate the nonlinear interaction of two beams, and pursue the switching of one plasma-wave train by another.

## Next Generation Natural Gas Adsorbent through Rational Design and Modeling

2015-091-R1

Di-Jia Liu and Rajesh K. Ahluwalia

## PROJECT DESCRIPTION

This project focuses on developing a new synthesis strategy and fundamental understanding that could lead to the next-generation, 3-D porous polymeric network (PPN) materials for gas adsorption and separation applications such as methane storage for a natural gas (NG) fueled vehicle. A PPN is an all organic framework, formed by crosslinking of a molecular “strut” with a stereo-contorted molecular node. The scaffolding through covalent bonds between these building units creates unique properties. PPNs have (a) high surface areas and porosity when properly prepared, which could be significantly higher than that of traditional zeolites; (b) light weight from hydrocarbon-only frameworks; and (c) extreme tolerance toward the heat (up to  $400^\circ\text{C}$ ) and contaminants in natural gas due to their covalent bonds.

Under this project, PPNs with high specific surface area will be prepared with controlled micro-porosity. Molecular struts with different chelating functional groups will be introduced to prepare PPNs with desirable surface properties. Advanced characterization techniques will be used to study how gas adsorbents such as  $\text{CH}_4$  interact with PPN and what are the optimal structural/physical properties for maximum usable storage capacity. The outcome of this project will be crucial in realizing the

full potential of a PPN-based gas adsorbent. The new PPNs will also have broader potential in gas separation, catalysis and other energy efficiency related applications.

### MISSION RELEVANCE

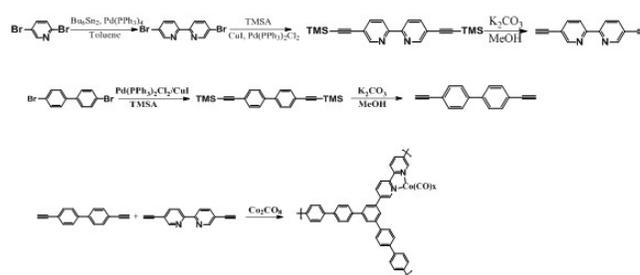
This project focuses on developing new natural gas storage technology for transportation applications. It aims at tapping into the vast NG reserve in the US as a replacement for petroleum. The project is therefore relevant to DOE's energy mission in securing national energy supply and reducing the dependence on foreign oil. In addition to gas storage, the new PPNs from this project could also be applied to gas separation, catalysis, and other applications related to energy conversion and environmental protection.

### FY 2016 RESULTS AND ACCOMPLISHMENTS

During FY 2015, we completed the experimental set up for PPN synthesis and prepared the first batch of polymers with bi-dentate ligation sites. We also collaborated with Shanghai Jiao Tong University and developed a new graphene-encapsulated hydride composite for on-board hydrogen storage.

In FY 2016, we achieved the following:

*Design and Synthesis of Both Metallated and Metal-Free PPNs:* Over 30 PPNs using different monomers and crosslinking chemistries have been developed during this period. The first round of PPN synthesis focused on using monomers containing the bipyridine functional group as a chelating site for transition metal ions. The concept is to promote PPN-methane electronic interaction through an unsaturated metal center. Such an interaction could increase the methane heat of adsorption, thereby improving the storage capacity of PPNs at ambient temperature. Figure 1 shows the synthesis schemes for preparing two monomers containing bipyridine and biphenyl functional groups, followed by crosslinking between the two using a cobalt catalyst to form a cobalt-doped PPN. In addition to these monomers, we prepared other monomers with different "strut" lengths and stereo-contorted configurations, leading to several different PPN compositions and properties. The surface properties of these PPNs were measured using the BET (Brunauer–Emmett–Teller) method, and specific areas as high as 600 meters-square per gram ( $m^2/g$ ) were found. In addition to metallated PPNs, non-metallated PPNs were prepared using a different crosslinking reaction. Such PPNs will be used as benchmark materials in comparing and understanding the impact of an unsaturated metal center.



**Figure 1. Synthesis scheme of one of the cobalt-metallated PPNs recently prepared in our laboratory.**

*New Electrocatalysts Derived from Metallated PPNs:* We also began investigating the conversion of metallated-PPN into efficient, platinum-group metal-free catalysts for the electrochemical oxygen reduction reaction (ORR). The ORR represents a critical step in fuel cell operation. At present, the catalyst material of choice for ORR is platinum, which is expensive with limited reserves worldwide. Finding an alternative catalyst using earth-abundant materials could greatly facilitate fuel cell commercialization. Metallated porous organic polymers (POPs) contain individually dispersed transition metal (TM) ions ligated by the nitrogen-containing coordination sites. Through thermal activation, such POPs can be converted to TM/N/C composites, which are known to be active with respect to ORRs. A number of POPs with Co ions ligated by the bipyridinic functional group were prepared, which were subsequently converted to Co/N/C composites through thermolysis. We found that such activated POPs showed promising catalytic activity for the ORR in both acidic and alkaline media. Figure 2 shows the rotating-disk electrode measurement of a representative catalyst derived from a Co-decorated POP in oxygen-saturated acidic and alkaline solutions. Good electrocatalytic half-wave potentials are observed in both cases, rendering the catalyst obtained from such an approach as a promising alternative to platinum.

*Graphene-Wrapped Complex Hydride for Hydrogen Storage:* We also expanded our effort on gas storage to hydrogen through the collaboration with Shanghai Jiao Tong University (SJTU). SJTU has been on the frontier of research on graphene-based hydrogen storage material. A new "graphene-wrapped" hydride composite was developed through the collaboration, in which individual sodium borohydride particles are encapsulated by monolayer graphene. Such a composite has demonstrated improved storage capacity for re-generable, clean hydrogen. The result from this collaboration was used to support a winning proposal to DOE-EERE for onboard hydrogen storage.

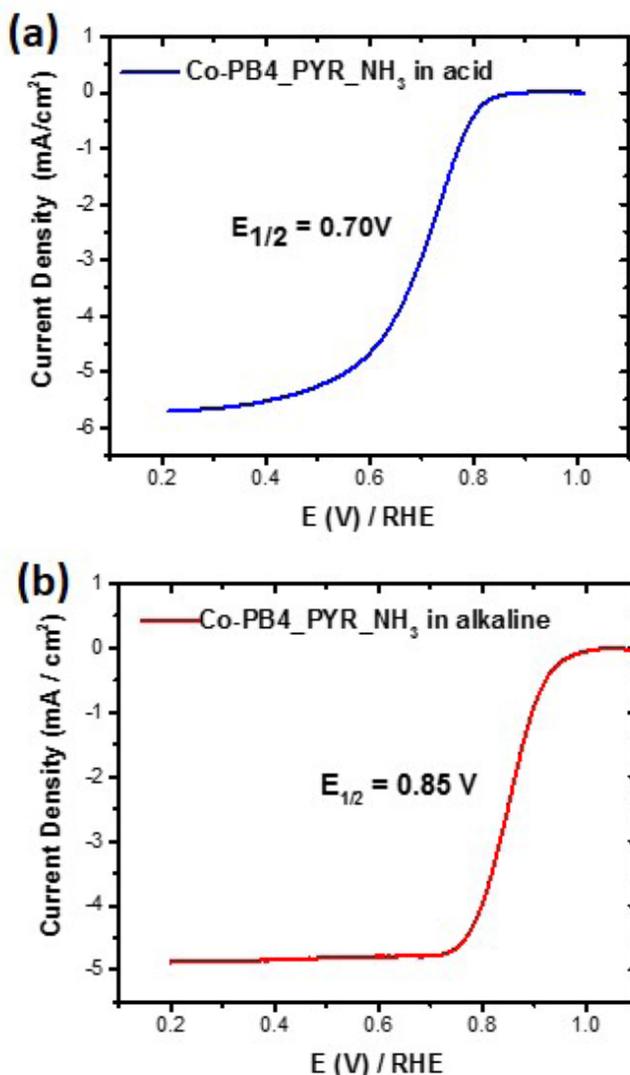


Figure 2. Linear sweep voltammetry of a catalyst derived from a Co-decorated POP after ammonia treating, Co-PB4\_PYR\_NH<sub>3</sub>, measured by rotating disk electrode in an oxygen-saturated (a) acidic solution and (b) alkaline solution. The performance in alkaline medium showed better activity with halfwave potential upshifted by 0.15 V, indicating that the catalyst performs better in alkaline electrolyte.

### PROPOSED FUTURE WORK

We will continue to design, synthesize, and improve different PPN systems according to our original project plan. We will prepare PPNs with new polymeric structures in an attempt to further improve surface properties and gas adsorption enthalpy. Other methods of enhancing surface properties and methane uptake capacity will also be investigated. In addition to gas storage, we will continue to maximize the value of surface-functionalized PPNs by exploring their usefulness in other clean energy-related applications. Advanced characterization tools will be employed to study the structure of the PPN framework and its interaction with gas adsorbents.

## Understanding Atomic-Scale Uranium Interactions under Severe Accident Conditions

2015-096-R1

Chris Benmore and Mark Williamson

### PROJECT DESCRIPTION

The Fukushima Daiichi nuclear reactor accident highlighted the importance of understanding nuclear fuel interactions at the atomic level, which precipitated our interest in establishing the fundamental properties of uranium dioxide (UO<sub>2</sub>) under severe accident conditions. The experimental challenges associated with measuring the structure of UO<sub>2</sub> at extreme temperatures, as well as sample contamination issues, were overcome by developing a laser-heated aerodynamic levitation system with a remote-handling sample changer and sample spinner for obtaining powder averages. We made the first measurement of the structure of molten UO<sub>2</sub> with a view to obtaining a realistic assessment of the multitude of atomistic models in the literature. The work focused on understanding the fundamental interaction of UO<sub>2</sub> with its surroundings, i.e., the bonding between uranium and its oxidized Zircaloy cladding at temperatures up to and beyond 3000 K and the deviation from stoichiometry of uranium in different reducing (oxygen-poor) atmospheres. Understanding material behavior under these extreme conditions is important for assessing safety considerations in meltdown scenarios and for developing realistic models of the behavior of uranium at ultrahigh temperatures. Moreover, our experiments rely heavily on the use of the high-energy beamlines at the Advanced Photon Source and the ability of hard X-rays to penetrate complex sample environments.

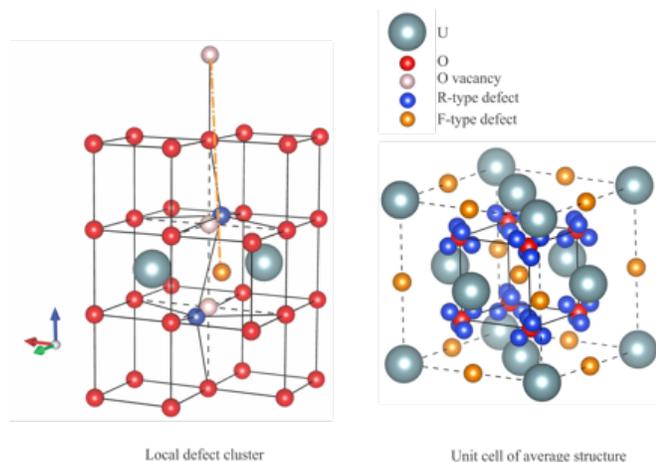
### MISSION RELEVANCE

This project is relevant to DOE's mission in energy. The development of so-called "accident-tolerant" nuclear fuels represents a necessary step forward for the DOE Office of Nuclear Energy in improving nuclear safety. Considering that mixed-oxide fuels are typically 90 wt.% UO<sub>2</sub>, insight into the atomic-scale behavior of its high-temperature solid and liquid phases will provide guidance in the selection of an optimum fuel composition, the selection of additives needed to stabilize the fuel, and the improvement of cladding materials. In addition, computer modeling of materials plays a key role in the fuels development program, and this project has directly led to a DOE INCITE 2016 Leadership Computing award of 75 million processor-hours on the IBM Blue Gene/Q

machine at Argonne. In addition, reactor safety codes under development by the U.S. Nuclear Regulatory Commission will benefit from the state-of-the-art experimental X-ray data obtained from this research.

## RESULTS AND ACCOMPLISHMENTS

The structures of high-temperature, crystalline and molten  $\text{UO}_2$  samples were probed using high-energy X-rays at the Advanced Photon Source. At the start of the project in FY 2015, we found that, upon melting, the average U-O coordination number decreased from 8 to  $6.7 \pm 0.5$ . The measured U-O bond length was found to contract upon heating up to the melting point, despite normal volume expansion. These results indicate that a substantial change from the  $\text{UO}_8$  cubic polyhedra of the  $\text{CaF}_2$ -type crystal structure in the solid (see Figure 1) occurs in the melt.



**Figure 1.** The crystal structure of  $\text{UO}_2$ . Left: a Frenkel defect (yellow) clustered with two R-type defects (blue), which distort the perfect cubes of the average oxygen sublattice (red) at high temperatures. Right: the crystallographic unit cell averages over all possible R and F defect sites. The U atoms are silver, and the O vacancies are white.

Rietveld refinements of our X-ray diffraction data on pure  $\text{UO}_2$  show that we are in excellent agreement with previously measured  $\text{UO}_2$  lattice and thermal-displacement parameters. However, our thermal expansion results are systematically located in the upper bound of the uncertainties in the standard model, indicating a slightly steeper trend of thermal expansion compared to established values. This finding has important implications for the choice of new cladding materials. We also observed a small pre-peak in the melt spectra, indicating the existence of medium-range topological ordering in the melt. This is unexpected because  $\text{UO}_2$  is mainly governed by ionic interactions. Using a Voronoi tessellation procedure, the domination of 4-fold Voronoi coordination polyhedra was found to be the origin of this peak. Changing the levitation gas has

allowed us to investigate departures from stoichiometry in the molten  $\text{UO}_2\text{-X}$  system. Changes in composition (represented by X) are known to significantly reduce the melting temperature. Classical molecular dynamics simulations have been used to interpret structural differences in the nearest-neighbor U-U correlations. Structural differences are found when liquid  $\text{UO}_2$  is exposed to carbon monoxide and hydrogen atmospheres rather than pure argon gas. These are attributed to an increase in the population of  $\text{UO}_7$  and  $\text{UO}_8$  polyhedra at the expense of  $\text{UO}_6$  polyhedra in oxygen-deficient environments. X-ray diffraction experiments on mixed-liquid  $\text{UO}_2\text{-ZrO}_2$  samples have shown that the pair distribution functions can be represented by a linear combination of the end-members, indicating that the melt can be treated as an ideal associated solution. The structural information derived from melt behavior provides definitive data for constraining models in a wide range of meltdown scenarios, particularly in reduced-oxygen environments.

## PROPOSED FUTURE WORK

The development of accident-tolerant fuels has become a priority for DOE. Accordingly, we propose to focus our work on the study of mixed-oxide fuels, such as  $\text{UO}_2\text{-PuO}_2$ . To achieve the goal of measuring the structure of  $\text{PuO}_2$  up to and above its melting point, changes in instrumentation and safety procedures will be made in the last year of the project. Given the increased radioactivity associated with  $\text{PuO}_2$  fuels compared to  $\text{UO}_2$ , additional containment levels will be implemented. With this capability, we will be in a position to study the vast majority of nuclear fuels.

## Development of Advanced $\text{VO}_2$ Nano-Composite Thermochromic Materials for High-Performance Smart Windows

2015-121-R1

Jie Li, Leah Guzowski, Ralph Muehleisen, and Xiaojie Yan

### PROJECT DESCRIPTION

Buildings consume approximately 30 to 40% of the world's energy; heating/cooling and lighting account for a primary portion of that energy consumption. An emerging solution to overcoming energy consumption/loss is to apply thermochromic (TC) films on windows, so-called "smart windows," such that the film selectively blocks the heat (infrared light) when the ambient temperature

reaches a transition temperature, while allowing visible light to pass through. At the transition temperature, TC materials experience a reversible structural change from the semiconducting phase to the metal phase accompanied by a significant change in optical properties. Among various potential candidates, M-phase vanadium dioxide ( $\text{VO}_2$  [M]) materials receive considerable attention because of their sharp and fast response at the transition temperature. However, three technical barriers restrict the use of  $\text{VO}_2$  (M) materials for practical applications: (1) the transition temperature is too high ( $68^\circ\text{C}$ ), (2) the luminous transmission (LT) is too low ( $<40\%$ ), and (3) solar transmission modulation (STM) is limited ( $<10\%$ ). A theoretical calculation predicts that these limitations can be overcome when  $\text{VO}_2$  particle size is reduced to the nanoscale, with particle size and morphology properly tuned. However, mass production of high-quality  $\text{VO}_2$  (M) particles with properly maintained optical and thermal properties at a low cost is problematic. New and efficient process technology is required to obtain the target materials with the required particle size/shape homogeneity.

The purpose of this project is to synthesize advanced TC  $\text{VO}_2$  (M) micro-nanoparticles for smart window film applications. By developing a novel continuous flow reaction system, our goal is to massively synthesize such nanoparticles. After nano-coating with transparent silicon dioxide ( $\text{SiO}_2$ ) shells to enhance durability and reduce light scattering, the nanoparticles will be incorporated into a dielectric host to make a novel window film to boost both transparency and solar modulation ability (i.e., the ability to reduce heat transmission at high temperature in the metal state). The particle size and shape are flexibly controlled by tuning experimental parameters, including temperature/pressure, resident time, reactor dimension, and reactant ratio. Our continuous flow technology not only enables the mass production of the particles and the feasibility of process scaling up, it intensifies the reaction, thus significantly reducing synthesis time.

Collaborators on this project have been Yugang Sun of Temple University (surfactant-assisted hydrothermal synthesis of  $\text{VO}_2$  nanoparticles using a microwave reactor and a quartz micro-reactor) and Samuel Dull of Northwestern University (material syntheses using a continuous flow reactor).

### MISSION RELEVANCE

This project supports DOE's missions of energy security and environmental quality. It aligns well with the DOE's Energy Efficiency and Renewable Energy (EERE) Building Technology Office's focus. Our advanced green

processing technology also supports the EERE Advanced Manufacturing Office's mission in additive manufacturing in which nanopowders are typically used as raw materials. The potential beneficiaries of this technology include building owners, window film manufacturers, automobile makers, sensor and detector producers, and the aerospace industry, as well as the defense industry where this  $\text{VO}_2$  material can be used for equipment protection from a high-power laser.

### RESULTS AND ACCOMPLISHMENTS

In FY 2015,  $\text{VO}_2$  nanorods were synthesized through a microwave-assistant hydrothermal reaction by using an existing Center for Nanoscale Materials (CNM) batch microwave reactor. However, after the post annealing process, the results showed that the final product is  $\text{V}_6\text{O}_{13}$  rather than  $\text{VO}_2$  (M), which was found to be due to the low synthesis temperature ( $190^\circ\text{C}$ ) of the microwave reactor. To address this issue, a micro-reactor was identified and ordered to conduct the synthesis since it is capable of operating under much higher temperature ( $400^\circ\text{C}$ ) and pressure (200 bar). The as-synthesized products from this micro-flow reactor are A-phase  $\text{VO}_2$  (A) nanorods, which can be converted to  $\text{VO}_2$  (M) after the post-annealing process at an elevated temperature. This finding shed light on the feasibility of using a continuous flow process for synthesizing target nanomaterials.

In FY 2016, we systematically investigated the influence of the flow reactor diameter on syntheses of  $\text{VO}_2$  nanomaterial. The results indicate that  $\text{VO}_2$  particles with varying sizes and shapes (from nano- to micro-scale and from spheres to rods; see Figure 1 left and center) can be synthesized by using such flow reactors. Materials obtained were well crystallized (see Figure 1 center), typically  $\text{VO}_2$  (A) phase nanorods under experimental conditions. We discovered that M phase  $\text{VO}_2$  can also be successfully synthesized in a single step when proper conditions of temperature, pH value and resident time are used. All syntheses required a significantly shorter time compared to those using a conventional autoclave reactor. Prepared particles were surface-modified by sol-gel coating with tunable thickness ranging from a few nanometers to tens of nanometers as can be discerned from Figure 1 right. The annealed  $\text{VO}_2/\text{SiO}_2$  composites proved to be pure M-phase Figure 2 top with a transition temperature of  $65^\circ\text{C}$  during heating and  $57^\circ\text{C}$  during cooling Figure 2 bottom. The semiconductor-to-metal phase transition is reversible.

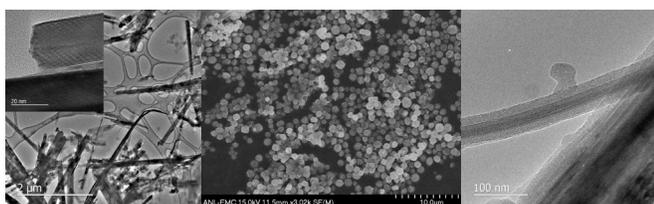


Figure 1. Scanning electron/transmission electron microscopy (SEM/TEM) images showing VO<sub>2</sub> nanorods and micro-spheres as-synthesized in continuous flow reactors (left and center) and VO<sub>2</sub>/SiO<sub>2</sub> core-shell structure after the sol-gel coating process (right).

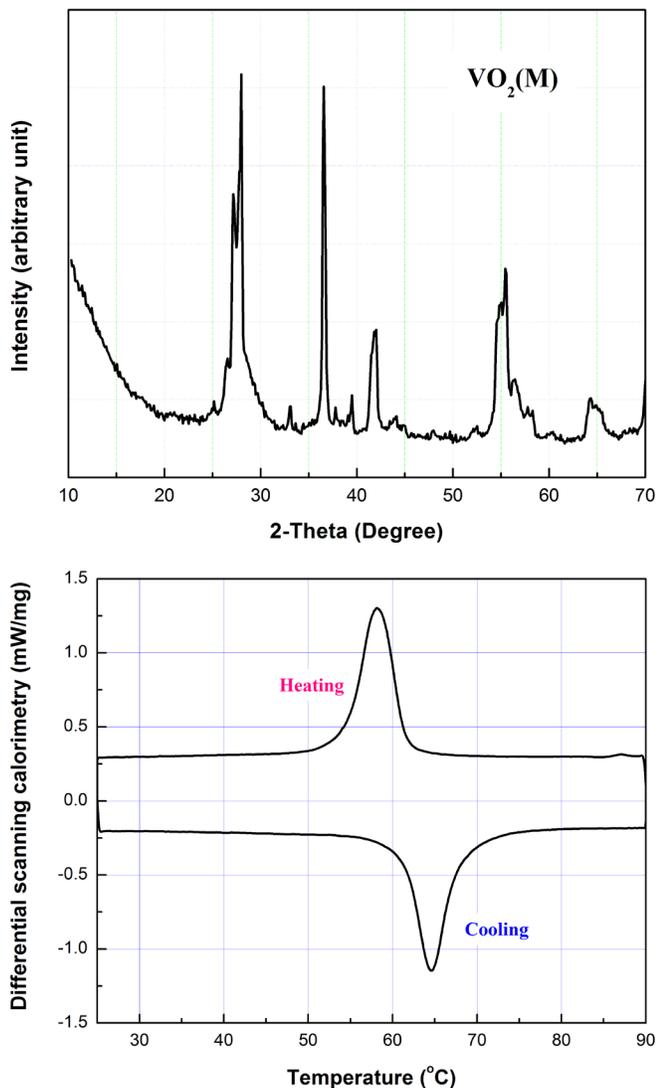


Figure 2. X-ray diffraction (XRD) (top) and differential scanning calorimetry (DSC) (bottom) results show that VO<sub>2</sub> particles after coating and annealing are M phase with transition temperature at around 65°C (heating) and 57°C (cooling).

With a small coil tubing reactor, particles are intended to be nucleated and then deposited onto the wall of the tube, which hampers the smooth carry-out of the nanoparticle product and eventually clogs the reactor tubing. After analyzing wall-sticking mechanisms and

reaction kinetics, we redesigned our reactor system and identified the corresponding optimized synthetic conditions. The experimental results show that our improved system can now smoothly manufacture nano-size M-phase VO<sub>2</sub> nanoparticles in a single step without any clogging issue. The influence of additives on flow synthesis was also investigated. The results indicate that additives can effectively alter and control the particle size, shape, and surface properties, which help control material properties, while facilitating solid product carry-out with the effluent. Our process is safe, convenient, and can easily be scaled up. The material synthesized has a good quality control in terms of particle size, shape and narrow size distribution, yet low cost owing to our wetting process. Our technique can be employed to make other nanoscale powder materials as well, an increasingly important capability since (nano) powders are the raw and feedstock materials for additive manufacturing (3D printing).

A provisional patent was filed in April 2016, and we plan on filing the patent (“Continuous Flow Synthesis of VO<sub>2</sub> Nanoparticles or Nanorods by Using a Micro-reactor”) by early FY 2017.

#### PROPOSED FUTURE WORK

In FY 2017, major project activities include the following:

1. Continuously optimize our newly fabricated, continuous-flow reaction system to grow target VO<sub>2</sub> nanomaterials with controlled size, shape, morphology, and uniformity, as well as surface properties.
2. Integrate magnesium (Mg) and tungsten (W) doping in the flow synthesis of VO<sub>2</sub> (M) nanoparticles to reduce the transition temperature.
3. Scale up the process to obtain VO<sub>2</sub> (M) nanoparticle production of tens of grams per hour by developing appropriate scaling methods; and
4. Fabricate and integrate the sol-gel coating process into our continuous flow system to continuously coat as-synthesized nanoparticles with a thickness-controlled SiO<sub>2</sub> shell.

To demonstrate our VO<sub>2</sub> powder product, we plan on making 1 × 1 ft<sup>2</sup> window films by dispersing core-shell nanoparticles into a transparent dielectric polymer matrix and then depositing them on a polymer substrate. Optical tests will be conducted and the results employed to optimize processing conditions. The ultimate goal is to have an optimized core@shell VO<sub>2</sub>/SiO<sub>2</sub> nanopowder product that is ready for a follow-on stage of manufacturing/production.

# Structure and Dynamics of Chiral Molecules and Radicals

2016-001-NO

Stephen T. Pratt and Ananya Sen

## PROJECT DESCRIPTION

The deoxyribonucleic acid (DNA) nucleosides and many of the amino acids that form proteins are chiral molecules with non-superimposable mirror images, or handedness. For the most part, the chemical and physical properties of the two forms, or enantiomers, are the same, although they interact differently with polarized light. They may also have very different biological activity. For example, most amino acids in living systems are of a specific (L) form, and most sugars in DNA nucleosides are of a specific (D) form. As a result, the different enantiomers of many chiral molecules can react very differently with biological systems. In this project, we are using photoelectron imaging techniques, tunable ultraviolet (UV) light, and photoelectron angular distributions to study the stability, reactivity, and selective detection of chiral molecules, as well as of chiral radicals formed by the photodissociation of these chiral molecules. We are also investigating molecules that only become chiral following excitation to excited states. If successful, this project will result in the development of new tools to monitor and characterize chiral molecules and radicals.

## MISSION RELEVANCE

The stability and reactivity of chiral molecules are important for both fundamental and practical applications. For example, understanding the source of chirality in the universe is essential for determining the origin of life, and understanding the reactivity and fate of chiral molecules in biological systems will almost certainly have important consequences for drug discovery and design. Development of the photoelectron circular dichroism (PECD) technique, particularly with respect to time-resolved applications, could result in new methods that could be used at DOE synchrotron user facilities, where circularly polarized UV light and X-rays are routinely available, and where time-resolved techniques are advancing to ever-shorter time scales. If our approach for characterizing chiral molecules and radicals proves successful, the work will have significant implications for the National Institutes of Health. The National Oceanic and Atmospheric Administration or the U.S. Environmental Protection Agency may also sponsor studies of the reactions of chiral radicals in the atmosphere. The work on excited-state chirality may also lead to interest from potential sponsors regarding stereospecific synthesis.

## RESULTS AND ACCOMPLISHMENTS

We initially set out to record photoelectron images following single-photon ionization of chiral enantiomers of methyl oxirane by using tunable vacuum UV (VUV) light generated by two-photon resonant, four-wave mixing in krypton (Kr). Our initial images of methyl oxirane were recorded with linearly polarized light, and their reconstructions showed good electron kinetic energy resolution in the resulting photoelectron spectra. Generating the circularly polarized VUV light necessary for PECD experiments required the addition of some polarization optics in the two-color, four-wave mixing scheme, and we have developed an approach that uses a combination of half-wave plates and a single Fresnel rhomb to produce linear polarization in the first color and circular polarization in the second color. Preliminary PECD experiments were hindered by the scattered light, and we are now working on a system of baffles to reduce scattered UV and VUV light. In the meantime, we have performed PECD experiments using a two-color pump-probe technique. In contrast to the single-photon experiments, this approach can be applied to both chiral and non-chiral molecules, although the signatures of the process are very different in the two cases. These experiments were pursued to test our ability to generate circularly polarized light and to assess the signal levels expected in future one-color experiments. Our initial experiments were performed on nitric oxide (NO), in which the first laser prepares an oriented excited electronic state, and the second laser probes this orientation by using the PECD technique. We are comparing these results with theoretical calculations performed by Katherine Reid (University of Nottingham, UK). Figure 1 shows the relatively good agreement between experiment and theory, and the strong PECD signal observed for some rotational branches in the photoelectron spectrum. This work has bolstered our confidence in our approach to producing circularly polarized light, and a publication based on this work is in preparation.

## PROPOSED FUTURE WORK

In the coming year, we will return to our VUV studies of chiral molecules and radicals. We will focus on some simpler chiral molecules such as methyl oxirane and 2-methyl-1-bromobutane. Photodissociation of the latter will produce the chiral 2-methyl-1-butyl radical, which should be relatively stable. Both the parent and radical can be ionized with low-energy VUV light, and the experiment can be simplified by tuning below the parent ionization threshold to observe photoelectrons produced only by the radical. This approach will allow us to study the time dependence of the PECD signal from the chiral radical.

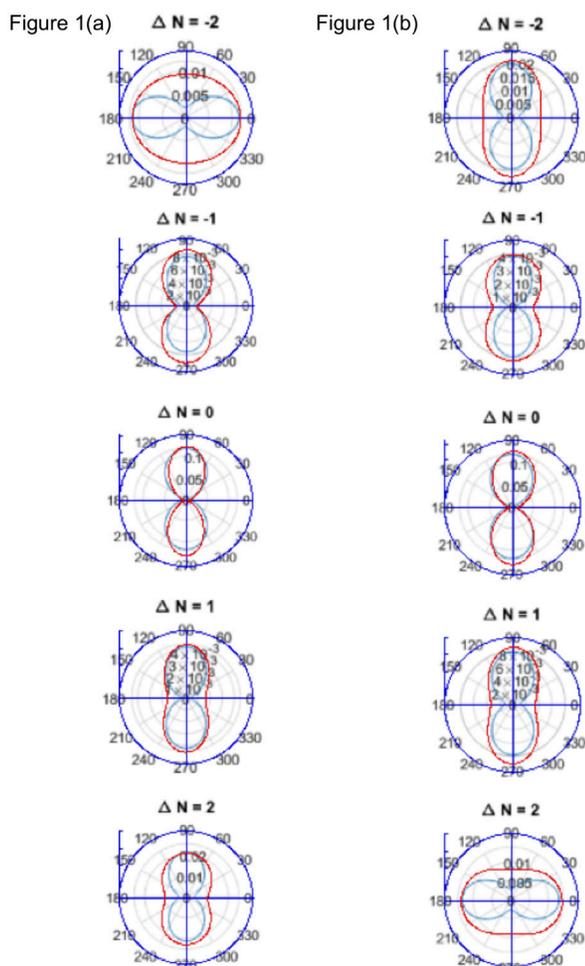


Figure 1. (a) Photoelectron angular distributions following ionization of the  $A, v' = 0, N = 15$  level of nitric oxide (NO) with a photon wavelength of 326 nm, and with a left circularly polarized pump beam and a right circularly polarized probe beam. (b) The same distributions, but with a left circularly polarized probe beam. Note that the orientation of  $\Delta N = \pm 2$  peaks reverses when the polarization of the probe is reversed, a clear signature of circular dichroism. The red curves are theoretical and the blue curves are experimental. The numbering in the plot indicates the angle between the propagation direction of the light and the direction of the detector.

## A Theory of Out-of-Equilibrium Phase Transitions

2016-010-NO

Valerii M. Vinokour and Alexey Galda

### PROJECT DESCRIPTION

The goal of the project is to develop a new direction of research that will embrace important recent developments in the physics of non-equilibrium states and that will lead to an innovative transformational science describing energy and spin transmission. The basis of this science will be the theory of strongly non-equilibrium macroscopic

quantum systems. The prospective theory will provide a quantitative description of far-from-equilibrium quantum phenomena and enable us to discover new effects, ultimately allowing us to build new energy technologies.

A general idea behind our proposed approach is that, contrary to the orthodox pessimistic viewpoint, a rigorous theoretical formalism *can* be developed and successfully applied to describe a wide range of non-equilibrium quantum systems by means of a non-Hermitian extension of the standard Hamiltonian approach. Our seed studies indicate that this goal can be achieved by introducing a complex “Hamiltonian”—the mathematical non-Hermitian operator corresponding to the total energy of the system. All dissipation mechanisms and non-equilibrium forces in the system can then be incorporated in its imaginary part. In addition, this approach provides a unique recipe to compensate for the inevitable losses in real experimental systems.

### MISSION RELEVANCE

This project is relevant to DOE’s basic science mission. It will enable researchers to exercise control over far-from-equilibrium processes. Because these processes are heavily involved in the behavior of energy and environmental systems, the project will also have long-term relevance to DOE’s energy security and environmental quality missions.

### RESULTS AND ACCOMPLISHMENTS

The idea of the approach is illustrated by the linearized Ginzburg-Landau Hamiltonian:  $H = -D \partial_x^2 - \tau^{-1} - 2i\varphi$ , where  $D$  is the diffusion coefficient,  $\tau$  is the relaxation time, and  $\varphi = E\chi$  is the potential of the electric field responsible for the non-hermeticity of the Hamiltonian. It is evident that this Hamiltonian is endowed with parity-time (PT) symmetry, given that it is invariant under the joint transformation of  $x \rightarrow -x$  (parity) and complex conjugacy (time reversal). It appears that as long as the electric field does not exceed some critical value  $E_c$ , the Hamiltonian maintains the PT-symmetry. As soon as  $E \geq E_c$ , the PT-symmetry gets broken, and nonstationary current flow accompanied by phase slip starts. In terms of the general spectral problem, the loss of the PT-symmetry means that the pairs of eigenvalues merge at the respective critical drives (see Figure 1). Thus, the loss of the PT-symmetry and the transition from the stationary to nonstationary dynamics are described as bifurcations at the spectral problem of the non-Hermitian quantum mechanics.

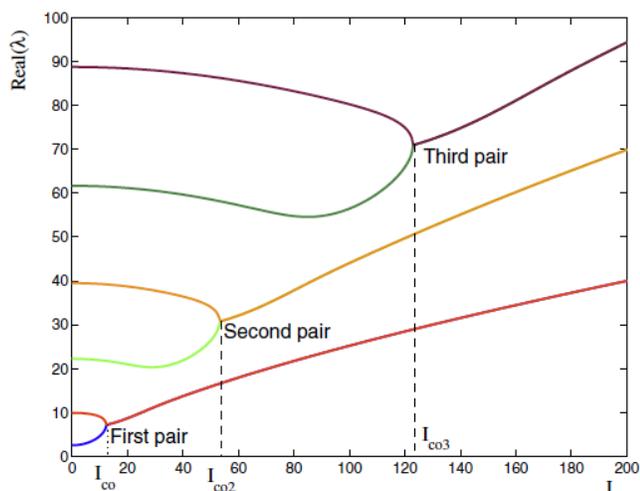


Figure 1. Real part of the first six eigenvalues of the  $PT$ -symmetric spectral problem. The parameter  $I$  is the driving current, the subscripts  $co$ ,  $co_2$ , and  $co_3$  denote the threshold currents at which the first pair of energy levels (the ground state and the first excited state), the second pair (second and third excited states), and the third pair (fourth and fifth excited states) merge, respectively.

The remarkable feature of this spectral problem is that expansion can be constructed near the bifurcation point and can describe the spectrum in the vicinity of the bifurcation. Thus, an analytical tool is provided for quantitative description of the system in the critical vicinity of the dynamic phase transition.

Another remarkable feature of the problem is that from the general viewpoint of catastrophe theory, these bifurcations belong in the so-called fold catastrophe topological class. This class of bifurcations is (topologically) protected with respect to small local perturbation of the Hamiltonian, thus preserving the symmetry of the system. Therefore, in order to establish the existence of the bifurcation and to find its type (and the corresponding expansion in the critical region), it would suffice to investigate the effective linearized Hamiltonian given above. This realization is the essence of our breakthrough in the quantitative description of out-of-equilibrium phase transitions. In the framework of this project, we intend to further develop and apply this technique to the dynamic Mott transition and to dissipative dynamics of the quantum spin systems.

In FY 2016, our specific project activities comprised:

- Developing a general theory of the dynamic vortex Mott transition with the integer frustration factor, and
- Developing a general theory for dynamic phase transition for the classical linear spin system.

## PROPOSED FUTURE WORK

In FY 2017, project activities will include:

- Performing numerical simulations of critical behavior of the dynamic Mott transition for integer fillings,
- Studying dynamic phase transitions in the Bose-Einstein condensate,
- Revealing the interconnection between the critical behaviors of dynamic and thermodynamic phase transitions, and
- Conducting in-depth investigation of the dynamic transitions in Ising models.

## Nano-Mechanical Delivery of Biomolecules into Live Bacterial Cells

2016-020-NO

Philip D. Laible and Andrey Sokolov

### PROJECT DESCRIPTION

Our understanding of the mechanisms leading some bacteria to be beneficial and some detrimental (e.g., disease-causing) to the host is limited by the fact that over half of their sequenced genes have unknown functions. Linking genes to specific microbial functions generally requires the ability to engineer the organism so as to inactivate target genes and observe the consequences. However, techniques to deliver biocompatible molecules into the bacterial cell for characterization efforts are very limited. They are mainly available for only a small number (a few dozen) of bacterial species. Here, we propose to develop a novel, potentially universal method for delivery of biomolecules into bacterial cells that is based on nano-mechanical disruption of the bacterial cell wall. Such a method has the potential to harness the diverse, mostly untapped biosynthetic capabilities of environmental microbes for biomanufacturing.

### MISSION RELEVANCE

The project addresses problems that are at the core of the DOE Office of Biological and Environmental Research (BER) Genomic Science program. These problems include understanding the basis of bacterial communities and ecosystems at a molecular level and discovering protein functions at large scale. The proposed method fits current objectives of both the Bioenergy Technologies Office in the Office of Energy Efficiency and Renewable Energy and biotechnology companies, as it opens new avenues for biomanufacturing and industrial biotechnology.

## RESULTS AND ACCOMPLISHMENTS

Novel proprietary materials, exhibiting “rough” nanoscale topologies, were fabricated using a reactive-ion etching technique. The dimensions and spacing of the surface features were similar to those of the waxy nano-protrusions found on insect wings. These wing attributes are associated with antimicrobial properties. The nanotopology (attributes and spatial arrangements of the roughness) of the material can be varied with controlled modification of the fabrication process conditions. The topography was characterized by scanning electron microscopy (Figure 1). The interaction, including bactericidal properties, of the new materials with a range of bacteria—possessing differences in the thickness and composition of cell walls and outer membranes—was also investigated (Figure 2).

Scanning electron microscopy showed directly how protrusions on the rough materials’ surface penetrated the cells and caused mechanical disruption of the specialized biological interface. In addition, fluorescent confocal microscopy revealed brightly fluorescent cells after interaction with the materials, when the cells were stained with benign dyes that label only the DNA of dead cells. These dyes penetrated the cells through holes introduced by the nanostructured material surface. Cells that interacted with smooth surfaces were non-fluorescent. The bactericidal effect appears to be generic and was confirmed for all bacteria types studied to date. Incorporation of these types of surfaces may prove to be an important design consideration in medical applications using abiotic components. We are now testing materials with surface modifications (e.g., aminosilane linkers) to facilitate noncovalent interactions of the nano-pillars with biocompatible molecules to promote adsorption from free solutions and subsequent release into the interior of cells.

## PROPOSED FUTURE WORK

We plan to discover materials attributes and process conditions for delivery of biocompatible molecules into a range of bacterial cell types. These approaches will be miniaturized and generalized to expand the application beyond the well-characterized laboratory strains that have been tested to date. The short-term focus will be proof-of-principle demonstration, with a longer-term objective of development of a microfluidics-based device. During this development phase, appropriate submissions will be made to protect any intellectual property that may arise.

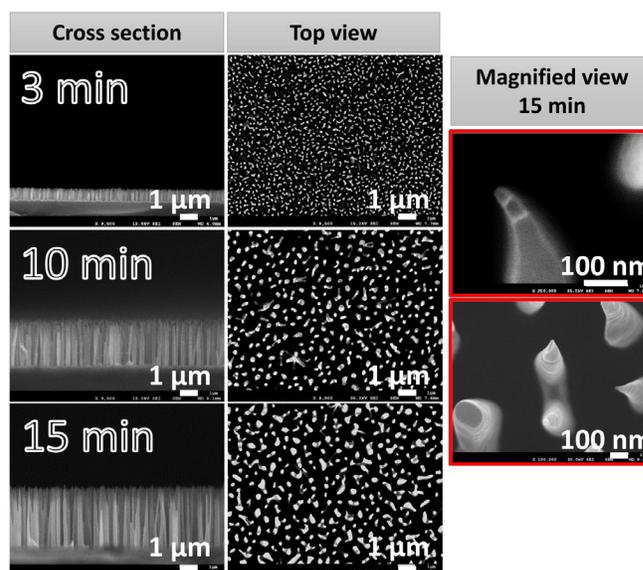


Figure 1. Scanning electron micrographs of attributes of novel materials that were etched for various periods of time and employed in bactericidal screening experiments.

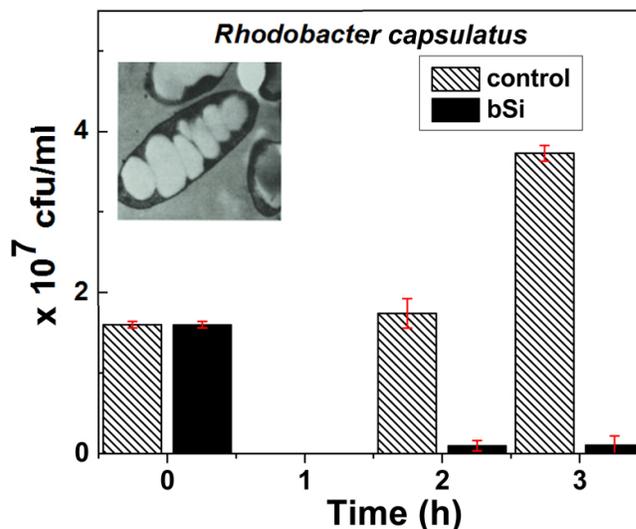


Figure 2. The abundance of cells, in terms of viable colony-forming units (cfu) per milliliter (ml), on control (smooth) and etched (rough, denoted bSi) surfaces as a function of time. Data are shown for the Gram-negative bacterium *Rhodobacter capsulatus*, for which cell death was quantitative after only a brief incubation period (<2 hours). Inset: electron micrograph of *Rhodobacter capsulatus* cells used in initial phases of materials testing.

# Real-Time Monitoring of Material Structure Evolution in Additive Manufacturing Processes

2016-023-NO

Tao Sun, Kamel Fezzaa, and Haidan Wen

## PROJECT DESCRIPTION

Additive manufacturing (AM, also known as 3D printing) refers to processes that build up parts by adding materials one layer at a time on the basis of 3D computer models. Compared with traditional manufacturing techniques, such as machining and stamping, which fabricate parts by removing materials from the bulk, AM creates customized complex products and replacement units by adding materials together with satisfactory geometric accuracy. AM exhibits unique advantages, including more efficient use of raw materials, less generation of hazardous waste, lower consumption of energy, shorter supply chains, and reduced time to market.

Most importantly, AM largely overcomes tooling constraints, and allows optimized design and fabrication of extremely complex products without the need to sacrifice the parts' functionality for ease of production. Although laser metal AM techniques have been developed over the past three decades, precisely controlling the dimensions and microstructure of the end products remains a challenge. In addition, porosity, anisotropic microstructures, surface roughness, and cracks are often found in additively manufactured parts, all of which can cause significant deterioration in their performance. To address these issues, in this project, we use high-speed synchrotron X-ray imaging and diffraction techniques to probe the laser metal AM process (specifically, the laser powder bed fusion process) *in situ* and in real time. The objectives of our study are to (1) measure the dynamic evolution of melt pool size/shape and powder ejection velocity/direction, and (2) understand the physics underpinning porosity formation.

## MISSION RELEVANCE

In the United States, manufacturing accounts for about 40% of total energy consumption, and half of the reduction in energy consumption achieved in manufacturing over the past 30 years has been through energy efficiency improvements. AM can effectively reduce energy consumption by using raw materials more efficiently, generating less waste, and reducing tooling considerably.

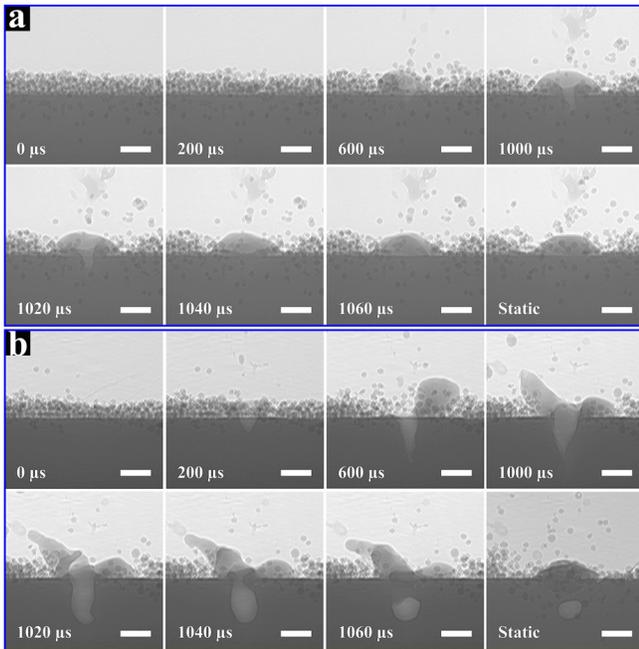
The outcome of this project will greatly advance AM techniques by providing dynamic structural information that could never be measured before, as well as the necessary physics and materials science knowledge for validating and improving current numerical models for AM processes. These project objectives dovetail with the core mission(s) of the Advanced Manufacturing office of DOE's Office of Energy Efficiency and Renewable Energy (EERE). Meanwhile, the aerospace and automotive industries have been among the early adopters of AM technology. In recent years, an increased number of parts in air and ground vehicles have been fabricated using AM.

Our work will shift the paradigm for AM R&D from the traditional trial-and-error approach, and help these industries to use AM technology to fabricate parts with higher performance and lower cost. This outcome is closely related to the goals of the DOE-EERE Transportation program. In addition, the DOE National Nuclear Security Administration, the U.S. Department of Defense (DoD) Office of Naval Research, the DoD Air Force Research Laboratory, and the National Institute of Standards and Technology have all laid out plans for supporting research on AM. Indeed, manufacturing permeates the R&D initiatives established by the President's Office of Science and Technology Policy.

## RESULTS AND ACCOMPLISHMENTS

In FY 2016, we designed and built a laser sintering apparatus as a miniature powder bed fusion system. High-speed X-ray imaging and diffraction experiments were successfully performed at the 32-ID-B beamline at the Advanced Photon Source. The results demonstrated that the dynamics of the laser powder bed fusion process could be probed with extremely high spatial and temporal resolutions (Figure 1). Algorithms were developed for identifying multiple microstructural attributes in X-ray images and tracking their evolution. Specifically, the following transient phenomena associated with laser-metal interactions were captured and quantified:

- Dynamic evolution of melt pool
- Powder spatter ejection
- Formation of process-induced and powder-induced pores; and
- Rapid metal solidification



**Figure 1.** High-speed X-ray images of laser powder bed fusion process of Ti-6Al-4V. The laser powers are 340 W for image group (a) and 520 W for group (b), respectively. The laser beam size is  $\sim 220 \mu\text{m}$ . The powder size is in the range of 5–45  $\mu\text{m}$ , and the powder layer thickness is  $\sim 100 \mu\text{m}$ . The numbers indicate the time nodes. The laser impinged the sample at  $t = 0$ , and lasted for 1000  $\mu\text{s}$ . The data were taken with a frame rate of 50 kHz. The exposure time for each individual image is 350 ns. All the scale bars are 200  $\mu\text{m}$ . In the case of higher laser power, more violent powder and melt pool motions, as well as the formation of a “keyhole” pore, can be observed.

### PROPOSED FUTURE WORK

In FY 2017, we will replace the laser head with a laser scanner in order to better emulate the powder bed fusion process. We will investigate the effects of multiple processing parameters on melt pool development, porosity, and powder ejection. These parameters will include laser power, laser scan speed and strategy, chamber environment, sample temperature, powder size and morphology, powder layer thickness, and others. We will also work with colleagues on materials simulation to build high-fidelity models for AM processes.

## A Novel Gas-Filled Microchannel Plate (GF-MCP) X-ray Polarimetry Imager

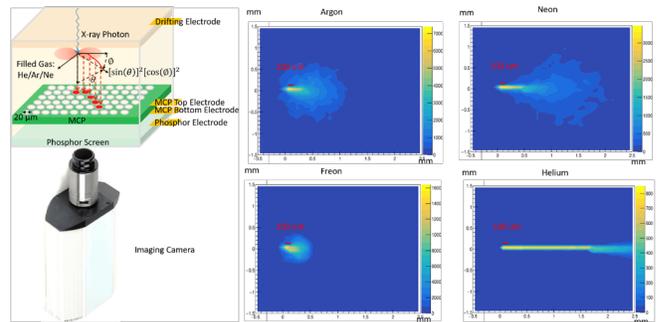
2016-027-N0

Shaolin Liao, Marcellinus Demarteau, Daniel Haskel, and Anil Mane

### PROJECT DESCRIPTION

We are studying a gas-filled microchannel plate (GF-MCP) X-ray polarimetry imager for measuring the horizontal/vertical polarization of X-ray photons. The development of the GF-MCP X-ray polarimeter is a unique extension of conventional vacuum-type MCP technology and thus can contribute to Argonne’s High Energy Physics Division’s (HEP’s) Large-Area Picoseconds Photodetector (LAPPD) effort.

The working principle of the GF-MCP X-ray polarimeter is to use MCPs to detect electron-gas ionization trajectories (from hundreds of microns to a few millimeters long) which form along the polarization direction of an energetic polarized X-ray photon (Figure 1). According to quantum physics, the coupling of the electric field of the X-ray photon with electron orbital dipole moment of an atomic electron yields a cosine squared probability distribution of an ejected photoelectron’s direction oriented along the X-ray polarization direction.



**Figure 1.** (left) Schematic of the GF-MCP X-ray polarization imager: the energetic X-ray photon ionizes the helium/argon/neon (He/Ar/Ne) gas molecule which emits a photoelectron in a direction whose probability distribution is centered at the polarization direction of the X-ray photon. The emitted photoelectron ionizes gas molecules along its trajectory. The electrons generated by that ionization drift toward the MCP, influenced by an applied electric field. Inside the MCP’s 20- $\mu\text{m}$ -diameter pores, an electron avalanche (multiplication) process occurs accompanied also by emission of photons. The amplified electron cloud drifts toward and impinges on phosphor screen, along with the emitted photons. A high-resolution (micron-level), high-sensitivity camera records the visible light emission from the phosphor screen. (right) Simulation of ionization trajectories of photoelectrons initiated by polarized X-ray photons incident upon different fill gases: argon, neon, Freon, and helium.

The GF-MCP polarimeter has impact on two R&D areas: (1) polarized X-ray spectroscopy, e.g., at the Advanced Photon Source (APS), where the GF-MCP polarimeter is expected to dramatically increase detection efficiency; and (2) X-ray polarimetry astrophysics, for which the GF-MCP array can form a large-area (square meters), panel-type polarimeter. The polarimeter can also be modified for detection and tracking of other types of particles, such as fast neutrons. The GF-MCP will operate at from 1 to 5 atmospheres pressure, depending on gas species and X-ray energy.

### MISSION RELEVANCE

Our project contributes both to DOE's science mission and to national security. It will directly add to capabilities at DOE's light sources, such as the APS, by enabling detectors/imagers for magnetic materials structure determination and for any other phenomena sensitive to X-ray polarization. Also, it contributes to HEP's programs, such as polarized X-ray astrophysics. Finally, it is also relevant to DOE's security mission as a detector/imager of fast neutrons.

### RESULTS AND ACCOMPLISHMENTS

We have performed simulations of the X-ray photon-initiated electron-gas ionization trajectories for various gas species (see Figure 1 for simulation results for argon, neon, Freon, and helium) using Garfield++, a 3D drift chamber ionization simulation software package developed at CERN for the detailed simulation of two- and three-dimensional drift chambers. Freon fill-gas was included as a potential buffer gas that could tune the ionization of the detection gas. A gas-filled test chamber was assembled for GF-MCP tests. And, we experimentally verified the spatial resolution of two cameras (the CoolSNAP HQ camera and the OWL 640 "Mini" VIS-SWIR InGaAs camera) for readout of the GF-MCP X-ray polarimeter (Figure 2).

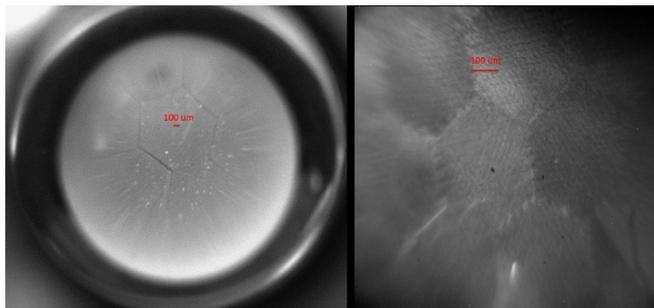


Figure 2. Experimental demonstration of micron-level spatial resolution of two cameras for imaging, via the phosphor screen, of the MCP with a pore diameter of 20  $\mu\text{m}$ : (left) CoolSNAP HQ CCD camera; and (right) OWL 640 "Mini" VIS-SWIR InGaAs camera.

### PROPOSED FUTURE WORK

In FY 2017 we will (1) design and assemble an initial version of the GF-MCP polarimetry imager; (2) evaluate the performance of different cameras for the best readout of the GF-MCP polarimeter; (3) perform laboratory tests to obtain optimized GF-MCP parameters such as gas mixture, pressure, and bias voltage; and (4) carry out polarized X-ray tests at the APS.

## A Missing Protein in the Bacterial Methylmercury Pathway

2016-048-NO

P. Raj Pokkuluri, Marianne Schiffer, and Rosemarie Wilton

### PROJECT DESCRIPTION

Some species of bacteria have the ability to transform mercury (Hg) into the extremely toxic compound methylmercury. Although some of the biochemical steps of the bacterial methylmercury transformation pathway have been elucidated, one key step, the uptake mechanism by which mercury is transported into the cell, remains unidentified. Our study is designed to elucidate the molecular determinants of this process.

Recently, two proteins, designated HgcA and HgcB, have been shown to be essential for the formation of methylmercury by two mercury-methylating bacteria. The genes for these proteins have been found in all the genomes of known mercury-methylating bacteria. However, it is not known how mercury from outside the bacterial cell is transported into the cytoplasm where these two proteins reside. One potential clue to this process may lie in the observation that mercury uptake requires energy; this finding suggests an active transport mechanism. Second, it has been shown that binary compounds of zinc, Zn(II), and of cadmium, Cd(II), are significant inhibitors of mercury uptake by these bacteria, which implicates metal ion transport mechanisms in mercury uptake. On the basis of these studies, we hypothesized that periplasmic solute-binding proteins (SBPs), known to bind and transport Zn(II) into the cytoplasm, could be involved in mercury transport in these bacteria. Therefore, we undertook the study of the metal ion-binding properties of potential Zn(II)-binding SBPs from two mercury-methylating bacteria, *Geobacter sulfurreducens* strain PCA and *Desulfovibrio desulfuricans* strain ND132.

## MISSION RELEVANCE

Transformations of the pollutant mercury into its various forms in the ecosystem is of significant interest to DOE Subsurface Biogeochemical Research part of the Office of Biological and Environmental Research, the National Institutes of Health, and the U.S. Environmental Protection Agency. Mercury pollution poses serious environmental and human health risks; the main concern is the formation of methylmercury that makes its way up the food chain. Methylmercury is a potent neurotoxin that is shown to cause neurodegeneration. The research proposed will contribute to delineation of the molecular pathways leading to the formation of methylmercury.

## RESULTS AND ACCOMPLISHMENTS

**Cloning Zn(II)-binding SBPs from *G. sulfurreducens*, *D. desulfuricans*, and *E. coli*:** We identified two potential Zn(II)-binding SBPs, one from *G. sulfurreducens* and another from *D. desulfuricans*, on the basis of sequence similarity to the known Zn(II)-binding SBP from *E. coli*, designated as “Zn uptake protein A” or ZnuA. Genes encoding ZnuA proteins were cloned into expression vectors using synthetic deoxyribonucleic acid (DNA) optimized for expression in *E. coli*. Examination of ZnuA from *G. sulfurreducens* indicated possible disorder at the N-terminus region of the protein; therefore, to enhance crystallizability of the expressed protein, in addition to the full-length protein, a second variant of ZnuA from *G. sulfurreducens* was constructed by deleting the first 12 amino acids.

**Protein Expression and Purification:** Good expression of *D. desulfuricans* ZnuA and both the constructs of *G. sulfurreducens* ZnuA were obtained, with yields ranging from 26 to 74 mg per liter of starting culture. Expression of the control protein, *E. coli* ZnuA, was poor under all conditions tested; we are exploring other strategies to express and purify this protein. The target proteins were purified from bacterial lysates by standard affinity chromatography, and the final purified proteins were concentrated and used for the experiments described below.

**Differential Scanning Fluorometry (DSF):** Assays to determine the effect of various divalent metal ions on the protein thermal stability were carried out using DSF. We demonstrated that the metal ions Zn<sup>2+</sup>, cobalt (Co<sup>2+</sup>), and Hg<sup>2+</sup> increase thermal stability, suggesting a significant interaction between these metals and the protein (data for Zn<sup>2+</sup> and Hg<sup>2+</sup> are shown in Figure 1). The metals magnesium (Mg<sup>2+</sup>), calcium (Ca<sup>2+</sup>), manganese (Mn<sup>2+</sup>), nickel (Ni<sup>2+</sup>), and Cd<sup>2+</sup> did not have any effect on stability, indicating that binding of these metals is unlikely. The

DSF assay results support our hypothesis that the Zn(II)-binding SBPs bind Hg<sup>2+</sup>, and we are continuing studies to determine the details of the interaction.

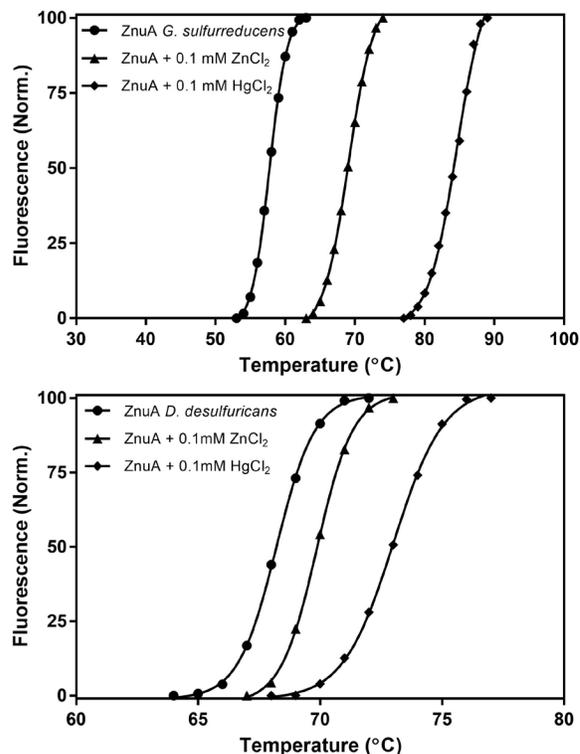


Figure 1. Effect of metal ions, Zn<sup>2+</sup> and Hg<sup>2+</sup>, on thermal stability of the solute binding proteins studied. Top: ZnuA from *G. sulfurreducens*. Bottom: ZnuA from *D. desulfuricans*

**Crystallization:** The SBP proteins produced in *E. coli* are known to bind endogenous ligands during their production. Therefore, it was imperative to identify any ligands associated with these proteins before proceeding to determine their role in mercury binding. The structural information obtained can establish the ligand status of the proteins as isolated from *E. coli*. Crystallization trials of the purified SBPs were carried out. Crystals of suitable size were obtained from both constructs of ZnuA from *G. sulfurreducens* but not from ZnuA of *D. desulfuricans*. Although SBPs have been known to produce well-diffracting crystals in many cases, the crystals of ZnuA that we obtained diffracted X-rays poorly (to about 6 Å resolution).

## PROPOSED FUTURE WORK

**Mercury Binding Studies:** We will use inductively coupled plasma-atomic emission spectroscopy to determine whether there is any metal ion bound to the SBP proteins as isolated from *E. coli*. In case the proteins isolated do have a bound metal ion (e.g., Zn<sup>2+</sup>), the ethylenediaminetetraacetic acid (EDTA) extraction method

will be used to prepare protein samples devoid of metal ions (ApoZnuA) for mercury binding studies. If the EDTA extraction proves unsuccessful in removing the metal ion bound to the protein, the more drastic approach of unfolding and refolding the proteins will be carried out using common protein denaturing agents, such as urea or guanidinium hydrochloride. The binding affinity of  $\text{Hg}^{2+}$  will be determined by isothermal calorimetry.

*Characterization of Mercury Binding Site:* When conditions for mercury binding are refined, EXAFS will be used to characterize the mercury binding site in these SBPs. Extensive crystallization trials will be carried out with the Hg-bound SBP samples. Upon obtaining suitable crystals, X-ray diffraction data will be collected and structures will be determined to fully delineate the mercury binding site (i.e., to identify protein residues binding mercury and the binding geometry) in these proteins.

## Perovskite Halide-Based Intermediate-Band Solar Cells

2016-054-N0

Alex Martinson and Maria Chan

### PROJECT DESCRIPTION

Intermediate-band (IB) solar cells are designed to retain the high-output voltages of large-bandgap semiconductors while harvesting significantly more of the solar spectrum, thereby approaching the Shockley-Queisser limit of solar conversion efficiency. By using the IB as a stepping-stone, electron-hole pairs may be generated from photons with insufficient energy to pump electrons directly from the valence band to the conduction band. However, it appears likely that an absorber base with outstanding photophysical properties and novel substitutional control will be required to achieve the excited-state lifetimes necessary for successful charge extraction. We propose to computationally screen, synthesize, and characterize the optoelectronic properties of a new class of bulk IB materials based on perovskite halides. By utilizing the rapidly expanding base of perovskite halide materials known to exhibit exceptional optoelectronic properties (e.g., methylammonium lead iodide,  $\text{MAPbI}_3$ , or  $\text{CH}_3\text{NH}_3\text{PbI}_3$ ) and the predictive power of *ab initio* density functional theory (DFT), we will develop an IB absorber with nearly ideal band gap and IB energy level spacing. The objective of this work is to probe the extent to which substitutionally doped hybrid perovskites satisfy the demands of an IB solar absorber, and to demonstrate their use in a photovoltaic (PV) device that operates according to IB

principles. We further propose to investigate the complex photophysics expected from the multilevel system using time-resolved optical spectroscopies. The objective of this task is to probe, for the first time, the mechanism of excited-state excitation and relaxation as a function of material composition.

### MISSION RELEVANCE

This project supports DOE missions in energy and the environment. From a practical perspective, if a perovskite halide IB material can be fabricated into an efficient PV device, there is an opportunity to extend the remarkable rise of PV efficiency beyond the 30% ceiling. Increases in efficiency are more important now than at any time in PVs' history, owing to balance-of-system costs (siting, permitting, installation, etc.) that now exceed module costs. Higher PV efficiencies have a compounding effect because of reductions in the *overall cost/watt* of PVs, which includes land use, hardware, installation, and maintenance. Indeed, even small gains in efficiency, combined with the outstanding scalability, cost, and efficiency (20%) of existing hybrid perovskite PVs, would exceed the economics needed to drive widespread displacement of the current energy infrastructure.

### RESULTS AND ACCOMPLISHMENTS

The substitution of transition metals for lead (Pb) in  $\text{ABX}_3$  hybrid perovskite halides was undertaken computationally and experimentally. DFT calculations predict that a significant density of states may be generated between the parent compound valence band maximum and conduction band minimum with appropriate transition metal substitution—here, cobalt (Co) and iron (Fe). We find striking experimental evidence for Co incorporation at up to 33% of Pb sites without significant changes to crystal structure, lattice constants, or radiative recombination rate (Figure 1). Steady-state absorption spectroscopy (Figure 2) reveals a new, apparently unfilled density of states, as revealed by new ground state absorbance between 1.6 and 2.0 eV, which we hypothesize to be closer to the parent conduction band. As such, the substitutional alloy represents a promising new perovskite material with an additional mid-gap absorption, with potential application as a future IB absorber. Although proper IB principles require the IB to be half-filled, with further investigation into means of tuning the occupancy of the Co-related mid-gap states, a material may be realized that is suitable for use in an IB solar cell.

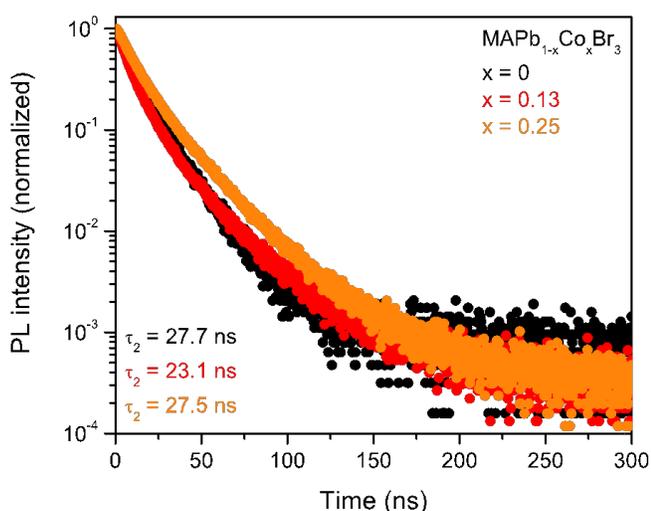


Figure 1. Time-resolved photoluminescence (PL) of Br-only ( $y = 0$ ) films revealing very little dependence on  $x$ .

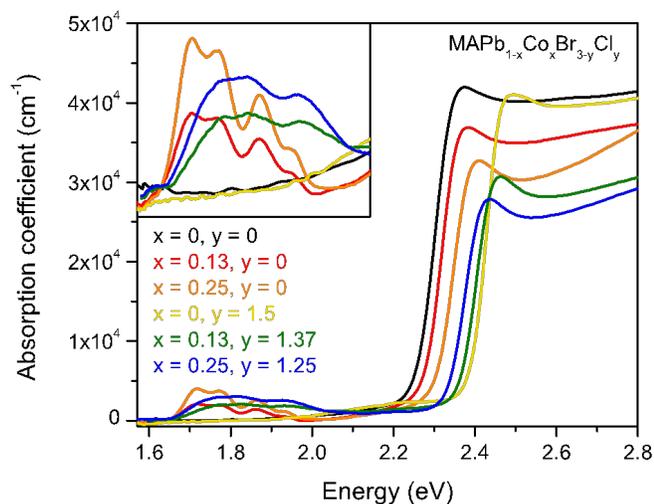


Figure 2. Ground state absorption spectra of  $\text{MAPb}_{1-x}\text{Co}_x\text{Br}_{3-y}\text{Cl}_y$  thin films.

### PROPOSED FUTURE WORK

Future studies will focus on moving the Fermi level into the IB in order to achieve the second ground state sub-gap absorption required for efficient IB PV operation. The novel materials are outstanding candidates for study of the unique and complex photophysics expected from the multilevel system. To the best of our knowledge, no time- and energy-level-resolved spectroscopic work has been performed on bulk IB materials, likely owing to their complexity and typically short lifetimes. The time-resolved dynamics of absorption, free carrier generation, charge separation, and relaxation are, of course, of paramount importance to IB PV device operation. Ultra-fast transient absorption and time-correlated single photon counting of luminescence will be used to probe carrier dynamics as a function of composition.

## Efficient Droplet-Based Environmental Mechanical Energy Harvesting through Reverse Electrowetting

2016-063-N0

Oleksiy Snezhko and Gasper Kokot

### PROJECT DESCRIPTION

Microfluidic-droplet-based energy harvesting, exploiting the reverse electrowetting process, promises a high areal energy harvesting efficiency. The method is based on generating electrical energy by changing the overlap between the droplet and the electrode interface. When voltage is applied to conductive droplets on an electrically insulating dielectric layer covering a flat electrode, they spread on the surface. This phenomenon is known as electrowetting. Extra electrostatic energy provided by applied voltage partially compensates for the droplets' interfacial energy. If a constant bias voltage is applied to the electrodes and the interface overlap between the droplets and the electrodes is decreased by other means (for instance, mechanically), the excess charge generates current—a mechanism also known as reverse electrowetting. The energy is generated by a mechanical actuation coming from a vibration, shear, or pressure.

The goal of this project is to develop and optimize a microfluidics-based environmental mechanical-energy harvester with an enhanced efficiency compared to currently available realizations for two different mechanical actuation mechanisms (i.e., shear and vibrations). To maximize the efficiency of the portable droplet-based energy harvesters, the surface-to-droplet volume ratio for the electrodes, electrode patterning schemes, and energy-harvesting layer stacking will be optimized. Typical sizes of the droplets will be scaled down to the microscale. These advances will enable an important step toward viable droplet-based energy harvesting.

### MISSION RELEVANCE

One of DOE's primary missions is the development of novel, renewable energy sources. Energy harvesting from mechanical movements opens up the possibility of extracting energy from vibrating car engines, buildings, bridges, or land next to a highway. Gaining electricity from dispersed local sources in this way would reduce the burden on the U.S. electric grid. The project, therefore, is related to one of DOE's core missions.

## RESULTS AND ACCOMPLISHMENTS

To generate microdroplets of a liquid metal (Galinstan) in microfluidic channels, microfluidic junctions based on the T-junction method have been designed and fabricated. In this method, two immiscible liquids are pushed into separate channels with external pressure sources (microfluidic pumps). The carrier solution follows the straight channel, and the droplet solution meets the T-junction at 90°. By varying the differential pressure of the inlets, a regime is achieved where the liquid material breaks off into droplets. The differential pressure is also used to control the droplet size and the spacing between the generated droplets. T-junction microdroplet generators with square channels down to 10  $\mu\text{m}$  deep were fabricated. To minimize the pinning of the generated droplets to the microfluidic channels, the walls of the device have to be coated with fluoropolymers. For this purpose, a fluoropolymer vapor coating setup has been developed. The operation of the setup was tested at temperatures up to 220°C with a flow of inert gas ( $\text{N}_2$ ) under medium vacuum conditions (15 Torr). Corresponding software has been developed in LabView to run the system.

## PROPOSED FUTURE WORK

During FY 2017, the project will focus on high-resolution measurements of contact angle dynamics in low-voltage and saturation regimes in order to optimize the channel coatings and carrier solutions and thus minimize contact angle pinning and charge trapping in the channel with droplets. We will also design and fabricate droplet-generating channels with dimensions down to 1  $\mu\text{m}$ .

# GO-IN-EM – Genetic algorithm Optimization of Interface structure from Electron Microscopy

2016-069-NO

Maria Chan, Fatih Sen, and Jianguo Wen

## PROJECT DESCRIPTION

Solid-solid interfaces are important for determining materials properties in a wide variety of systems, yet characterizing these interfaces via both experiments and computational modeling remains challenging. In particular, the interfacial region is often poorly imaged by electron microscopy, even if atomic resolution is achieved away

from the interface. In this project, we use a combination of atomistic modeling and a multi-objective genetic algorithm in conjunction with transmission electron microscopy (TEM) and image-matching algorithms to solve this problem and produce three-dimensional atomistic structures of complex solid-solid interfaces.

## MISSION RELEVANCE

Enhancing materials understanding, design, and development is central to DOE's energy security and scientific discovery missions. As use-inspired science, the present work falls under the purview of DOE's Office of Basic Energy Sciences. This work improves materials characterization, including *in situ* and *operando* studies, by automating the construction of three-dimensional atomistic models from two-dimensional electron microscopy data, thereby allowing for rapid understanding of solid-solid interfaces and prediction of properties based on the atomistic structure. The central theme of rapid materials understanding and design is also a key focus of the Materials Genome Initiative and the National Strategic Computing Initiative.

## RESULTS AND ACCOMPLISHMENTS

In FY 2016, we developed approaches, equipment, and software which (1) improved the resolution and dynamic capturing of TEM images, (2) effectively compared and matched computed and measured TEM images, and (3) improved the speed and scalability of construction of interfacial models from the two crystal structures on each side of the interface and genetic algorithm optimization of atomistic structures.

### (1) TEM Resolution Improvement and Dynamic Imaging

Our project requires that high-resolution TEM images meet two basic requirements: high resolution (HR) and high contrast. In FY 2016, we developed a new electron microscopy imaging mode that exploits atomic-resolution amplitude contrast imaging (ACI) to provide atomic-scale elemental and structural information in one directly interpretable image. ACI was achieved on solid-solid interfaces of perovskite oxide superlattices (Figure 1) by correcting the values of spherical and chromatic aberrations of the objective lens to very low levels. We also obtained, adapted, and tested a Gatan double-tilt heating stage to directly observe the motion of solid interfaces under electrical biasing using HRTEM. We modified the heating stage for application of an electrical bias voltage across a TEM specimen.

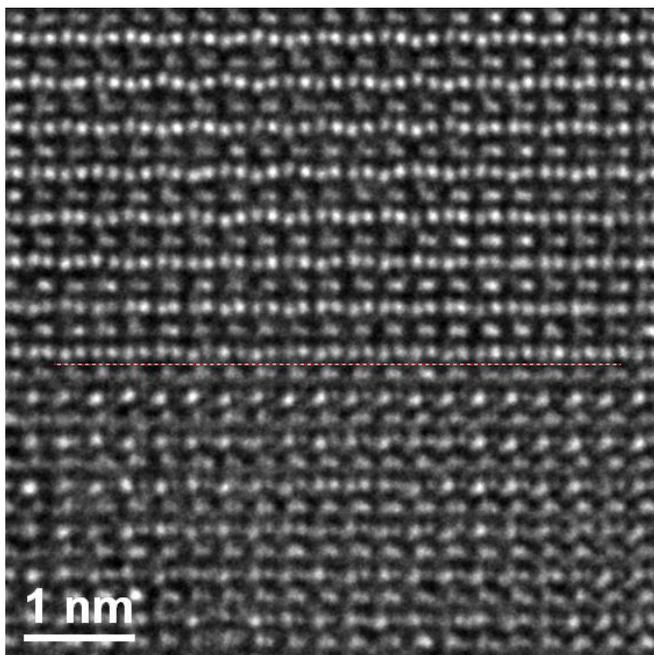


Figure 1. HRTEM image of a domain wall (red line) in bismuth ferrite ( $\text{BiFeO}_3$ ). Solid-solid interfaces such as this have important effects on the properties of functional materials.

## (2) Image-Matching Algorithms

We must be able to computationally assess the matches between a large number of simulated S/TEM images (queries) and a corresponding measurement (target). Toward this goal, a set-to-set similarity definition is needed. In FY 2016, we implemented four methods and assessed their utility and effectiveness in this image similarity task. We found that scale-invariant feature transform (SIFT), which provides a coherent framework for detecting and describing local image feature in a translation-, scale-, and rotation-invariant manner, is a suitable approach for image comparisons and is capable of selecting, out of hundreds of candidates, a match for a dislocation structure (Figure 2).

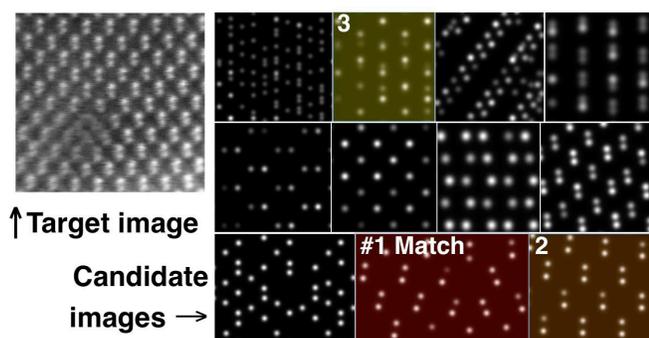


Figure 2. SIFT was used to find a match for an experimental TEM image of a dislocation core in cadmium telluride (CdTe) among a library of images of bulk and defected CdTe.

## (3) Grain Boundary Genie and Genetic Algorithm Codes

In order to efficiently automate the building of interfacial atomistic models, we have ported the Grain Boundary Genie code (previously co-developed in our group at Argonne) to the Python programming language and performed extensive testing by creating thousands of grain boundary structures. We have also developed and improved our genetic algorithm code for low-symmetry configurations including nanoparticles.

## PROPOSED FUTURE WORK

In the coming year, we plan to:

1. Carry out the *in situ* experiment to record dynamical motion of domain walls. The time scale for domain motion is in the range of  $10^{-3}$  seconds, which is the range of our Gatan K2 camera recording capability. Using the ACI technique, we expect to produce TEM images that indicate oxygen octahedral rotations when domain walls move.
2. Continue the development of image matching algorithms by SIFT and integration of image comparison and simulation codes into a high-throughput framework.
3. Extend the current single-objective genetic algorithm code to treat constrained multi-objective optimization at solid-solid interfaces, and integrate image simulation, matching, and energy evaluation codes into a complete software package.

## Top Down Fabrication of Large Area Monolayers of 2D Materials

2016-082-N0

Subramanian Sankaranarayanan, Mrinal Bera, and Mathew Cherukara

### PROJECT DESCRIPTION

The search for novel two-dimensional (2D) materials beyond graphene has attracted considerable attention because of their exotic physical properties like room temperature quantum Hall effect, charge density waves, high-temperature superconductivity, superlubricity, and high carrier mobility when the thickness is reduced to a monolayer or a few layers. Although these unique properties have led to prototype devices and applications, the eventual transition into commercially viable technologies would require large-area, scalable, and controllable growth of monolayers or a few layers.

Fundamental insights into the growth and synthesis of 2D materials are therefore needed to enable scalable and rapid formation of possibly monolayer and single-crystalline 2D materials. The current state of the art relies heavily on chemical vapor deposition (CVD), which has recently been optimized to grow large-area 2D materials.

The success of CVD is, however, dependent on the availability of precursors and optimized conditions like temperature, pressure, and air flow. Also, the CVD-grown samples may suffer polycrystallinity and non-uniform thicknesses, which limit the quality of the samples. So far, the best-quality samples of 2D materials have been obtained with mechanical exfoliation from naturally occurring single crystals, which by its very nature can produce randomly distributed flakes of different thicknesses ranging from monolayers ( $\sim 0.6$  nm) to a few layers ( $\sim 50$ – $100$  nm). Also, the lateral dimensions of the flakes are limited to only a few micrometers, and the probabilities of getting thinner layers are quite low and uncontrollable.

To overcome these challenges, we propose to develop a new top down fabrication electrochemical exfoliation method that would allow for synthesis of large area monolayers of a broad class of 2D materials.

### MISSION RELEVANCE

Achieving an eco-friendly, large-scale synthesis route to exfoliate 2D materials down to single/few atomic layers will help realize unique functional flexibility, new properties, and novel applications. The major limitation of using 2D materials, except graphene, in consumer products is the synthesis of high-quality large-area uniform mono- or few layers. The success of the proposed research will overcome enormous technological barriers and open the door for the industrial implementation of 2D materials, which will find application in large screen displays for TVs and smartphones, tunable optical detectors, mechanical resonators, and even gas sensors. Our project will strengthen materials research in the low-power electronics area, which is a strategic mission of DOE programs such as Advanced Power Electronics and Electric Motor R&D Program and broadly within programs supported by Advanced Research Projects Agency-Energy (ARPA-E), the Office of Energy Efficiency and Renewable Energy (EERE), and the Office of Science. This development could be used in the design and fabrication of innovative devices. In addition, the success of the project would create the opportunity for basic scientific research in terms of recently observed proximity effects for all 2D materials.

### RESULTS AND ACCOMPLISHMENTS

During FY 2016, we developed (experimentally and theoretically) a very simple, cheap, fast, and scalable process for preparing large-area single-crystalline monolayers of 2D materials based on electrochemical exfoliation. Simultaneously, we explored, via reactive atomistic simulations, the role of substrate interactions in the growth of large-area 2D materials via both the CVD and electrochemical exfoliation methods. Overall, our experimental and theoretical findings afford valuable insight for the first rational route to preparing practical quantities of monolayer, processable single-crystalline and large-area 2D materials.

We demonstrated an electrochemical technique, hereafter referred to as the electro-ablation (EA) technique, for room-temperature synthesis of monolayers of semiconducting transition metal dichalcogenides (TMDs) on a conductive substrate. The lateral dimensions of the monolayers obtained within a few seconds at room temperature were as large as 0.5 mm. The temporal and spatial dynamics of this physical phenomenon, studied on MoS<sub>2</sub> flakes using *ex situ* atomic force microscopy (AFM) imaging, Raman mapping, and photoluminescence measurements, trace the origin of monolayer formation to a substrate-assisted self-limiting electrochemical ablation process. Electronic structure and atomistic calculations point to the interplay among three essential factors in the process: (1) strong covalent interaction of monolayer MoS<sub>2</sub> with the substrate; (2) electric field-induced differences in Gibbs free energy of exfoliation; and (3) dispersion of MoS<sub>2</sub> in an aqueous solution of hydrogen peroxide. We are in the process of extending the EA process to obtain monolayers of other 2D TMDs.

Our initial results show that the EA technique is generic and can be applied to the synthesis of monolayers of most of the semiconducting TMDs. As shown in Figure 1, the EA technique was also applied to other semiconducting TMDs, e.g., WS<sub>2</sub>, WSe<sub>2</sub> and MoTe<sub>2</sub>. The optical micrographs and Raman shift data show monolayer formation for WS<sub>2</sub> and MoTe<sub>2</sub>. Consistent with these findings, our density functional theory (DFT) calculations showed that similar to MoS<sub>2</sub> the binding energy of these monolayers with a substrate such as TiN is much stronger than the interlayer van der Waals interactions; e.g., the binding energy between WS<sub>2</sub> and TiN was found to be -1.63 eV, while the interaction energy between consecutive layers was much lower (-0.16 eV). However, in the case of transition metal diselenides (e.g., WSe<sub>2</sub>), our EA technique removed the monolayer as well, despite DFT binding energy trends similar to those for MoS<sub>2</sub>.

This finding suggests that for the case of diselenides, there are additional factors (apart from binding energies) that play a major role in governing the EA process. These key atomic-scale factors are most likely (a) the specific chemistry of selenium interactions with  $\text{H}_2\text{O}_2$  and (b) sluggish kinetics of diselenide monolayer binding with TiN as compared to the rate of removal under electrochemical conditions; a comprehensive investigation of such factors is beyond the scope of this report.

Given the importance of substrate-monolayer interactions, we have also developed atomistic models of growth of 2D materials. We are studying vapor phase deposition as a stepping-stone towards understanding the more complex EA process. These studies will help us better understand the interactions between the substrate surface and the 2D material of interest. As a representative case, we investigated the growth of a monolayer of silicene on an Ir(111) surface via atom-by-atom deposition of Si (similar to CVD) using large-scale molecular dynamics simulations at 1000 K.

### PROPOSED FUTURE WORK

During FY 2017, detailed studies of the impact of the substrate and electrolyte solution are required to optimize the EA technique for other material systems and to provide a full understanding of the mechanism leading to the formation of monolayers of semiconducting TMDs. For instance, the nature of the passivation of TiN and its role in the EA technique are open-ended issues. We will perform controlled experiments to address these issues.

We will also develop atomistic models to study the vapor phase growth of 2D materials on substrates (Figure 2). Our preliminary study of silicene growth on Ir(111) suggests that the formation of extended defects such as line defects and multiple grains is controlled by the competition between the rate of deposition of Si atoms and the diffusion of Si on the Ir(111) surface. A systematic study of this competition is currently underway. More importantly, as suggested by previous DFT calculations, the Ir-Si interactions are primarily of the non-bonding type, and the growth of silicene does not entail disruption of the Ir(111) surface or pull-out of surface Ir atoms (as is necessary for other substrates like Ag). Such detailed molecular dynamics models will be developed in FY 2017 for the various proposed 2D materials as well.

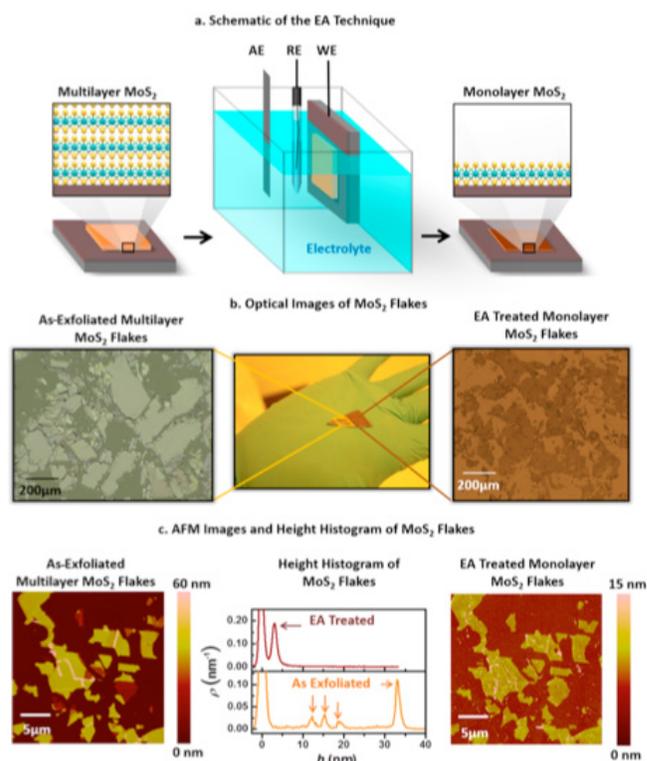


Figure 1 (a) Schematic illustrations of the electro-ablation (EA) technique, which involves the exfoliation of large-area multilayered MoS<sub>2</sub> flakes (left panel) on a silicon (Si) substrate coated with 100-nm conducting TiN film, followed by an EA process carried out in an electrochemical cell (middle panel), which results in the formation of monolayers of MoS<sub>2</sub> (right panel). The TiN/Si substrate with exfoliated MoS<sub>2</sub> flakes acts as the working electrode (WE), the Ag/AgCl half-cell acts as the reference electrode (RE), and Grafoil (Graftec Corp.) acts as the auxiliary electrode (AE). (b) Optical images of mechanically exfoliated large-area MoS<sub>2</sub> flakes on a TiN/Si substrate before (left panel) and after (right panel) the EA treatment. (c) Atomic force microscopy (AFM) images of mechanically exfoliated MoS<sub>2</sub> flakes of different thicknesses (left panel) and uniformly thick monolayers of MoS<sub>2</sub> after the EA treatment (right panel), along with histograms of the height profiles of both images (middle panel).

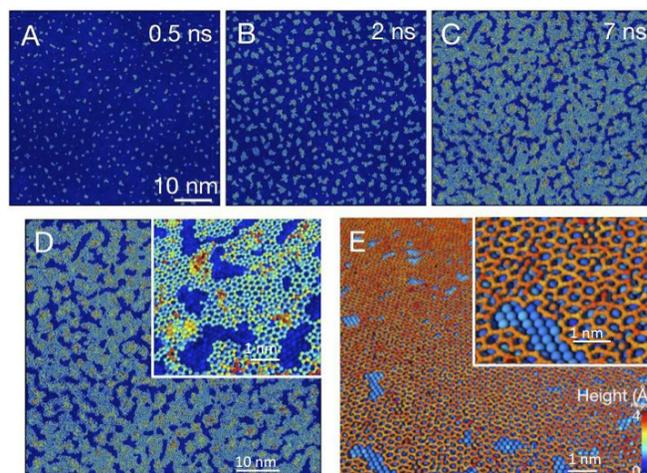


Figure 2. Growth of silicene on metal substrates. The silicene atoms are colored according to their height from the substrate; the substrate atoms are shown in blue. (A–C) Temporal evolution of structure during our molecular dynamics simulations of atom-by-atom growth. (D) Sub-surface growth and formation of multiple layers of silicene when grown on Ag(111). (E) On Ir(111), a near-perfect uniform deposition of monolayer silicene is observed.

# Spin Vortex-Based Non-Volatile Superconducting Memory

2016-092-N0

Valentine Novosad

## PROJECT DESCRIPTION

We are developing a hybrid memory architecture that marries the best features of magnetic memory with high-fidelity superconducting electronics. The concept has significant advantages over existing memory architectures. First, it requires much lower power to alter the state of a memory element than the state-of-the-art spin-torque-based systems, because our scheme relies on resonant spin excitations. Second, the dynamic switching is in the range of microwave frequencies, so pulses with these frequencies are readily available in the logic boards. Third, a multiplexed SQUID readout scheme makes the integration density scalable with the Q-factor of the cells and the reduced nanomagnet size (increased resonant frequency of vortex core oscillation). Finally, the memory is nonvolatile up to the Curie temperature of the magnetic structure (i.e., even above the cryogenic temperatures). This memory would ultimately be operating at low temperatures; one target application is a memory component in a low power quantum computing architecture (where all processing hardware is inherently cryogenic). The fact that the memory is nonvolatile even at elevated temperatures (e.g., at room temperature) may be an added benefit as it prevents the data from being lost during the cryostat warm up.

## MISSION RELEVANCE

The scope of this proposal is well aligned with DOE Office of Science missions to advance our understanding of nature and the energy, economic, and national security interests of the United States. This proposal also addresses the materials sciences and engineering mission of the Office of Basic Energy Sciences through development of materials with novel structures, functions and properties. Superconducting computers could solve problems impossible for today's and even tomorrow's most anticipated powerful supercomputers. The ability to design, develop, test, and implement novel superconducting memory architectures will be a major step forward, opening up new and exciting possibilities for future R&D on superconducting computing.

## RESULTS AND ACCOMPLISHMENTS

This project aims to develop a hybrid memory architecture based on spin vortices (Figure 1, inset in the lower left corner) and compatible with cryogenic temperatures. Thus, the main focus is to explore the dynamic response and the manipulation of spin vortices at low temperatures. We performed extensive micromagnetic modeling and experimental work at room temperature in order to explore the magnetic phase diagram of radio frequency (RF) magnetic field-driven vortex core reversal. We have established that the core ordering can be achieved even when the excitation frequency is off-resonance, provided that the excitation amplitude is increased accordingly.

This finding is important, as it confirms that some (inevitable) dot-to-dot variations in the realistic memory array will not prevent selectively "writing" or "reading" the magnetic state via resonant excitation. We have also found that the vortex core eigenfrequency will be influenced by the magnetic field screening effect from the superconducting stripline. Therefore, we have explored how to control the resonant frequencies by, for example, altering the dot topography (i.e., without changing the overall geometry of the element). By using pre-patterned substrates, we were able to obtain a strong geometric confinement effect, which was confirmed experimentally and numerically. This result allows us to significantly expand the dynamic range of future memory cells. Furthermore, several kinds of magnetic materials, including nanocrystalline iron-nickel-molybdenum (Fe-Ni-Mo), amorphous iron-cobalt-boron (Fe-Co-B), and single-crystal iron-cobalt-manganese-silicon (Fe-Co-Mn-Si) Heusler alloy thin films, were prepared; these are being characterized now in terms of their overall magnetic properties and high-frequency losses. In addition, we have modified an existing cryogenic measurement setup for performing high-frequency measurements at low temperatures. This system will allow us to further optimize the microfabrication procedures via feedback from cryogenic measurements of the devices.

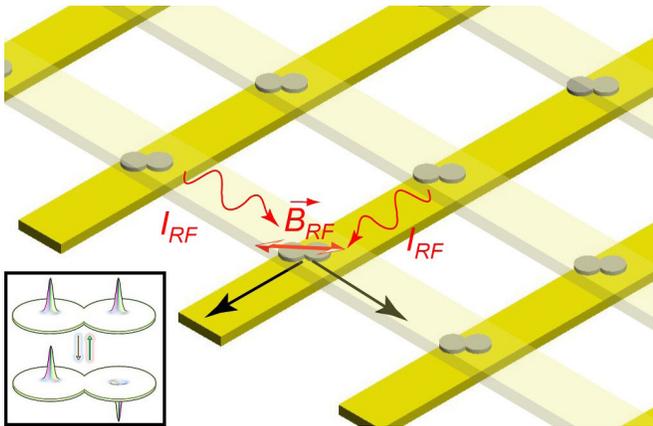


Figure 1. This schematic depicts setting up the vortex polarities (lower left corner inset) in a single double-dot ferromagnet by application of two synchronized RF pulses ( $I_{RF}$ ) along the microstrip lines leading to the desired memory element. The geometrical anisotropy of the double-dot is used to selectively trigger the vortex core flip by the resonant RF magnetic field produced by the two pulses. Note the direction of the resulting  $B_{RF}$  with respect to the “easy” axis of the magnetic double-dot. The inset shows two different magnetic states.

### PROPOSED FUTURE WORK

We are in the process of finalizing the microfabrication protocols and shifting toward optimizing the memory performance from the standpoint of writing speed and power by optimizing geometries and materials. We will also start designing the memory-containing chain of elements, compatible with low-temperature-readout electronics. Two different readout schemes will be tested.

## Ordered Core-Shell Nanostructure for Transverse Thermoelectric Applications

2016-094-N0

King Chen, Dileep Singh, and Ziyao Zhou

### PROJECT DESCRIPTION

Over the past 10 years, experiments have shown that both the Thermoelectric Figure of Merit (ZT) and the Power Factor (PF) can be higher in transverse thermoelectric (TTE) devices made from core-shell nanostructured materials, such as nanofibers, nanowires, or nanotubes, than from conventional materials. The primary focus of this project is to develop well-oriented core-shell nanostructured materials for (TTE) applications. The core will be made of a highly conductive, low Seebeck coefficient metal nanowire, whereas the shell will be a uniform layer of insulating oxide material with a high Seebeck coefficient. Numerical modeling will aid in understanding and exploring the design space for potential applications.

### MISSION RELEVANCE

This project is related to DOE’s missions in energy and science. Specifically, it is relevant to: two DOE goals. The first goal is to transform our energy systems. The new materials and technologies developed during this project will enable new, more energy-efficient technologies for thermal-electric cooling, thermal-electric generation, and other applications. With respect to the second goal, supporting the science and engineering enterprise, the new materials and processes developed in this project will lead to many new applications that require smaller form factors.

### RESULTS AND ACCOMPLISHMENTS

We have completed the theoretical and modeling study to illustrate the working concept. Over the past year, we also demonstrated the synthesis of highly ordered magnetic nanowires with diameters of about 20 nm, and developed heat treatment, oxygen reduction, and atomic layer deposition (ALD) processes to synthesize the metallic core and oxide shell nanostructures. And, we developed technology to further align the nanowires into highly oriented structures. The alignment technology is based on applying an external magnetic field to the magnetic nanowires. The developed ALD process deposits 6 nm of a smooth and uniform zinc oxide (ZnO) layer over a metallic cobalt iron (CoFe) nanowire, forming the core-shell nanostructure.

### PROPOSED FUTURE WORK

We will focus on developing new materials with high ZT and high PF for TTE materials. In addition, to further exploration of materials choices, we will investigate processes beyond the existing patented approach, which may lead to better quality control of the process and improved materials properties. Consolidation methods that involve using less binding agent will be investigated to improve the thermoelectric properties of materials. We will assemble and test core-shell nanostructure TTE material based on ALD-coated nanofibers. One key challenge will be alignment of the core-shell nanofibers at a specific angle, which may be achievable using tilted external magnetic fields during consolidation. Relevant design and modeling work will provide guidance and understanding.

# Images from Inner Space: Exposing Quantum Mechanics within Nucleons and Nuclei

2016-098-NO

Ian Cloët and John Arrington

## PROJECT DESCRIPTION

Almost all the universe's visible matter is comprised of protons and neutrons; but even after a century of striking progress in subatomic physics, we still lack an intimate understanding of these principal building blocks. The challenge resides in quantum chromodynamics (QCD), the strong-interaction aspect of the Standard Model of particle physics. A comprehensive approach to describing the internal structure of protons, neutrons, and other subatomic particles formed by the strong interaction (collectively known as hadrons) has recently emerged.

This framework encodes our knowledge of hadrons and even nuclei in the Wigner distributions of the fundamental constituents (the quarks and gluons of QCD); these distributions are a quantum mechanical concept analogous to the classical notion of a phase space distribution. From the Wigner distributions, a natural interpretation of measured observables is provided via construction of quantities known as generalized parton distributions (GPDs) and transverse momentum-dependent parton distributions (TMDs): GPDs are the key to a spatial tomography of hadrons, and TMDs allow for their momentum tomography. A new generation of experiments at, for example, Thomas Jefferson National Accelerator Facility (Jefferson Lab) in Newport News, Virginia, and the COmmon Muon Proton Apparatus for Structure and Spectroscopy (COMPASS) at CERN will provide the empirical information necessary to develop a phenomenology of Wigner distributions. However, these experiments will only provide detailed information about the Standard Model's strong interaction sector if these distributions are also calculated in a framework with a well-defined connection to QCD. The goal of this project is to fulfill this role by directly calculating the tomographic images of the quarks and gluons inside hadrons and nuclei.

## MISSION RELEVANCE

The mission of the DOE Office of Nuclear Physics is to discover, explore, and understand all forms of nuclear matter. To further this mission, Jefferson Lab has just undergone a \$370 million upgrade through which the energy of its electron beam has doubled from 6 to 12 GeV. More than 50% of allocated running time at the upgraded Jefferson Lab is dedicated to exposing the quark and gluon tomography of nucleons and nuclei. However, access to this tomography is not direct, and developing these 3D images will require significant theoretical guidance, such as that undertaken as part of this project.

## RESULTS AND ACCOMPLISHMENTS

The starting place for QCD-based calculations is often the pion, which is a bound state of a dressed quark and a dressed antiquark in quantum field theory and the Goldstone boson associated with dynamical chiral symmetry breaking (DCSB) in QCD. The Argonne Physics Division Theory Group leads in the study of pion structure. Under this project, their studies have now been extended to a spatial and momentum tomography of the quarks inside the pion. The calculations proceed using the formalism provided by QCD's Dyson-Schwinger equations, which are none other than QCD's equations of motion, to first determine the light-front wave functions (LFWFs) of the pion. LFWFs encode how the quarks and gluons are distributed inside a subatomic particle, and have many remarkable properties: for example, they are Lorentz boost-invariant and yield a probability interpretation.

Therefore, LFWFs provide a quantum field theoretical framework that is as close to quantum mechanics as possible. In Figure 1, we illustrate our result for the pion's quark-antiquark LFWF at a typical hadronic scale. We find a broad concave function in the light cone momentum fraction  $x$ , which is linked to DCSB in QCD, and at large transverse momentum the LFWF is power-law suppressed. The tomography of the quarks inside the pion can then be revealed by taking various overlaps of these LFWFs. A key example is the pion's transverse momentum-dependent parton distribution function, which is illustrated in Figure 2. With these results, we have now developed an unprecedented level of understanding of the pion and how DCSB drives its structure and dynamics.

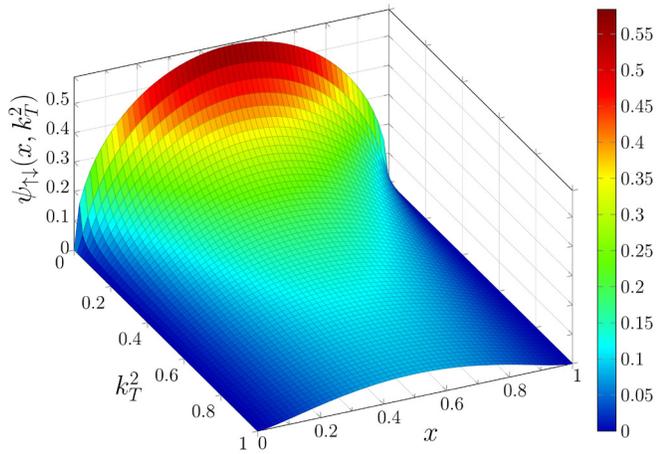


Figure 1. Pion's light-front wave functions, where the broadening in  $x$  is associated with mass generation in QCD.

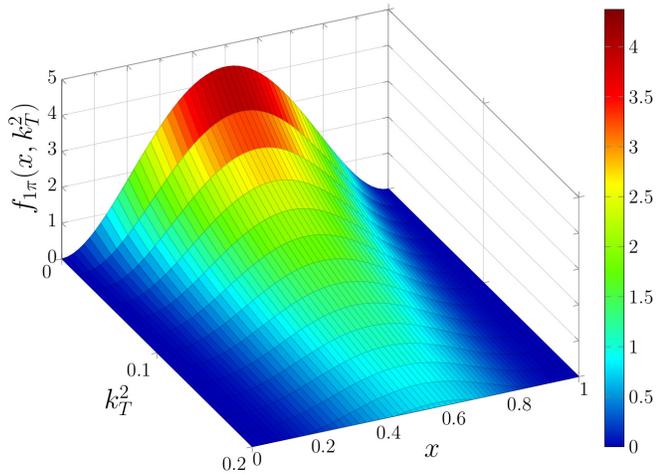


Figure 2. A momentum-space tomography of the pion provided by a transverse momentum-dependent distribution function.

### PROPOSED FUTURE WORK

With the development of a detailed tomography of the pion, the focus now is on further extending the tomographic studies of nuclear matter and its basic constituent, namely, the nucleon. These investigations will address questions at the very heart of QCD, specifically: how more than 98% of the visible mass in the universe is created; how the strongest known forces in nature arrange partons within protons, neutrons, and nuclei; how the measurable properties of such subatomic particles are shared between the partons from which they are composed; and can the partons be removed, namely, is confinement absolute? The formalism with the greatest potential to answer these questions is the one that provides for a tomography of nucleons and nuclei. Once the LFWFs of the nucleon are determined, a quark and gluon tomography becomes possible. These results will help guide the spatial and momentum imaging programs at Jefferson Lab and other facilities worldwide.



# LDRD SWIFT

# Recovery of Critical Materials from Post-Consumer Electronics

2016-240-NO

John Hryn and Jeffrey Spangenberg

## PROJECT DESCRIPTION

The specific objective of this project is to adapt technology developed at Argonne for the separation and recovery of polymers from mixed automotive plastics to the separation and recovery of polymers and materials that are present in obsolete electronics. Process operating conditions will be developed to demonstrate proof-of-concept for recovering value and critical materials from obsolete electronics. The key technical barriers to the development of this process technology include the yield and selectivity of the process for specific polymers relative to the market requirements for product purity and consistency. The research conducted in this project directly addresses these barriers. We will undertake characterization of materials, development of a process model and design configuration, and development and verification of process operating conditions.

The basic process configuration for separation and recovery of materials from obsolete consumer electronics consists of two primary systems: Mechanical Separation, which is comprised of conventional magnetic separation and size reduction technology to produce a metal-free polymer concentrate from the bulk electronics scrap (e-scrap), followed by Polymer Separation, which is comprised of a series of modular wet separation tanks (designed and patented by Argonne) in which the polymer concentrate is sequentially separated into constituent polymers using flotation/elutriation techniques (patented by Argonne) to selectively recover the polymers at high yield and at the purities necessary for their re-use in value-added market applications.

Most of the metals in the obsolete electronics will be recovered in the Mechanical Separation system (we also point out that owing to their intense magnetic properties, rare earth magnets that are used in electronics equipment can be isolated from the metals fraction for separate recycling if sufficient volumes can be recovered); any residual metals (primarily nonferrous) in the polymer concentrate will be recovered in one of the downstream separation tanks.

The process is effective for selectively recovering polymers of similar densities through surface modification of the specific polymers by pH and surface tension

adjustment combined with the appropriate elutriation velocity of the solution. The elutriation process is controlled by solution flow into a process tank in which the plastics are isolated in a column through which solution flow occurs.

Solution flow is controlled by recirculating solution pump rates. Plastics that sink to the bottom of the tank are conveyed out with a screw conveyor and then discharged or conveyed to the next separation stage. Plastics that rise in the elutriation column are carried with the solution to a conventional spin dryer that discharges the plastics and recovers the solution to be pumped back into the separation tank. Process solutions are continuously recycled in the process.

## MISSION RELEVANCE

The mining and processing of energy-intensive materials consume more than 8 quads annually; up to 50% of these materials (equivalent to 4 quads) is estimated to be disposed of in landfills within one year of production. Internal DOE analysis shows that by increasing the recycling rate of key material classes by 30% and improving the energy efficiency of secondary feedstock processing by 30%, energy savings of up to 1.6 quads can be achieved, thereby addressing DOE missions in energy and the environment.

## RESULTS AND ACCOMPLISHMENTS

A bulk sample of post-consumer e-scrap was processed. The material was shredded to less than 6 millimeters (nominal), and magnetically separated using the Argonne technology described above. The two largest material fractions (ferrous and plastics) were separated and analyzed. The ferrous fraction amounted to 60.0% of the sample by weight, whereas the plastics fraction accounted for 29.3% of the sample. The remaining fractions consisted of oversized material that could not be shredded, and undersized materials, mostly dusts. The compositions of the two largest fractions were determined in the lab by analyzing the entire sample using magnetic separators, air classifiers, and when necessary, microscopic examination and hand sorting. From the results, it appears that Argonne technology can adequately separate and isolate the two major material fractions in e-scrap. The next step is to analyze the composition of the plastics fraction to determine the specific types of polymers present. Each polymer particle will be weighed and subjected to Fourier transform infrared spectroscopy analysis to determine its polymer family.

### **PROPOSED FUTURE WORK**

Once the plastic fraction components are identified, a proposed process scheme to maximize recovery of individual polymers, based on our existing knowledge of plastics separations, can be developed. We can then estimate the economic viability of the process. Once it is clear that the process is economically viable, the plastic fraction will be separated into individual polymers to demonstrate proof of concept for the separation process.



# LDRD NAMED FELLOWS

# ***In situ* Polarized Spectroscopy of Optically Transparent TRGO-Polymer Solar Cells**

2016-180-NO

Muge Acik

## **PROJECT DESCRIPTION**

This project seeks to understand the interfacial chemical reactions that alter device power efficiencies in graphene-based perovskite solar cells by examining the interfaces between thin films of methylammonium ( $\text{CH}_3\text{NH}_3$ ) lead halide ( $\text{MAPbT}_x$ , T = I, Br, Cl) perovskite (the light-harvesting layer) and graphene oxide (GO) (the hole-transporting layer). The two main goals of the work are (1) to derive the mechanisms of degradation of reduced GO (RGO) during perovskite growth and (2) to analyze the impact of the halide anions of  $\text{MAPbT}_x$  crystals, which modify the graphene/perovskite interfaces. Ultimately, this research will help to determine the key factors in poor solar power conversion efficiencies in perovskite photovoltaics. In addition, the experimental findings will contribute to addressing stability challenges for high-performance solar devices. Improvement of perovskite/graphene-derived thin films, combined with new device designs, will offer novel next-generation engineering opportunities for photovoltaics, light-emitting devices, and photodetector applications if experimental data analysis is successful.

## **MISSION RELEVANCE**

This project is relevant to DOE's energy mission. To identify the key factors that challenge photovoltaics fabrication, this project explores the interfacial mechanisms that degrade the film properties of GO/perovskite thin films grown in a device stack. This work combines interface chemistry with materials science and engineering knowledge. These scientific efforts introduce new opportunities for different approaches in next-generation solar technology and demonstrate the incorporation of graphene-based thin films into energy-related applications.

## **RESULTS AND ACCOMPLISHMENTS**

The initial experiments involved the fabrication of single-layered GO thin films to study interfacial chemical interactions upon perovskite growth, using *in situ* infrared spectroscopy combined with annealing studies (at  $\sim 60$ – $300^\circ\text{C}$ ). Thin-film uniformity with continuous film deposition was found to be necessary to achieve high device performance.

Three-layered GO was used because of its optimum film uniformity. A thin film of perovskite was grown on these layered GO thin films (Figure 1), resulting in a stack thickness adjusted to  $\sim 100$  nm to conform to the depth resolution limit of the X-ray photoelectron spectroscopy (XPS) technique. Interfacial defect formation at the GO/ $\text{MAPbI}_x$  interfaces was found to begin when the perovskite precursors, such as MAI and  $\text{PbI}_2$ , were initially deposited on the GO thin films. Meanwhile,  $\text{PbI}_2$  precipitation occurred on the GO, resulting in iodine vacancies in the form of point defects or interstitials, as confirmed by the XPS studies (Figure 2).

Annealing also generated oxygen-induced chemical reactions, and produced Pb-O bond formation, hindering  $\text{MAPbI}_x$  growth on GO. Metallic Pb species were also observed during  $\text{MAPbI}_x$  growth on Si/SiO<sub>2</sub> upon precursor deposition. In addition to the oxidation of Pb, precursor deposition from a dimethylformamide solution resulted in defect formation in RGO, initiated by the ring opening of out-of-plane epoxide and hydroxyl groups from the basal plane. The disappearance of the (220) orientation peak of the perovskite revealed that cubic-to-tetragonal phase transitions had occurred. Broadening of D (defect) and G (chemical doping) bands observed by Raman analysis confirmed that for  $\text{MAPbI}_x$  growth on GO, oxygen-induced defect formation occurred in both the RGO and oxidized perovskites (Figures 2a, b).

However, such defects were not present during  $\text{MAPbBr}_x$  growth on GO (Figures 2c, d), following a different growth mechanism. Defects related to the symmetry disorder were not observed for the latter case upon precursor deposition.

As a result,  $\text{MAPbBr}_x$  growth was successfully obtained on GO without the incorporation of defects in RGO. At GO/ $\text{MAPbCl}_x$  interfaces (Figures 2e, f), oxygen impurities in RGO drove oxygen-induced defect formation through negligible functionalization of RGO during annealing; however, interfacial Pb-O was not observed at such interfaces. Consequently, the type of halide functioning as the anion in these organo-lead halide perovskites has been found to determine the chemical modifications at the graphene interfaces.

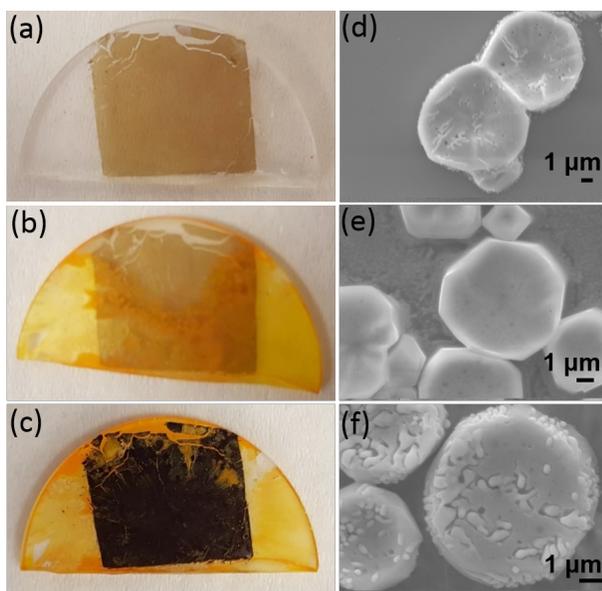


Figure 1. Photos of as-prepared GO (3–5 layers) (a) deposited on a quartz piece, (b) after deposition of spin-coated MAPbBr<sub>3</sub>, and (c) after annealing at 130°C. Scanning electron microscope images show (d) MAPbBr<sub>3</sub> on Si/SiO<sub>2</sub> at 130°C; and GO/MAPbBr<sub>3</sub> thin films (e) prior to annealing and (f) at 130°C.

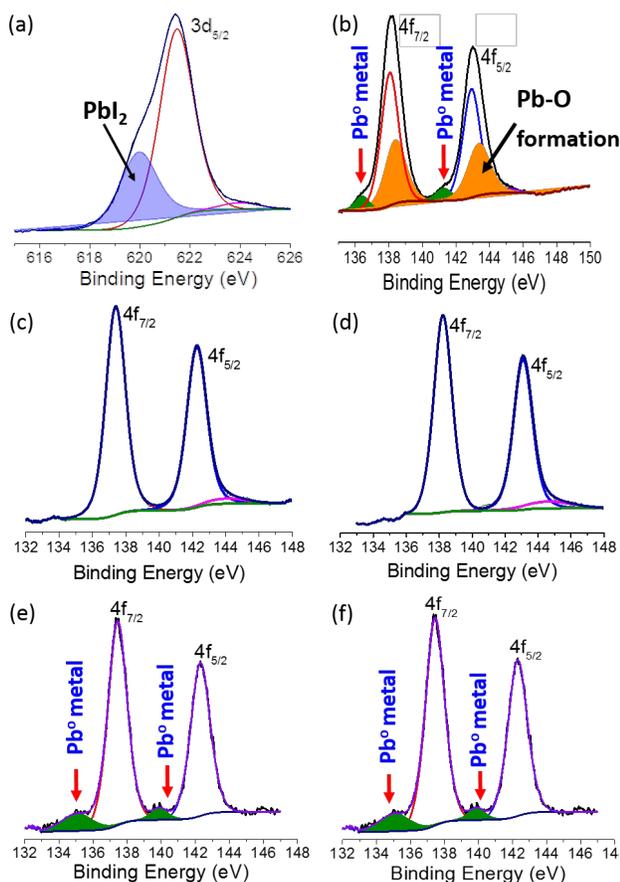


Figure 2. X-ray photoelectron spectroscopy (XPS) analyses of GO/MAPbI<sub>3</sub> (a) as deposited given with I (3d) and Pb (4f) at 130°C in (b), thin films of GO/MAPbBr<sub>3</sub> and GO/MAPbCl<sub>3</sub> as deposited, shown with Pb (4f) (c) – (e), and with Pb (4f) at 130°C (d) – (f), respectively.

## PROPOSED FUTURE WORK

This research to improve perovskite growth on oxides is ongoing. We have initiated new routes to eliminate both the annealing process and the use of high-boiling-point solvents from the perovskite growth methods. In the next step, these methods will be examined by solution processing. A new design for producing these perovskites will benefit novel device designs in FY 2017.

## The Search for Weyl Semimetals

2016-181-N0

Nirmal Ghimire and John F. Mitchell

### PROJECT DESCRIPTION

Graphene is the most celebrated example of a two-dimensional (2D) semimetal, where valence and conduction bands touch at the Fermi energy at a point known as the Dirac point. These 2D Dirac points near the Fermi level are responsible for many important properties in graphene such as its high electron mobility and conductivity, and underpin its promise for next-generation electronics.

However, Dirac nodes in graphene are susceptible to small perturbations such as disorder, external magnetic field, or spin orbit coupling, and, consequently, are easily “gapped out” as the valence and conduction bands lose contact, thus forming a semiconductor. A close cousin of graphene is the so-called Weyl semimetal. Like graphene, its band structure has a pair of bands crossing at certain points called Weyl nodes at the Fermi energy; unlike graphene, this system is three dimensional (3D) and is more stable than graphene against small perturbations, making it more attractive as a candidate platform for low-power electronics. The objective of this project is to explore these novel materials and their properties.

After the discovery of the TaAs family of compounds as Weyl semimetals, subsequent investigations showed promising functionalities in these compounds, including extremely large magnetoresistance (XMR), high charge carrier mobility, quantum oscillations, and negative longitudinal magnetoresistance (LMR). However, similar properties found in some other compounds, not expected to be Weyl semimetals, complicated the understanding of the true transport properties of Weyl semimetals. We thus focused our work toward addressing the following key issues in Weyl semimetal physics: (1) understanding the origin of the above-mentioned exotic behaviors in the compounds not expected to have Weyl behavior,

(2) studying the effect of magnetism in such compounds, and (3) discovering and studying new, simpler Weyl semimetals (i.e., Weyl semimetals with fewer Weyl nodes). This study will allow us to understand the true transport behavior of Weyl semimetals and to test their applicability in future technology.

### MISSION RELEVANCE

This project lies at the intersection of two recently identified high-priority Basic Energy Sciences (BES) research directions—quantum matter and crystal synthesis. Both topics have been emphasized through recent Basic Research Needs workshops, as impacting the DOE science mission of understanding and controlling matter at the atomic level.

### RESULTS AND ACCOMPLISHMENTS

We synthesized single crystals of YSb, and carried out transport properties measurements together with electronic structure calculations. Through the magnetotransport studies, we found that YSb, like isostructural LaSb and LaBi, has a large unsaturating magnetoresistance that reaches 75,000% at 1.8 K and 9 tesla (T), large Hall mobility ( $6.2 \times 10^4$  cm<sup>2</sup>/volt-sec at 1.8 K), quantum oscillation, and magnetic-field-induced metal-insulator-like transition followed by the resistivity saturation plateau. These behaviors previously observed in LaSb were questioned as to whether they are related to surface conduction, possibly resulting from some sort of topological protection on the surface. Our experimental results indicated that the saturation plateau cannot be unambiguously assigned solely to the surface conduction in YSb. Later, reports of some angle-resolved photoemission spectroscopy (APRES) studies have claimed the presence of the surface states in LaSb and LaBi. The XMR behavior of these compounds has been explained in terms of the electron-hole compensation effect.

To examine this issue further, we carried out ARPES studies on YSb with Professor Z.-X. Shen at Stanford University, where we observed that both electron and hole pockets are at the Fermi energy, as expected from the first principles calculations. But the electron-hole concentration ratio estimated by the experimentally measured volume of electron and hole pockets is  $\sim 0.81$  at 10 K, which clearly deviates from perfect carrier compensation. Upon further investigation, we found that when there is a substantial difference between electron and hole mobility, the cooperative action of that difference with the moderate carrier compensation observed in YSb could contribute to XMR. This study has thus identified a new mechanism for the XMR behavior.

### PROPOSED FUTURE WORK

Future work will focus on the noncollinear magnetism in topological materials. The motivation is that these two areas of noncollinear magnetism and topological materials, which are being studied independently, have a connection through a geometrical phase of electrons known as Berry's phase. The candidate materials for such a study are topological semimetals with noncollinear magnetic ordering.

We have identified several systems of interest. The examples are frustrated magnetic semimetals, noncentrosymmetric semimetals, and magnetic impurity doped noncentrosymmetric Weyl semimetals. There are also some new compounds that we have screened through the calculated band structure and available magnetic properties.

Noncollinear spin textures such as skyrmion (a hurricane-like spin texture) and magnetic bubble are expected in frustrated magnets with weak anisotropy. Noncentrosymmetric magnets are known to host noncollinear spin structures such as a magnetic helix, a magnetic soliton (magnetic kink), or a magnetic skyrmion. These types of magnetic textures provide Berry's phase to electrons either in momentum or in real space depending on the size of the magnetic structure. In a topological semimetallic state, electrons can acquire Berry's phase in momentum space because of the features in energy band topology. Berry's phase manifests in Hall effect measurements. We will study these compounds by measuring transport properties, the Hall effect in particular, and by investigating their magnetic structures to understand the role of the magnetic texture and band topology in the transport properties.

## Core-Shell Nanowire Magnetic/Ferroelectric Multiferroic Heterostructure for Voltage-Tunable RF Devices

2016-182-NO

Ziyao Zhou and Xing Chen

### PROJECT DESCRIPTION

Obtaining voltage control of magnetism through multiferroics (materials exhibiting both ferroelectricity and ferromagnetism traits simultaneously) is of great fundamental interest and technical importance for fast, compact, and energy-efficient next-generation tunable

magnetoelectric (ME) devices, such as radiofrequency (RF) circuit components, memory devices, and sensors. This project will synthesize scalable core-shell nanowire (iron cobalt-hafnium oxide/zirconium oxide [CoFe/HfO<sub>2</sub>-ZrO<sub>2</sub>] or PZT (lead zirconate titanate)/CoFe) structures as multiferroic substrates for ME devices using the electrospinning technology we have developed. HfO<sub>2</sub>-ZrO<sub>2</sub> is an insulator (dielectric), whereas PZT has a large piezoelectric effect, enabling the material to change shape in an electric field. The core-shell nanostructured material is synthesized by first producing an electrospun nanofiber core followed by a coating using atomic layer deposition (ALD). The resulting core-shell structure is a ferroelectric nanowire with a ferromagnetic shell, or vice versa. This material has the potential to be used as multiferroic substrates in advanced voltage-tunable RF devices, where the ME coupling strength can be ten times stronger than in conventional ME devices.

#### MISSION RELEVANCE

This project is relevant to DOE's mission in science with likely applications also relevant to energy and national security. Based on the new materials and processes developed in this project, new applications such as voltage-tunable RF and memory devices can be realized. The new materials and technology developed will enable a smaller and more energy-efficient ME device. One can also envision this technology enabling applications in space, satellite, and defense-relevant technologies.

#### RESULTS AND ACCOMPLISHMENTS

We demonstrated that electrospinning technology can synthesize ferromagnetic iron-cobalt alloy nanowires with the desired composition. These nanowires were coated with aluminum oxide using ALD to maintain their high magnetic moment and large anisotropy. In addition, we demonstrated synthesis of PZT nanofibers coated by ALD with CoFe, the first core-shell magnetic/ferroelectric multiferroic nanowire. The total wire thickness is about 35 nm, as shown in Figure 1.

#### PROPOSED FUTURE WORK

We will investigate additional materials and process conditions to optimize this technology and realize improved multiferroic materials. In addition, we will explore uses of these materials in RF device applications. We anticipate engagement with Defense Advanced Research Projects Agency (DARPA) for a new opportunity based on this technology for RF/ microwave applications.

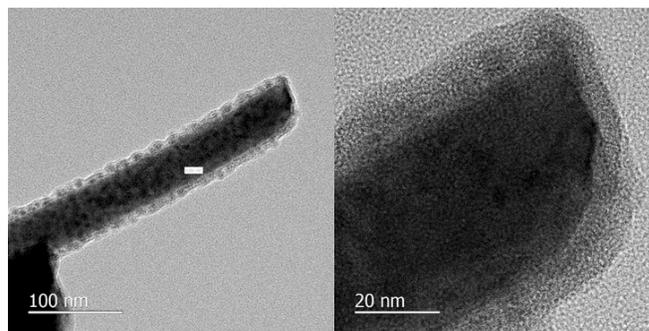


Figure 1. Transmission electron microscopy (TEM) images of a PZT/CoFe core-shell nanofiber.

## Understanding and Controlling Charge, Spin, Pseudospins, and Lattice Degrees of Freedom in Layered Transition Metal Dichalcogenides

2016-183-N0

Qi Zhang and Haidan Wen

#### PROJECT DESCRIPTION

A grand challenge for current electronic device technologies is how to reduce the increasing power consumption of the devices while enhancing their operating speeds. Among many contributors to power consumption, the interconnect has been identified as the major player, with an ever-increasing role. One promising solution is to apply optoelectronic devices, which have several physical advantages over electronic interconnects, including high information density for long-distance communication, low energy cost owing to the absence of charging lines, and precise timing for clocks and signal processing. Toward this goal, breakthroughs in photonics to overcome the power and bandwidth limitations and advance the state of the art of optical communications are likely to emerge from a new family of devices that will employ new materials and exploit principles and degrees of freedom other than charge and spin alone.

Recently, two-dimensional (2D) layered materials, in particular transition metal dichalcogenides (TMDs), have emerged as extraordinary systems because of their coupled quantum degrees of freedom, including spin, valley pseudospin, and layer pseudospin, with electrical and optical accessibility. To advance optoelectronics and new-concept devices for efficient and low-power

information processing, it is critical to understand the fundamental dynamics of these electronic degrees of freedom under optical excitation.

To address this challenge, we propose to (1) understand and control the dynamics of charge, spin, and pseudospins by low-energy excitation and explore the strong-field physics in layered TMDs with ultrafast terahertz (THz) pump-probe spectroscopy, and (2) utilize the unique laser pump and the hard X-ray nanodiffraction probe technique recently developed at the Advanced Photon Source (APS) to unveil the ultrafast lattice dynamics of the laser-induced phase transitions in TMDs. The energy scales of many optical excitations, such as charged exciton binding energy, are on the order of 10 meV, located well within the THz range (with 4.1 meV in photon energy at 1 THz). This characteristic makes THz spectroscopy an effective tool for probing and controlling these quantum degrees of freedom.

### MISSION RELEVANCE

This project supports DOE's mission in science-based innovation. The capabilities we will develop at the Nanophotonics Laboratory of Argonne's Center for Nanoscale Materials (CNM) will enable versatile pump-probe techniques at THz frequencies, which provide essential tools for ultrafast electronic characterization in nanoscale electronic materials. The study of ultrafast dynamics in layered TMDs will answer key questions on how the structural reconfiguration of 2D materials influences their electronic properties. The knowledge acquired from this work will advance the understanding of exotic magnetic phenomena which in turn portends advances in the electronic devices and characterization tools that support the broader spectrum of DOE technology-based missions in energy and security.

### RESULTS AND ACCOMPLISHMENTS

During FY 2016, we built two THz spectroscopy systems and conduct a successful experiment using ultrafast X-ray diffraction technique:

#### *Intense THz Pump-Probe Spectroscopy System.*

We generated intense single-cycle THz pulses with wavefront-tilted ultrafast laser pulses at a wavelength of 800 nanometers (nm). The peak THz electrical field is 300 kilovolts/centimeter (kV/cm). It can be further enhanced by a factor of 10, to 3 megavolts (MV)/cm, with a metamaterial split-ring resonator array. This intense THz system is the key experimental setup for our effort to gain ultrafast THz control of quantum degrees of freedom and strong-field effects in layered TMDs, as well as

novel THz control of magnetic dynamics in 2D spintronic heterostructure systems with ultrafast pure spin currents.

*Broadband THz Time-Domain Spectroscopy System.* We use one gallium phosphide (GaP) crystal to generate a broadband THz pulse via an optical rectification process, and another GaP crystal as the THz detector to encode THz electric field information into the polarization states of the optical sampling beam. The THz waveform is sampled and reconstructed in the time-domain by varying the optical path length of the sampling beam. We have established a functional broadband (0.2 to 5 THz) transmission setup. The next step is applying an ultrathin (30- $\mu\text{m}$ ) GaP crystal to achieve micron-level, near-field spatial resolution. The result will be the world's first cryogenic near-field THz spectroscopy system, which will open the door to a profusion of new physics of low-energy excitation of micron-scale layered TMDs.

*Ultrafast Lattice Dynamics in TMDs Revealed by Ultrafast X-ray Diffraction at the Linear Coherent Light Source (LCLS).* We discovered a surprisingly fast (5 ps) lateral lattice expansion in monolayer  $\text{WSe}_2$  flakes after intense optical excitation. This unusually fast lattice dynamics may be related to the rippling structure of the  $\text{WSe}_2$ . This work is in collaboration with teams from Stanford University and University of Washington.

In addition, we have discovered strong THz emissions from ultrafast spin and charge current pulses at a 2D Rashba interface (i.e., an interface lacking inversion symmetry along its normal direction). Ultrafast broadband THz radiation is highly desirable in various fields, ranging from fundamental research in condensed matter physics to biochemical detection. Conventional ultrafast THz sources rely on either nonlinear optical effects or ultrafast charge currents in semiconductors. Recently, however, it was realized that ultrabroadband THz radiation can be produced highly effectively by novel spintronics-based emitters that also make use of the electron's spin degree of freedom. These THz emitters convert a spin current flow into a THz electromagnetic pulse via the inverse spin-Hall effect. In contrast to this bulk conversion process, we found that a femtosecond spin current pulse launched from a cobalt-iron-boron (CoFeB) layer can also generate THz transients efficiently at a 2D Rashba interface between two nonmagnetic materials (i.e., silver/bismuth [Ag/Bi]). These interfaces have been proven to be efficient tools for spin- and charge-current interconversion.

## PROPOSED FUTURE WORK

We will focus our efforts in FY 2017 on the following two areas:

*Ultrafast THz Control of Quantum Degrees of Freedom and Strong-Field Effects in Layered TMDs.* We will study strong-field effects in TMDs with intense THz pulses. Matter in the presence of a strong laser field exhibits counterintuitive effects that cannot be understood by treating the field as a small perturbation. The interplay between the spatially periodic lattice potential and the intense temporally periodic laser field provides unique and fascinating possibilities for tuning the material properties.

*Control of Magnetic Dynamics in 2D Spintronic Heterostructures with THz-Induced Ultrafast Pure Spin Current.* We recently discovered strong THz emissions from spintronic heterostructures (Figure 1), where transient spin current is converted to transient charge current via the inverse spin Hall effect. Now we plan to investigate the inverse process, that is, to generate ultrafast charge current with intense THz pulses and convert it into ultrafast pure spin current at the interface of a ferromagnet and a normal metal. This technique will bring the whole spin-transfer-torque physics down to the sub-ps time scale, opening the door to new possibilities in the field of THz spintronics and magnonics.

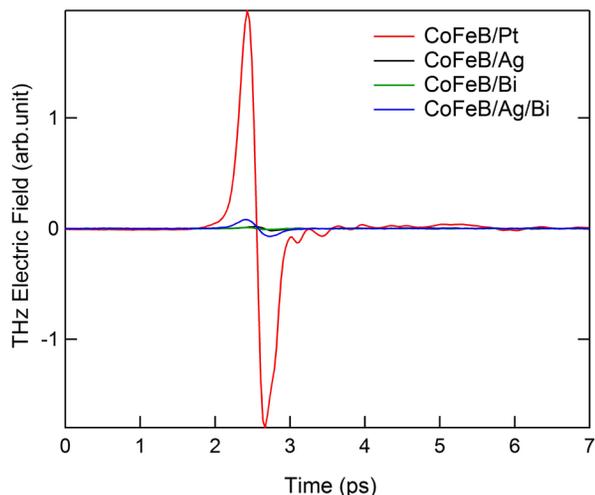


Figure 1. Emitted single-cycle THz pulses from spintronics heterostructures of a ferromagnet (CoFeB) and a normal metal (platinum [Pt] or Ag/Bi). The THz emission efficiency is comparable to that of the conventional THz emitter GaP.

## Investigation of Solid-Liquid Interfaces in Energy Materials: Interfacing Multi-Scale Modeling with Experimental Characterization

2016-184-NO

Kendra Letchworth Weaver, Maria Chan, and Paul Fenter

### PROJECT DESCRIPTION

Electrochemical energy storage and conversion devices such as batteries and solar-to-fuel technology must become more efficient and less costly. However, the complexity of the interface between the charged electrode surface and the fluid electrolyte presents a challenge. Studying these devices under operating conditions requires bridging length-scales from the atomic scale to the macroscopic scale of the devices themselves. Pursuing a complete understanding of these important energy systems therefore requires unprecedented effort that bridges disciplines and integrates theory with experiment. While various modeling techniques exist for describing solid-liquid interfaces, a predictive multiscale theory has yet to emerge. The highly scalable yet atomically detailed joint density functional theory (JDFT) approach proposed below enables far more systems to be studied in a limited time than any competing theoretical description. Pioneering work to obtain a complete description of the solid-liquid interface will broaden basic understanding of fundamental processes at the electrochemical interface, including ion solvation/desolvation and electrode stability to dissolution. Because of its far-reaching implications for processes like corrosion, this proposed research will offer crucial insights into a wide range of energy materials.

### MISSION RELEVANCE

The modeling of solid-liquid interfaces is of significance to various energy applications including energy storage, photocatalysis, corrosion, and dissolution—areas of concern to the DOE energy security mission. In addition, predictive modeling, especially from first principles, is a key focus of DOE's Computational Materials Science report. The proposed work targets both the Basic Energy Sciences and Advanced Scientific Computing Research programs of DOE. The theory and software developments complement and enhance research at existing Argonne centers, primarily the Center for Electrochemical Energy Science, but also the Midwest Integrated Center for Computational Materials, Argonne-Northwestern Solar Energy Research Center, and the Joint Center for Energy Storage Research.

## RESULTS AND ACCOMPLISHMENTS

### Theory and Software Development

**Benchmarking JDFT Performance:** JDFT performance in predicting liquid structure next to graphene was benchmarked relative to experimental measurements and other levels of theory, showing excellent agreement. Figure 1 displays the JDFT-predicted density of the oxygen in water as a function of perpendicular distance  $z$  to a graphene sheet located in the  $z = 0$  plane, compared with predictions from classical and first-principles molecular dynamics (MD).

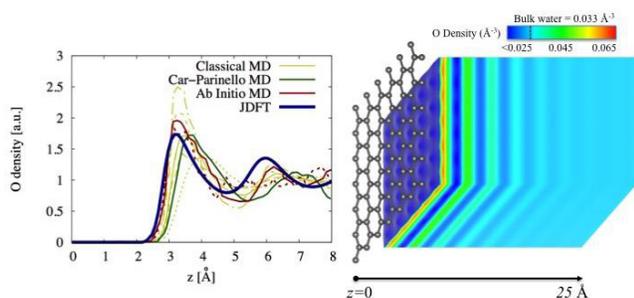


Figure 1. (Left) Comparison of liquid water structure next to graphene sheet, as predicted by JDFT and other theoretical techniques. (Right) Graphene-water interface (carbon atoms in grey).

**Building Models for Organic Electrolyte:** Because detailed experimental data (such as a full equation of state) are unavailable for battery solvents such as ethylene carbonate, we generated a phase diagram using classical MD. This phase diagram will be used to construct a molecular DFT to enable fundamental studies of the battery electrode/electrolyte interface within the JDFT framework.

### Structural Studies of Oxide Surfaces

**X-ray Reflectivity of  $\text{Al}_2\text{O}_3(0001)$  in Water:** Extending the approach to include dynamical information, we have computed structure factors from first-principles MD of the interface between water and the (0001) surface of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and compared them directly with experimental reflectivity measurements, gaining insight unavailable from either experiment or theory alone regarding chemical composition and bonding at the interface.

**Strontium Titanate ( $\text{SrTiO}_3$ ) under Growth Conditions:** By combining experimental measurements with DFT calculations, we computed the fractional coverage of the double layer of  $\text{TiO}_2$  on a  $\text{SrTiO}_3$  substrate at high temperature, enabling understanding of the atomic-scale processes involved in homoepitaxial growth of Ruddlesden-Popper stacking faults.

### Metal Oxide Battery Cathode Structure/Reactivity

Using JDFTx (the open-source implementation of JDFT), we studied how the composition and structure of the (001) and (111) surfaces of lithium manganese oxide spinel ( $\text{LiMn}_2\text{O}_4$ ) change upon exposure to liquid electrolyte (i.e., acetonitrile with 1.0 lithium hexafluorophosphate [ $\text{LiPF}_6$ ]). For the (001) facet, we studied a Li-rich termination with two surface Li atoms per unit cell, a stoichiometric surface with one surface Li atom per unit cell, and a Li-poor termination with no surface Li. The Li atom on the surface interacts significantly with the liquid, shifting the relative surface energies of the different terminations and altering the phase diagram. As shown in Figure 2, the most dramatic effect we observe is a widening of the voltage stability window of the stoichiometric surface termination.

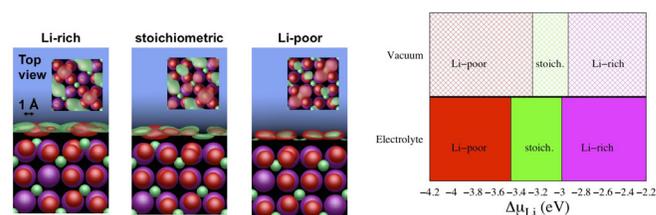


Figure 2. (Left) Negative (red) and positive (green) bound charge in the liquid electrolyte near the (001)  $\text{LiMn}_2\text{O}_4$  surface for several possible terminations (top). (Right) Predicted phase diagram as a function of the chemical potential of lithium.

### PROPOSED FUTURE WORK

In addition to continuing work on the topics above, we plan the following new research directions:

#### Nanocatalysts in Solution

**Catalytic Properties of Iridium Oxygen ( $\text{IrO}_2$ ) Nanoclusters and Surfaces:** Using low-index surfaces and energetically favorable nanocluster geometries as model systems, we plan to use JDFT to investigate the role of water in the shape and reactivity of  $\text{IrO}_2$  catalyst materials. Such studies will inform the design of more effective catalysts for oxygen reduction and evolution.

**Fundamental Studies of Platinum Electrochemistry:** JDFTx studies of hydrogen diffusion on a platinum surface, with and without an overlayer of graphene, will enable interpretation of experiments to probe basic reaction pathways for hydrogen evolution. These joint experiment-theory studies will elucidate the fundamental science underlying fuel cell technology.

### Understanding Trends in Ion Organization at Interfaces

Batteries with multivalent working electrolytes like magnesium ( $Mg^{2+}$ ) or aluminum ( $Al^{3+}$ ), which carry double or triple the charge of  $Li^+$ , could theoretically store much more energy. JDFT calculations of liquids and ions at graphene-liquid interfaces will help interpret data from X-ray diffraction-based techniques, which can resolve atomic positions with sub-Angstrom resolution. Because low-atomic-number ions are difficult to image, they will be replaced with heavier but chemically similar ions and the behavior of the lighter ions will be extrapolated from trends. JDFT-calculated solvation structure and free energies will validate these trends and predict the plating behavior of ions onto the model electrode surface, yielding fundamental insight into rate-limiting processes in electrodeposition, corrosion, and even ion transport through cellular membranes.

## Charge Transport in Nanostructured Materials from *ab initio* Simulations

2016-185-NO

Marton Andras Voeroes and Larry Curtiss

### PROJECT DESCRIPTION

One of the major challenges in predicting materials and processes for efficient conversion of solar energy or for energy storage is the optimization of charge transport through heterogeneous interfaces. We have proposed to develop a unified platform, based on first-principles methods, to investigate electron and hole transport in nanocomposite materials with complex interfaces. We are focusing on nanostructured systems for solar energy conversion; however, we are developing methods and codes that are general and may be applied to study other energy conversion or storage processes.

We plan to devise a unified scheme to investigate charge transport in both the band and hopping regimes, with the intermediate regime treated in an approximate, although nonempirical and hierarchical, manner. In the case of nanoparticle (NP) arrays, we are developing *ab initio* codes to optimize and tune material properties so as to achieve high carrier mobilities while maintaining the Coulomb interaction-enhanced carrier multiplication (CM) effect. This study builds on our previous experience in developing methods and codes to compute CM rates from first principles in NPs and in studying NP arrays and embedded NPs.

The band transport will be described in an *ab initio* formalism based on the Boltzmann transport equation, first in the constant-relaxation-time approximation, and then by including electron-phonon and impurity scattering lifetime effects.

In parallel, we will be working to adapt the Marcus theory of electron transfer to nanocomposites and to generate structural models of simple systems for validation purposes. An ultimate goal of the project is to connect the hierarchical model of electron transport with our previously developed CM code. Such a platform will be of general applicability to investigate transport at heterogeneous interfaces, including solid/electrolyte interfaces, that are relevant for optimization of batteries. The codes developed in the project will be made available to the public in open-source format.

### MISSION RELEVANCE

Our goals of understanding and engineering charge transfer and charge transport processes in complex nanostructured materials are highly relevant to the energy mission of DOE, as charge transport processes are ubiquitous in materials relevant to energy conversion and storage.

### RESULTS AND ACCOMPLISHMENTS

As a first step toward computing electron-phonon couplings (EPC), we have examined a materials family that is close to what we are planning to study and is well-characterized experimentally. Diamondoids are tiny clusters of diamond nanocrystals whose structure is exactly known; thus, they are ideal testbeds for developing new theories. Because it is known that bulk diamond has large EPC-induced renormalization in the band gap, it was thus naturally expected that small diamond nanocrystals could also show interesting physics. Working with researchers at the Institute for Material Science of the National Research Council in Italy, we have examined the effect of EPC in the photoemission spectra of some diamondoids using the code Yambo. We found that a dynamical theory of EPC is essential to describe the main features of the experimentally measured photoemission spectra. This work was published in *Nature Communications* very recently.

Another prerequisite for understanding electron transport in nanostructured composites is good structural models. Along with researchers at the National Renewable Energy Laboratory (NREL), we have designed a library of ligands for lead chalcogenide nanoparticles. In particular, we were able to engineer optical absorption and band alignment by changing the functional group on the ligands. A

manuscript summarizing the major findings of this work has been submitted.

With colleagues in Argonne's Materials Science Division and at the University of Chicago, we have started developing a computational framework based on constrained density functional theory (CDFT). CDFT can be used to compute charge-localized states and the electronic coupling between them, as well as other properties such as reorganization energies. These values, in turn, can be plugged into models of hopping transport and charge transfer, such as the Marcus theory. We have applied this framework to dimers of colloidal nanoparticles with and without defects, and we have submitted two papers based on the findings. Figure 1 summarizes the key result of one of the projects. We found that hydrogen treatment may passivate defective nanoparticles; this passivation is also beneficial for charge transport in nanoparticle films.

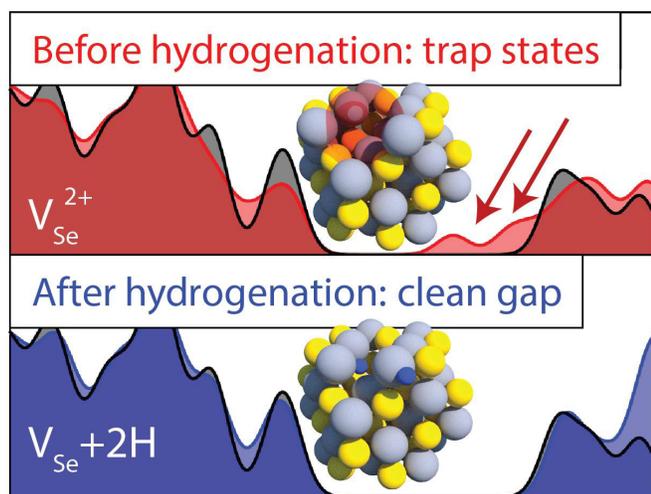


Figure 1. Electronic density of states of a defective lead sulfide (PbS) nanoparticle before (top) and after (bottom) hydrogen treatment. The hydrogen forms a complex with the vacancy, removing the gap states and recovering the charge transfer dynamics (not shown).

### PROPOSED FUTURE WORK

Nanoparticle arrays in most applications are quite disordered, and capturing disorder and the associated increase in size of the systems could be challenging for *ab initio* methods. We are thus planning to explore kinetic Monte Carlo-based approaches as well. In this framework, the electron dynamics are semi-classical and are governed by transition rates that are computed using first-principles theory.

We will also continue working on “designer nanoparticles” with NREL scientists. Combining design rules provided by our computational framework with their synthetic

approach, we can engineer a family of ligands that can lead to enhanced charge transport in nanocrystal arrays.

The computational framework we are developing to study charge transfer and charge transport is also highly relevant to understanding electron transfer reactions occurring in batteries, such as at the electrolyte/cathode interface. Preliminary results suggest that disproportionation, a detrimental process in spinel lithium manganese oxide electrodes, can be understood as a solid state chemical reaction, and the framework being developed can be used to study this process and eventually to generate strategies to lessen its impact or eliminate it. Along with collaborators at Purdue University, we will be actively investigating the relevance of this process.

## Ultrafast Spectroscopy of Nanometer-Scale Heterojunctions Fabricated by Self-Assembly

2016-186-NO

Benjamin T. Diroll and Richard D. Schaller

### PROJECT DESCRIPTION

This project concerns investigations using time-resolved spectroscopic techniques into the properties of solids constructed from colloidal nanomaterials. Junctions are at the heart of many technologies, and therefore understanding how they affect the transfer of charge and energy using nanocrystals offers a step toward designing higher-performance optoelectronic devices such as solar cells, LEDs, lasers, and detectors. Colloidal nanomaterials offer a scalable way to generate intimate contact between two types of materials through mixing of individual components. Close contact of these materials forms a junction at which the interaction between the two nanomaterials may generate the transfer of energy or charge or the emergence of collective phenomena, which this project studies using time-resolved spectroscopy.

In particular, we have used time-resolved emission and transient absorption studies to observe electron-transfer processes in nanomaterials-organic complexes following photoexcitation and the emergence of lasing in solid nanomaterial films, including heterostructured materials. To achieve a detailed microscopic understanding of the behavior of these materials, they are studied both isolated (colloidal solution) and condensed forms. Among the most promising lines of investigation in this regard

is the purposeful manipulation of effective temperature of electrons in heavily-doped materials studied using transient absorption spectroscopy.

### MISSION RELEVANCE

This project supports DOE's missions in basic science and energy storage. This work on the study of nanomaterial-based solid is specifically aligned on the DOE's support for solid-state lighting technology and devices with improved efficiency and solar energy generation.

### RESULTS AND ACCOMPLISHMENTS

In FY 2016, we pursued three lines of work with results that have been either published or submitted for publication.

1. Although electron transfer theory is well understood for molecular (point-charge) systems, its extension to colloidal nanocrystals, which have excited states delocalized over substantial volumes, has not been pursued effectively. In our work, we investigated electron transfer from two-dimensional (2D) cadmium selenide colloidal quantum wells to a molecular electron acceptor (methyl viologen). To execute these experiments, a novel procedure was developed to observe the transfer of electrons at stoichiometries of one quencher per particle. By using quantum wells with different dimensions but the same electronic structure, we showed that the size of the quantum well was inversely-related to the electron transfer rate. This result demonstrates that in addition to factors like driving force, the size of the electronic state is also important in determining electron transfer rates. This work was published in the *Journal of the American Chemical Society*.
2. A second area of study was the ultrafast optical properties of transparent conducting oxide nanocrystals. For this work, colloidal nanocrystals with various impurity doping levels were controllably-synthesized to demonstrate strong optical absorptions in the infrared spectrum. When we excited the sample at the energy of these absorptions using a laser and then probed the sample absorption immediately after the first pulse, we found that the materials underwent a very fast (<1 ps) change in the index of refraction, which made them dramatically more transparent. These results will be published in *ACS Nano*. In addition, an invention report based on these results was filed. A poster presentation of these results received the Robert G. Sachs Award for Outstanding Poster Presentation at Argonne's Annual Postdoctoral Research and Career Symposium.

3. A third area of study during this year has been the formation of heterojunction nanocrystals based on plates. 2D samples of cadmium sulfide were coated with shells of zinc sulfide, with control over the thickness at the level of single atomic layers. We found that these materials undergo relatively efficient lasing in the blue spectral region; this result has been submitted for publication. Along the same lines, we have also explored using the chemistry of alternating layers to build stacks of materials on 2D sheets of cadmium sulfide. This work is in progress.

### PROPOSED FUTURE WORK

Our work will build on that of the past year. In particular, work will continue on heterojunction nanocrystals with the goal of achieving superlattice structures in which alternating layers of material are built up in a plane. We will also continue to explore optical switching technologies using colloidal nanocrystals, especially those based upon silicon nanocrystals.

## Coherent X-ray Investigations of Defect Dynamics in Next-Generation Nanostructured Materials

2016-187-NO

Andrew Ulvestad and G. Brian Stephenson

### PROJECT DESCRIPTION

"Defect engineering," or the rational design and optimization of desired functionalities through deliberate defect manipulation, can be used to design new nanomaterial properties, but is limited in scope because of the inability of current probes to characterize defect dynamics under *operando* conditions in three-dimensional (3D) detail. The thrust of this project is to understand defect dynamics in nanomaterials by developing and employing Bragg coherent diffractive imaging (BCDI), an emerging technique that underpins the scientific impact of the Advanced Photon Source (APS) Upgrade. In BCDI, nanoscale shape and strain are imaged in 3D detail by using a computer algorithm to invert single-particle diffraction patterns obtained with a coherent X-ray beam. BCDI thus avoids the problems of ensemble measurements, which convolve effects of non-uniform particle shape and size. The technique is also capable of "4D imaging" of real devices in real time with nanoscale resolution to reveal strain evolution. We have chosen two focus areas—defect dynamics during phase transformations and defect influence on interfacial

processes—which will demonstrate the power of BCDI to provide the fundamental materials understanding needed to develop next-generation nanostructured materials.

### MISSION RELEVANCE

This project will further the DOE science mission to design, discover, and synthesize new materials through atomic-scale control. It addresses the Grand Challenge, “How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?” The results will contribute to the scientific case for high-brightness X-ray facilities such as the APS Upgrade.

### RESULTS AND ACCOMPLISHMENTS

In FY 2016, we realized these project findings and milestones:

- Defect formation was measured in palladium nanoparticles. The presence of defects changes the thermodynamics for hydrogen storage/release for this metal-hydride system and as such is very interesting for hydrogen storage, purification, and sensing applications. We discovered the critical size for defect formation, and how to model the defective particles. These findings resolved an outstanding question in the field and will impact other systems, including intercalating battery cathode materials.
- We developed a new phase retrieval algorithm. This algorithm improves the temporal resolution of coherent X-ray imaging experiments by incorporating knowledge of the entire time series into each individual state. We used the hydriding phase transformation of individual palladium nanocubes as an example and demonstrated a factor of 2–20 improvement in the temporal resolution. This result opens up new avenues for investigating fast processes using coherent diffractive imaging.
- We explored the influence of surface strain and defects on dissolution by using coherent imaging to investigate single particles in their reactive environments. Specifically, we looked at dissolution of silver due to applied voltage. We found that defects enhance relative dissolution rates; this finding will be important in improving the stability of highly active catalysts, particularly catalysts that are used in fuel cells.
- We showed that coherent imaging is sensitive to surface strains, and used coherent imaging to look at gold catalysts in reactive environments. This work was a step towards understanding the structure-activity relationship at the nanoscale.

### PROPOSED FUTURE WORK

In FY 2017, our efforts will include the following:

- Improving the three-electrode electrochemical cell for *operando* coherent X-ray diffractive imaging studies.
- Performing further BCDI studies of the dissolution of silver nanoparticles.
- Performing further BCDI studies of the dissolution of gold/copper nanoparticle alloys.

## Understanding the Structure of Matter

2016-188-NO

Cédric J. Mezrag and Craig D. Roberts

### PROJECT DESCRIPTION

While the fact that almost all of the visible mass of the universe comes from nucleons and nuclei is well established today, the underlying mechanisms generating it are still not deeply understood. Indeed, today we know that nucleons are composed from particles that are (almost) massless at very high energy, described by a theory called quantum chromodynamics (QCD).

A dynamical mechanism is, therefore, at work here to generate both the mass and the structure of the nucleon in terms of its almost massless constituents. Uncovering this mechanism is the role of hadron physics. The goal of this project consists in understanding the structure of the nucleon, and more generally of hadrons, to shed light on the above mentioned mechanisms. Three complementary distributions are therefore considered: distribution amplitudes (DAs), generalized parton distributions (GPDs), and transverse momentum distributions (TMDs). The DAs describe the one-dimensional structure of the nucleon in momentum space, whereas GPDs and TMDs describe its 3D structure. More precisely, GPDs deal with the positions of quarks and gluons inside the nucleon, while TMDs focus on their momenta.

The project is therefore dedicated to the computations of these distributions using state-of-the-art, nonperturbative techniques that allow us to compute observables with a direct connection to QCD. This treatment is a significant step forward in a research field which, until now, has mainly relied on phenomenological parametrizations. The results will be achieved at a critical juncture in the evolution of nuclear and particle physics, that is, at a moment when (1) a greatly enhanced hadron physics facility at the Thomas Jefferson National Accelerator Facility (Jefferson Lab) is about to begin operations with

programs dedicated in large part to the measurement of GPDs and TMDs, and (2) the community is developing the science case for an electron-ion collider, which must be informed by reliable predictions from continuum-QCD.

### MISSION RELEVANCE

This work addresses issues that are basic to the programs sponsored by the DOE Office of Nuclear Physics. For example, the results are enabling concrete predictions to be made for basic properties of the proton and neutron that will be measured using the upgraded accelerator at the Jefferson Lab; and these predictions would have been impossible had the new techniques not been developed.

### RESULTS AND ACCOMPLISHMENTS

The first accomplishment of the project has been the completion of calculations related to the pion GPDs. This success has paved the way for future computations of nucleon GPDs, and it has led to the publication of a review paper. The second achievement concerns computations of the DA of the nucleon. While the computation of the DA is a mandatory first step before proceeding to the GPDs and TMDs, it is also of great interest in itself. Surprisingly enough, the nucleon DA has hardly been studied until now. So in the first months of the project, the computation technology required to obtain the nucleon DA was successfully developed. This milestone has allowed us to compute, for the first time, a nucleon DA in the continuum, using a framework with unambiguous connections to QCD. We have unraveled the key roles of different kinds of strong correlations inside the nucleon, understood as diquarks.

We now understand how the relative strength of these correlations modifies the entire shape of the nucleon in momentum space. The results are shown in Figure 1. They confirm the ones obtained through heavy computer simulations, which are only able to compute the mean of the distribution, and not the distribution itself. On top of this, our results provide an intuitive understanding of the nucleon structure in terms of probability distributions, similarly to what is usually the case in quantum mechanics. The results obtained for the nucleon DA have been generalized to the first radial excitation of the nucleon, known as the Roper resonance (Figure 2). The results show significant differences (e.g., changes of sign). This finding is interesting, as it means that some combinations of momentum sharing are strictly forbidden inside the Roper resonance. This is quantum field theory expression of the “zeros” in the wave functions of hadron radial excitations. Although it will be a long time before lattice QCD can test these predictions, we will use them

to make concrete statements about existing and planned experiments at the Jefferson Lab.

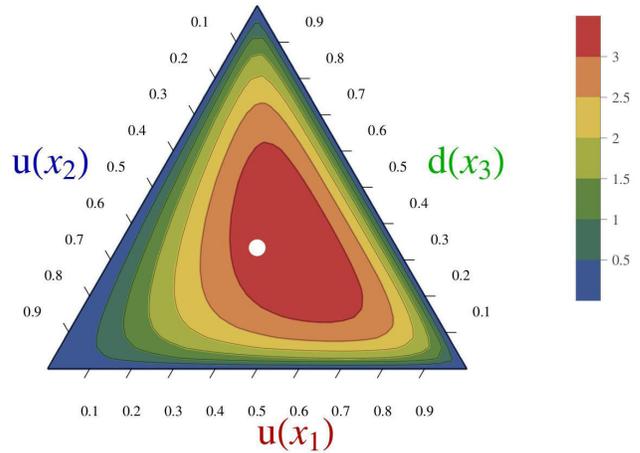


Figure 1. Ternary diagram showing the nucleon DA as a function of the momentum fractions  $x_1$ ,  $x_2$  and  $x_3$  carried by the  $u$ ,  $u$  and  $d$  quarks respectively. The white dot denotes the center of the triangle, where every quark shares one third of the total nucleon momentum. The momentum is more likely to be carried by quarks 1 and 3 rather than quark 2, as the red area indicates a larger probability amplitude. The fact that the distribution is positive-definite is consistent with the nucleon being the ground state of baryons.

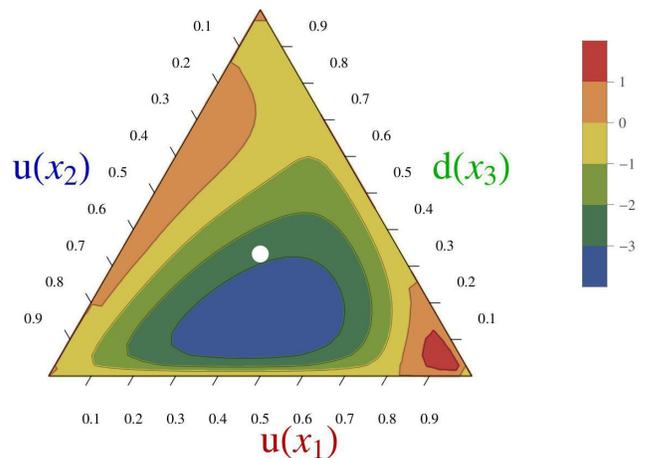


Figure 2. Ternary diagram for the Roper DA as a function of the momentum fractions  $x_1$ ,  $x_2$  and  $x_3$  carried by the  $u$ ,  $u$ , and  $d$  quarks respectively. The white dot denotes the center of the triangle, where every quark shares one third of the total Roper resonance momentum. The result exhibits sign changes as red and orange colors indicate positive areas, whereas yellow to blue are negative ones. This behavior is expected for the first radial excitations of the nucleon. In addition, the two non-connected positive areas are fully consistent with what has been observed in the case of mesons.

**PROPOSED FUTURE WORK**

The computations of the nucleon and Roper DA can actually be refined using state-of-the-art nonperturbative techniques. This refinement will reinforce the connection of our results with QCD. It requires us to extend our algebraic approach to a full numerical one. This extension is possible, and has already been realized in the past in the simpler case of the mesons. Once we have computed the DA using the most refined techniques, we will consider applying the tools and knowledge we gained from the DA studies to more complicated objects like GPDs and TMDs in order to compute the 3D structure of the nucleon. While simple contact-interaction (Nambu–Jona-Lasinio-like) models are now being used in this connection, there is no way of telling whether their failure to explain existing data is a weakness of the model or the computational techniques, or a challenge to the data. Our QCD-connected approach will answer this and related questions.



# LDRD PRIME – APPLIED ENERGY AND SUSTAINABLE TRANSPORTATION

# Grid-Level Energy Storage for Integration of Renewable Energy

2014-120-R2

Audun Botterud, Julie Bessac, Emil M. Constantinescu, Kevin Gallagher, Fernando de Sisternes, Prakash Thimmapuram, and Canan Uckun

## PROJECT DESCRIPTION

Energy storage is widely considered as a key solution for the large-scale expansion of renewable energy. However, most energy storage technologies are expensive and do not scale up to the storage magnitudes required for grid-level storage. To better understand the role of energy storage in the power grid, we are conducting a detailed analysis of the possible applications of such technologies in power systems dominated by variable renewable resources. Toward this end, we are developing advanced methods for storage and grid planning and operations considering the uncertainty and variability of wind and solar power. This comprehensive modeling framework enables us to analyze the potential benefits of different energy storage technologies in the power grid to enable a low-carbon electricity supply with high levels of renewable resources. We are also investigating the economics of energy storage and the extent to which investor incentives for storage investments are aligned with the benefits provided to the power system.

## MISSION RELEVANCE

The comprehensive analytical framework and advanced methods developed in this project directly support the DOE in its mission to ensure America’s security and prosperity by addressing its energy, environmental, and nuclear challenges through transformative science and technology solutions. DOE’s Offices of Electricity Delivery and Energy Reliability (OE) and Energy Efficiency and Renewable Energy (EERE) are both very interested in energy storage for the power grid and have relevant programs in this area of research. Moreover, energy storage is receiving increasing levels of attention from the electric power industry, and our work is also of high interest to developers of batteries and other energy storage technologies.

## RESULTS AND ACCOMPLISHMENTS

In the first two years of this project we developed several methods and algorithms to investigate the role of energy storage in future electric power grids with increasing shares of renewable energy.

Building on this extensive analytical framework, in the final year we have focused on conducting case studies and documenting algorithms and results in a series of publications.

We investigated the value of energy storage as a system asset providing energy and operating reserves in a power system with renewable energy. We developed a novel stochastic programming approach for day-ahead scheduling along with a new flexible operational strategy for batteries in real-time dispatch. In a case study of a small-scale power system with high wind penetration levels, we found that the proposed operational strategy provides better results than multiple benchmarks, and we also found significant benefits for battery storage. An important input to the stochastic scheduling model is a consistent set of forecast scenarios for renewable generation. This is an area where we have made further advances by developing a novel Gaussian multivariate space-time framework that combines multiple sources of past physical model outputs and measurements along with model predictions in order to produce a probabilistic wind speed scenario forecast that reflects spatiotemporal correlations.

We analyzed the potential value of energy storage in reducing greenhouse gas emissions from the power sector. We found that energy storage can reduce total generation costs by increasing utilization of generation assets and enabling greater penetration of the lowest-cost carbon-free resources. However, investments in shorter-duration storage technologies, such as Li-ion batteries under current cost assumptions, are only economically justified under stringent carbon emission limits (Figure 1). Hence, continued innovation and cost reductions for battery technologies will be necessary for the economic justification of large-scale deployment.

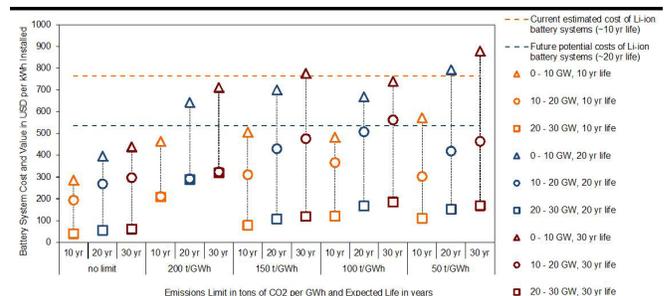
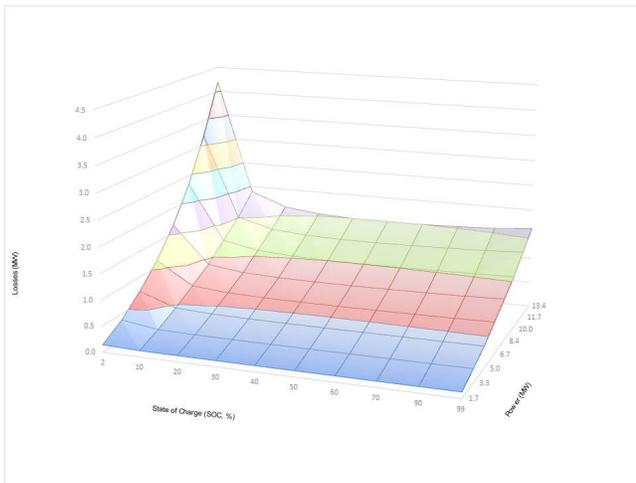


Figure 1. Estimated grid benefit of 2-hour energy storage for various CO<sub>2</sub> emission limits compared to current and future battery costs (Li-ion), based on projected wind, solar, and load for Texas in 2035.

The largest potential application of energy storage in the power grid is for energy arbitrage. We have developed a novel optimization model for bidding battery storage into

electricity markets under uncertainty in energy prices. The proposed model helps storage owners in optimizing the operation of their assets in day-ahead and real-time markets for electricity. We validated the stochastic bidding model in several case studies with realistic data, finding that the proposed bidding algorithm performs significantly better on average than deterministic benchmarks.

Energy storage is typically represented simplistically in power grid models. We have therefore focused on improving battery representations by developing more realistic battery models that consider the electrochemistry in batteries, yet are sufficiently simple to be implemented within mixed-integer linear programming models for grid optimization. We developed a model for improved representation of losses and power limits as a function of battery state of charge (Figure 2). We show that errors in energy arbitrage profit estimates using standard assumptions may be as high as 10% compared to a more realistic representation of losses. Moreover, we have developed a representation of battery degradation, and we show that this is a critical consideration for storage investors. We find that battery degradation may reduce arbitrage profit estimates by as much as 12 to 46% compared to the idealistic case with no degradation. In sum, these efforts contribute to more realistic assessments of the roles and benefits of energy storage in the rapidly evolving electric power grid.



**Figure 2. Illustration of battery losses as a function of state of charge and charge/discharge power.**

## Magneto-Dielectric Composite Substrates Comprised of High Aspect-Ratio Magnetic Nanofibers for Smart Antennas Operating at Microwave Frequency

2014-169-R2

Xing Chen

### PROJECT DESCRIPTION

Scalable magneto-dielectric composites, comprised of high aspect-ratio magnetic nanorods in a dielectric matrix, are being developed for microwave antennas and other radio frequency (RF) devices. Magnetic permeability  $\mu$  and dielectric permittivity  $\epsilon$  of the magnetic and dielectric phases, respectively, dictate microwave (MW) properties. Materials with high  $\mu$  and matched  $\epsilon$ , which may be tuned for specific antennas, are highly desirable in MW communications and wireless/MW power transmission (W/MPT) as a next-generation antenna. In this project, we developed magnetic nanofiber materials to enable RF devices. The target applications were for microwave communications in the GHz frequency region. The overall goal was to produce magnetic nanofibers, develop the technology to align the nanofibers, and demonstrate that the material properties can be suitable for MW applications.

### MISSION RELEVANCE

This project is related to DOE's missions in energy, national security and science-based innovation. The new materials and technology developed will enable better communication technology with more energy-efficient devices. The materials, processes, design, and other technologies developed from this project have excited commercial interest, leading to work to further extend this technology to device-level demonstrations. The technology developed through this project will enable more sensitive devices to be implemented in various applications, including many applications in the defense industry.

### RESULTS AND ACCOMPLISHMENTS

In FY 2014, we fabricated magnetic nanofibers with diameters less than 30 nm and quantified the magnetic properties as a function of fiber diameter. Electrospinning produced metal-salt-containing polymer fibers, which

were heat-treated to produce metal oxide fibers and then reduced to metal nanofibers. X-ray diffraction, electron microscopy and direct-current (DC) magnetic measurements were used to characterize their morphology and magnetic properties.

In FY 2015, a scalable and robust process of fabricating magnetic nanowires was established. The fibers were consolidated to test the magnetic properties at DC and microwave frequencies. The microwave property results guided our enhancement of the fiber morphology. Initial trials were also made to embed magnetic nanofibers and dielectric nanoparticles in polymer matrices.

In FY 2016, magnetic nanofibers with diameters less than 30 nm were fabricated using the integrated electrospinning process developed in prior years. Once completed, alignment technology based on exploiting the magnetic properties of the metallic nanowires was developed to align the magnetic nanofibers and measure their bulk magnetic properties. The aligned magnetic nanofibers and selected dielectric nanoparticles were embedded in polymer matrices to generate proprietary ink formulations, and 3-D printed to produce bulk samples containing in excess of 70% by weight nanofibers. 50  $\mu\text{m}$  deep trenches 0.2 mm in diameter in silicon wafers were filled with printed nanofibers. The technology is being scaled to produce a sample device module.

We have engaged industrial partners to implement this technology for MW communication, which has led to two projects funded by DARPA commencing in 2017, in which we will be participating with our industrial partners to develop model communication systems for defense and civilian applications.

## Chemical Vapor Processing for Additive Manufacturing

2015-151-R1

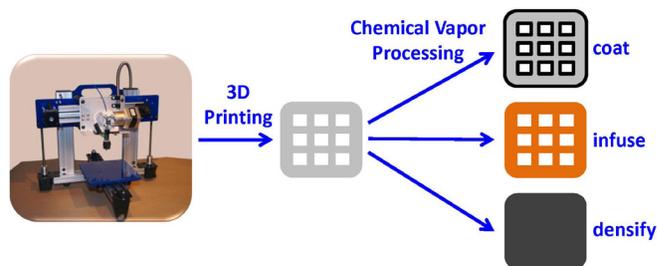
Jeffrey W. Elam, Seth B. Darling, and Randall Winans

### PROJECT DESCRIPTION

We are in the midst of what is arguably the most significant transformation in manufacturing since the industrial revolution—the advent and proliferation of additive manufacturing. Additive manufacturing, also called three-dimensional (3D) printing, creates solid, 3D objects from digital models by depositing a series of thin, patterned layers. Since the 1980s, 3D printing has been used primarily for rapid prototyping; but recent advances in printer size, speed, and printable materials are pushing this technology toward manufacturing in a

range of industries, including the defense, aerospace, automotive, construction, and medical industries. Although a variety of 3D printing technologies have emerged, all have limitations. For instance, the most common 3D printing medium is organic polymers, which are cheap, light, and versatile. But for applications such as engine parts, electronic components, or medical implants, polymers typically lack the necessary robustness, electrical properties, and chemical compatibility.

To address these problems, we propose to develop chemical vapor processing for additive manufacturing (CVPAM, Figure 1). In this technique, the desired part is first 3D-printed and then post-processed by treating with chemically reactive vapors either to (1) deposit a coating, (2) infuse the bulk of the part to enhance the material properties, or (3) densify the part. This project will develop CVPAM to the point of attracting industrial partners. The first task will be to perform a targeted survey of 3D printing media and chemical infiltration methods. This effort will allow us to evaluate suitability of CVPAM for surface coating, infiltration, and densification of 3D-printed parts. Next, we will down-select the most promising processes for development and refinement and evaluate coating equipment, chemistry, and methodology. Finally, we will pursue applications for CVPAM technology. We will work with industrial partners to identify opportunities where CVPAM will provide the greatest benefit and value.



**Figure 1. Chemical Vapor Processing for Additive Manufacturing (CVPAM):** After 3D printing, a part is subjected to chemically reactive vapors either to (1) coat all exposed surfaces (e.g., for biocompatibility), (2) infuse the part with inorganic material (e.g., for added stiffness or conductivity), or (3) densify the part (e.g., to fill voids in a sintered metal).

### MISSION RELEVANCE

This project supports the DOE mission of energy security. Additive manufacturing has great potential to reduce energy intensity by eliminating production steps, enabling re-use of by-products, and producing lighter products. In addition, remanufacturing of parts through additive manufacturing and surface treatment can reduce energy consumption by up to 25% compared to manufacturing new parts. Industrial beneficiaries will include 3D printer suppliers that can incorporate the

CVPAM technology into their products, industrial coating equipment manufacturers, and chemical suppliers. The aerospace, automotive, and medical industries will also benefit through the numerous advantages of additive manufacturing, including shorter lead times, easy customization, and reduced materials usage.

### RESULTS AND ACCOMPLISHMENTS

In FY 2015, we engaged local suppliers of 3D printers for production to discuss their needs and the relevance of our technology to their industry. We purchased and installed a development-scale 3D printer and printed a variety of test structures and coated them using atomic layer deposition (ALD). We examined the parts using scanning electron microscopy and four-point probe conductivity measurements, and studied the infusion of polymers by ALD precursors using *in situ* grazing incidence small-angle X-ray scattering.

In FY 2016, we examined the mechanical properties of infiltrated 3D-printed parts using nanoindentation measurements, and we explored the suitability of CVPAM to impart corrosion resistance to 3D-printed parts for an annular centrifugal contactor. Finally, we used CVPAM to impart electrical conductivity to create first-of-a-kind actual working 3D-printed particle detectors under development at Argonne.

### PROPOSED FUTURE WORK

In FY 2017, we will complete the fabrication and testing of a prototype 3D-printed particle detector that utilizes the CVPAM technology. We will continue our development of corrosion resistant coatings to provide durability to 3D printed structures under harsh chemical environments. Finally, we will complete our study of the mechanical properties of infiltrated 3D printed parts through collaborations with Northwestern University and the Tribology Group in Argonne's Energy Systems Division.

## Sustainable Transportation: Novel Bio-Derived Fuel Additives for Improved Vehicle Efficiency

2015-157-R1

S. Scott Goldsborough, Xing Chen, Stephen Ciatti,  
Philip D. Laible, Raghu Sivaramakrishnan, and Robert Tranter

### PROJECT DESCRIPTION

The objective of this project is to discover/develop novel, bio-derived fuel additives that can be used at small concentrations (e.g., ~1% by volume [v/v]) to tailor the chemical kinetic pathways controlling autoignition of petroleum-based fuels. Such additives could be employed in internal combustion (IC) engines to help meet evolving performance targets and legislated mandates, significantly increasing overall vehicle efficiencies, while at the same time augmenting the use of biomass feedstocks for, and reducing life-cycle greenhouse gas emissions of, the transportation sector. Though the replacement of IC engine-based powertrains is envisioned in the long term, this work will facilitate near-term gains.

Advanced IC engine designs are expected to employ a range of robust combustion systems, including downsized, boosted spark-ignition (SI) approaches, as well as low-temperature combustion (LTC) schemes. However, fuel-engine interactions can considerably constrain potential advances. SI configurations are knock-limited, while LTC schemes, which modulate the extent of mixing and fuel reactivity in order to mitigate pollutant formation, are limited by the difficulty in controlling ignition timing and rates of heat release over the entire engine operating map. Bioderived fuel additives, if appropriately designed, could be effective at facilitating improved engine design, and corresponding vehicle efficiencies.

Major tasks include (1) utilizing a heuristics-based approach to identify and screen molecules/classes of molecules that can boost octane or improve cetane, and evaluating the autoignition behavior of various additive/fuel blends via rapid compression machine (RCM) tests; (2) characterizing the decomposition kinetics of the targeted molecules using shock-tube experiments, *ab initio* theory, and modeling, and investigating additive-fuel interactions using chemical kinetic modeling; (3) biosynthesizing and separating bench-scale levels of select targets; and (4) scaling up sustainable, carbon-neutral biosynthesis efforts and chemical upgrading processes to produce sufficient volumes.

## MISSION RELEVANCE

This project directly addresses urgent national needs to improve the sustainability of the U.S. transportation system via improved IC engine/vehicle efficiency and the utilization of sustainably produced bio-derived components. Significant fuel economy gains are projected using bio-derived fuel additives compatible with combustion technologies that are expected to dominate in the near and medium terms. This work is related to the DOE energy and environmental mission areas and to a number of programs of DOE offices, including Energy Efficiency and Renewable Energy's Co-Optima initiative, Basic Energy Sciences, and Biological and Environmental Research.

## RESULTS AND ACCOMPLISHMENTS

In FY 2016, we conducted additional screening activities using the RCM, while chemical analyses were undertaken for the most promising additive candidate. Further progress was also made in improving the feedstock production and developing upgrading/synthesis pathways.

We investigated 40 different additive candidates using the RCM in FY 2015/2016, including alcohols, esters, ethers, ketones, furans, aromatics, and a few other molecule classes. Two compounds were specifically synthesized for this project, since they are not available commercially. Single-component additives were blended into a full-boiling-range gasoline at 10% v/v, and comparisons were made with ethanol, since it represents the current octane booster of choice. Wide ranges of temperature and pressure were tested to characterize perturbation effects at conditions relevant to conventional SI combustion as well as LTC schemes. The resulting database was data mined in order to distinguish structural features of the molecules that provide resistance to autoignition, or conversely, promote it. The measurements revealed a few promising candidates that could be employed at the target doping levels, especially for mixed-mode operation; that is, they boosted SI at high power and LTC at low power/idle. An invention report was filed for one of these, and due to the potential intellectual property, these are not disclosed here.

To better understand the underlying chemistry responsible for the perturbative characteristics of the additives, we initiated a chemical kinetic model for the most promising additive. This model will aid in interpreting the experimental measurements, allow us to investigate the possibility of creating toxic by-products during combustion, and help us identify other additive candidates. Initial effort already has provided feedback for

potential causes of the unique behavior observed in the RCM tests.

In strategies to produce novel and effective fuel additives biologically using negative value materials as feedstocks, additional strains of purple, non-sulfur bacteria were isolated that can grow on renewable waste streams and accumulate chemical precursors at up to 75% of their total cell mass. The bacteria were found to grow at rates comparable to those on purified carbohydrates. Additional interactions were initiated with local companies that can provide waste streams convertible by this bacterial platform. High-throughput fluorescent assays were established in order to conduct non-invasive quantitation of the chemical precursors in live cell cultures. In addition, we worked with chemists in Argonne's Energy Systems Division to develop and implement upgrading of 3-hydroxybutyrate to a unique additive in yields and qualities that were sufficient for testing.

Currently, the biopolymer from the cells is harvested via a two-step, one-pot chemical route that involves heat-assisted cell lysis to release the polymer, which is then broken down into monomers using an acid-catalyzed methyl esterification. The methyl ester monomers are then separated from cell debris via solvent extraction. Guided by initial RCM results and theoretical calculations, we identified at least a dozen molecules that can be produced via monomer valorization. One of these can be catalytically converted to the most promising additive discovered in the RCM tests. We also identified two to three candidates and structurally relevant analogues on the basis of optimal upgrading conditions, such as consideration of ease of synthesis (fewer steps, higher yield) and minimization of need for external additional carbon source (minimizing carbon footprint).

## PROPOSED FUTURE WORK

In FY 2017, the RCM database will be extended with a few additional compounds, and the functional behavior of two of the promising candidates will be further probed. Additional data-mining techniques will be applied to the dataset to better understand, empirically, the relationships between additive molecular structures and their perturbative performance. Comprehensive tests will be conducted in the RCM using the most promising additive over a wide range of conditions in order to acquire validation data for the chemical kinetic model. Engine tests will be conducted over a limited LTC operating range using this compound. The chemical kinetic model will be extended to cover the base chemistry of the additive, as well as interactions with the gasoline fuel.

With success in production of chemical precursors using several waste streams, experimental plans for FY 2017 include finalizing growth rates and precursor production levels such that a manuscript can be prepared for publication. In addition, we will continue to expand the repertoire of molecules available for upgrading, and we will explore conditions that lead to the biosynthesis of larger carbon chains or reactive substituents.

We have identified alternative methods for biopolymer and monomer extraction from cells, which will be further developed in FY 2017. Nano-adsorbent-based biopolymer/monomer separation from cell debris is more economically attractive than solvent extraction methods, while synthetic routes and upscaling optimization methods for monomer valorization will be identified for some of the most promising additives.

## Large-Scale Modeling and Simulation for an Adaptive and Resilient Power Grid

2015-159-R1

Jianhui Wang, Feng Qiu, Chen Chen, James Kavicky, and Sven Leyffer

### PROJECT DESCRIPTION

A well-prepared and well-executed response to extreme weather events can prevent possible outages, reduce the time to restore power to consumers, and potentially lead to significant economic savings. Maintaining the resilience of the power grid is critical to our nation's energy security and sustainability. This resilience effort becomes even more critical as climate change alters the frequency and severity of extreme weather events.

The core of our project will be development of a complete suite of solutions for enhancing power grid resilience. We start with the state-of-the-art, short-term weather forecasting or “Nowcasting.” We then investigate transmission-level power system restoration and distribution-level service restoration. In addition to short-term power grid operation and restoration, we also attack the problem from the long-term point of view, that is, how the system can be hardened and enhanced through an improved investment and planning process.

### MISSION RELEVANCE

The project is consistent with and supportive of DOE's Energy mission to ensure a resilient, reliable, and flexible electricity system.

## RESULTS AND ACCOMPLISHMENTS

### Milestone 1: Transmission-Level Restoration Tool Development.

In the first year of the project, we developed the framework and mathematical models for restoration at the transmission level. The framework and the models were thoroughly tested on Institute of Electrical and Electronics Engineers (IEEE) standard test cases and were ready to implement. In the second year of the project, we dedicated the majority of our time to implementing the framework and models.

The proposed software tool has two major components: the optimization module and the simulation module. The optimization module generates initial restoration plans considering operational constraints and objectives, such as generation capacities, earliest/latest start time, and minimization of restoration time. The simulation module takes the output of the optimization module and refines the operational plans to satisfy technical constraints (such as voltage stability and frequency stability). Figure 1 illustrates the difference between the operational plan and the restoration plan refined by simulation (an IEEE 118-bus test case). Note that the refined plan takes longer to restore generation capacity since line loss and voltage stability are considered. The overall restoration times are still similar.

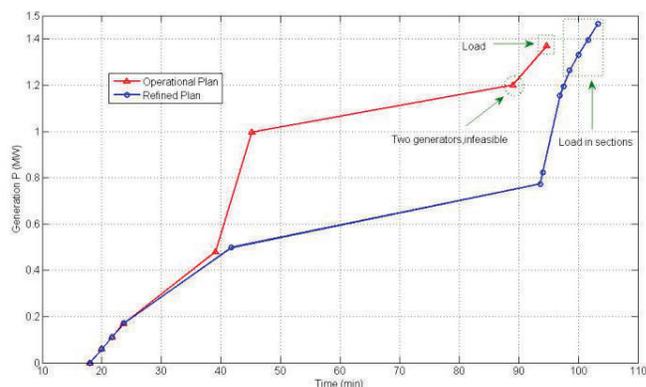


Figure 1. Comparison of operational plan (red) to refined plan (blue).

To create restoration plans for large-scale industrial-level data sets, we developed new procedures based on the original mathematical models to tackle the scalability issues. The computational complexity of the restoration problems (including network sectionalization and generator start-up sequencing) belongs to the NP (nondeterministic polynomial time)-complete category, indicating that the solution time will increase exponentially with regard to the size of the problem; therefore, solving an industrial-size restoration problem to global optimality is not realistic. We sought a trade-off between performance and optimality by decomposing

the integrated model into two separate problems: sectionalization and sequencing.

The simulation modules include Cranking Path Search, Generator Startup Plan Refinement, and Load Pickup. The three modules use alternating current optimal power flow (ACOPF) to generate and validate restoration plans. The modularized design offers the possibility of extending the functionalities (i.e., the functions can be re-assembled to perform new tasks).

The core of the simulation toolbox is the ACOPF routine, which is used to check the generator startup sequence and generate the feasible startup time considering transmission loss, reactive power support, power limits of generators, bus voltage constraints and thermal limits of lines. The ACOPF procedure is depicted in Figure 2.

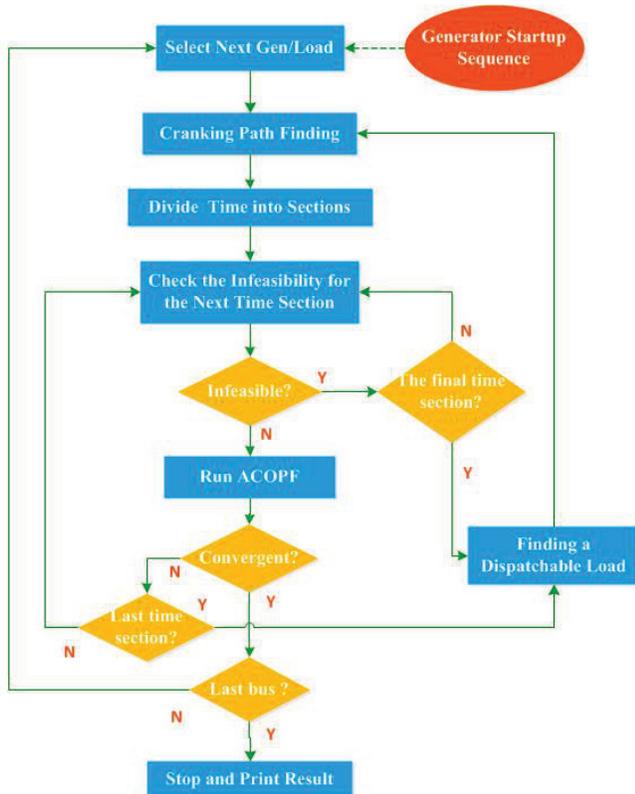


Figure 2. ACOPF-based restoration plan refinement.

The input files have two parts: the startup sequence produced by the AMPL optimization models and the electric power system power flow data, including line resistance, line reactance, and so on.

*Milestone 2: Restoration With Mobile Generators.* Truck-mounted mobile emergency generators (MEGs) are critical, flexible resources of distribution systems (DSs) for resilient emergency response to natural disasters;

however, they are currently underutilized. For better utilization, we propose dispatching MEGs as distributed generators in DSs to restore critical loads by forming multiple microgrids (MGs). As the travel times of MEGs on road networks (RNs) can greatly influence the outage duration of critical loads, a two-stage dispatch framework consisting of prepositioning and real-time allocation is introduced, and the traffic issue is considered via the vehicle routing problem. Prepositioning places MEGs in staging locations prior to a natural disaster, while real-time allocation sends MEGs from staging locations to restore critical loads by forming MGs in DSs after a natural disaster strikes. A scenario decomposition algorithm is applied to solve this problem. Illustrative cases demonstrate the effectiveness of the proposed dispatch scheme and algorithm.

## PROPOSED FUTURE WORK

The next stage of the project will focus on the following two directions:

1. Software tool development. Our ultimate goal is to create a deployable software tool for users to prepare restoration plans for their grids. Currently, the major functionalities have been completed. However, in order to make it deployable to our users, we have to accomplish the following tasks:
  - a. In order to improve user experience quality and make this restoration tool easier to use, we will develop a graphical user interface.
  - b. Cross-platform deployment packages: In reality, users may have different information technology (IT) infrastructures, including hardware, operating systems, and installed software. To reduce the deployment effort, we will develop cross-platform capability for our tool.
2. Restoration with renewable generation. As a type of renewable generation, wind power has advantages over conventional generation, such as quick ramping capability and the ability to start on its own. However, owing to its uncertainty and variability, it has not been used for black-start units (those power plants that can start without external power supply such as hydropower plants). As renewable generation continues to increase, the installed wind generation capacity has the potential to serve as a black-start resource during transmission-level restoration. We will investigate renewable generation duration forecasting, restoration with wind generation as a secondary black-start resource, and other relevant issues.

## Connected and Automated Vehicles

2015-176-R1

Aymeric Rousseau, Joshua Auld, Dominik Karbowski, and Vadim Sokolov

### PROJECT DESCRIPTION

Connected and automated vehicles (CAVs) are bound to transform on-highway transportation in the near future. Vehicles will be able to communicate with each other and with the surrounding infrastructure as some or all of the tasks incumbent upon drivers will gradually shift to automated controllers. Although the R&D on the underlying technology has been many years in the making, the impact that CAVs may have on energy use—whether it is positive through more efficient driving and reduced congestion or negative through increased travel demand—has been largely overlooked. Advanced high-fidelity simulation tools are needed not only to evaluate impacts before actual implementation, but also to identify system-level control strategies that will improve mobility and reduce energy use. The objective of this project is to develop an integrated model combining both traffic flow models and advanced vehicle models.

### MISSION RELEVANCE

Most of the research in the area of intelligent transportation systems has been targeted at mobility and safety. On another side, systems researchers have been focusing on energy efficiency on standardized cycles. However, it has not been possible so far to assess global energy performance in a real-world transportation network scenario. Thus, the main benefit of the integrated model we propose would be to quantify the energy impact of advanced vehicle technologies, one of the main focuses of DOE's energy mission.

### RESULTS AND ACCOMPLISHMENTS

During FY 2015, we focused on the development of new capabilities including the following:

- A new traffic flow model was developed in POLARIS to enable the analysis of platooning's effect on mobility. (POLARIS is a transportation system simulation tool used to model entire metropolitan areas to study the impact of new technologies on mobility.)
- The development of a new multi-vehicle platform was initiated to allow vehicle-to-vehicle simulations. The first application included the development of a Cooperative Adaptive Cruise Control algorithm.

- A POLARIS model for the Ann Arbor metropolitan area was developed to leverage existing vehicle datasets from deployments by DOE and the Department of Transportation.

The ability to assess the impact of advanced technologies from both a mobility and an energy point of view was significantly improved through the development of the new process shown in Figure 1. Initially, we used a commercial micro-simulator to disaggregate mesoscopic vehicle trajectories from POLARIS for input to Autonomie. (Autonomie is a vehicle system simulation tool focused on simulating the energy consumption and performance of advanced powertrain technologies.) This approach limited the scale we could consider during our analysis, both from a spatial point of view and from a number-of-vehicles point of view. In FY 2016, we developed an improved stochastic simulator for POLARIS-generated trajectories that allows us to bypass the commercial micro-simulator tool. We have developed a process to automatically and efficiently run and analyze hundreds of thousands or millions of runs through high-performance computing. The faster process allows us to handle scenarios that include much larger scales.

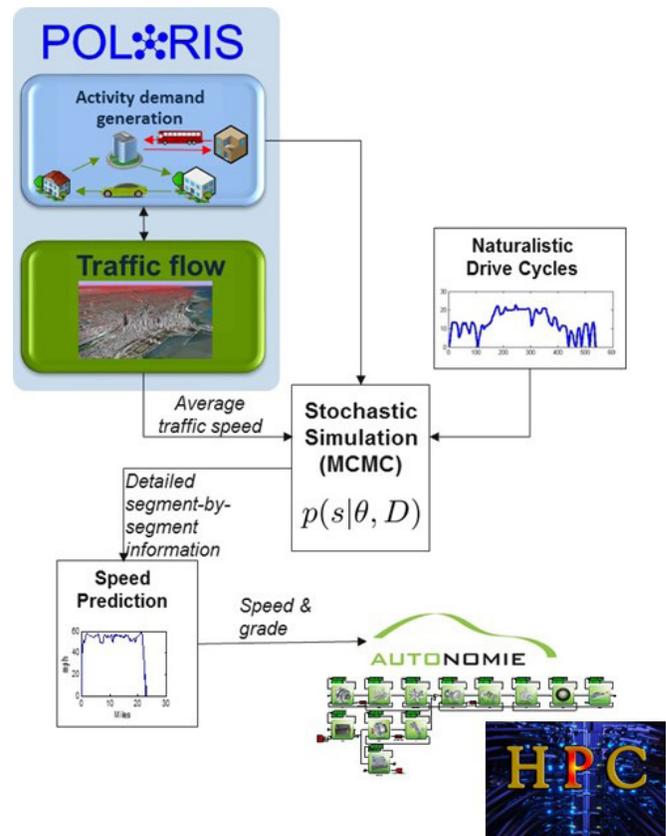


Figure 1. Newly developed process to simultaneously quantify the mobility and energy impact of advanced technologies at the regional level. HPC: high-performance computing

Multiple improvements were implemented in POLARIS, including the following:

- Router model improvements:
  - Incorporated historical observed travel times into route selection.
  - Implemented weighting of current vs. historical times in link selection.
  - Included routes from multiple potential starting links for better model fidelity.
  - Implemented analysis tool for estimating relative gap between simulated dynamic traffic assignment and actual shortest paths.
- Traffic flow model improvements:
  - Implemented microscopic queuing model for intersections with traffic lights.
  - Incorporated parameters that allow representation of human driving (reaction time, acceleration/ deceleration).
- POLARIS code/process improvements:
  - Developed a methodology to modernize and simplify code design to decrease model development time.
  - Identified, documented, and started implementing code changes needed to maintain up-to-date cross-compiler compatibility.
  - Developed a POLARIS testing environment for quality assurance/quality control.
  - Developed process document and support scripts for quickly starting new models.
  - Developed management tools for generating multiple runs for parametric studies.

One additional objective was to identify new engineering and analysis opportunities enabled by the increased vehicle sensing and connectivity. We were able to investigate several concepts, including the following:

- Traffic density estimation (using adaptive cruise control radar following distances + global positioning system [GPS] + speed).
- Detection of anomalous traffic events (distribution of pedal position vs. GPS).
- Environmental conditions (rain, temperature, road surface, etc.) versus location.

## PROPOSED FUTURE WORK

In FY 2017, we will pursue these objectives:

- *Traffic flow simulation.* Integrate microscopic traffic flow simulator into the integrated models so it is a feature of the software.
- *Autonomie integration.* Integrate Autonomie-light into POLARIS so that simulations are performed in a single shot.
- *Enhanced user interface for case study/model development.* Extend this enhancement (currently limited to the Network Editor) to all model inputs and parameter settings to replace the scenario file system currently in place. Network Editor Python code can be used as a platform.
- *Scenario manager.* Redevelop this manager in higher-level language (Python). Possibly integrate with Network Editor as above.
- *POLARIS capabilities.* Enhance POLARIS capabilities to expand the list of potential CAV use cases to evaluate.

The work performed in this LDRD project has been solely focused on the development of new capabilities (from both a model and a software point of view) that will then be applied to specific problems.

Our work to date has allowed us to gain new potential sponsors and partners, including the DOE Vehicle Technologies Office, the University of Michigan, the City of Detroit, U.S. Department of Defense Tank and Automotive Research, Development and Engineering Center, the DOE Clean Energy Research Center-Clean Vehicle Consortium, and a DOE small business voucher led by Connected Signals.

# Advanced Control Algorithms for Improving Energy Consumption of Connected and Automated Vehicles

2016-126-NO

Jeffrey Larson, Dominik Karbowski, Todd Munson, and Vadim Sokolov

## PROJECT DESCRIPTION

We are studying the effects of connected and automated vehicles (CAVs) on traffic patterns and fuel use in metropolitan road networks. We are developing algorithms for routing vehicles through metropolitan road networks in a fuel-optimal fashion by exploiting the savings provided by platooning of CAVs. Platooning vehicles collectively uses 10–20% less fuel because trailing vehicles experience less aerodynamic drag.

## MISSION RELEVANCE

This project contributes to DOE's energy security mission to develop and deploy large-scale, energy-efficient solutions in all of the nation's energy sectors. Individuals and companies use billions of gallons of fuel every year; decreasing this usage will lead to significant economic savings and environmental benefits.

## RESULTS AND ACCOMPLISHMENTS

For any network and a set of vehicles with origin/destination nodes/times, we developed a model that defines the platooning routing problem. By solving this optimization problem, we find a coordinated routing of vehicles that routes them to their destinations on time while using the lowest amounts of fuel (Figure 1). While common approaches to this problem decompose the platoon coordination and vehicle routing into separate problems, our model addresses both problems simultaneously in order to obtain better solutions. We use modern modeling techniques and constraints, inferred from analyzing the platoon routing problem, to address larger numbers of vehicles and larger networks than previously considered in the literature. We also obtain excellent solutions in approximately one minute for much larger networks and vehicle sets than previously considered. We demonstrate our methodology by evaluating the benefits of a coordinated solution, then comparing it to the uncoordinated case where platoons only form in an *ad hoc* manner. When vehicles are willing to wait for a short time to coordinate their travel with other vehicles, fuel savings approaching 10% are possible for platooning vehicles.

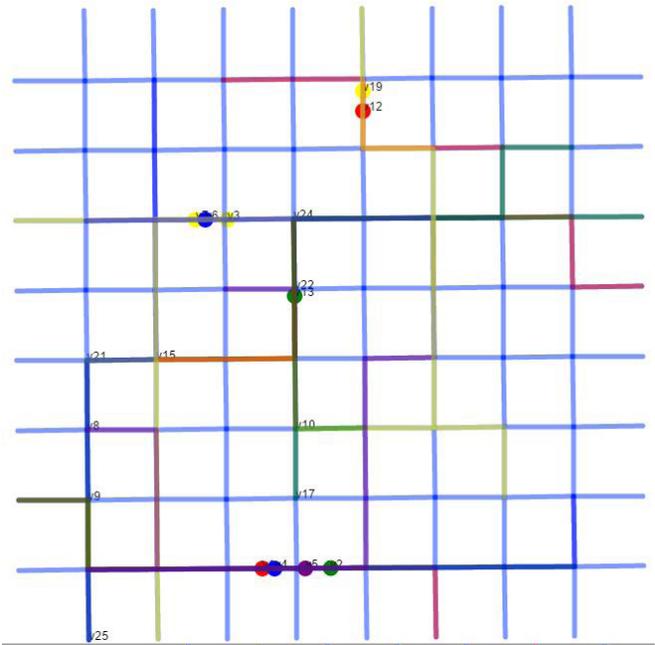


Figure 1. A snapshot at one instant of an animation of an optimal platoon routing of vehicles with random starting and ending points in the network. The color of the paths that each vehicle will traverse matches the color of the vehicle (represented by a circle). The complete animated simulation can be observed here: [http://polaris.es.anl.gov/cav\\_map\\_notiles/](http://polaris.es.anl.gov/cav_map_notiles/)

## PROPOSED FUTURE WORK

We are currently working on expanding the number of vehicles that we can route through a network in a fuel-optimal fashion. We will use our previous results to route small subsets of vehicles and combine these routes into a large-scale routing for the Chicago metropolitan road network. We will also be simulating the results in the POLARIS traffic simulation software in order to better understand the effects that platooning CAVs will have on metropolitan traffic patterns as the percentage of platooning-capable CAVs increases. For example, as the fraction of CAVs on major highways increases, congestion should only occur at higher traffic densities than we experience today. Long trains of platooning vehicles may themselves introduce traffic issues; however, our POLARIS studies will help us better understand their effects.

# Integrated Water-Energy Systems Assessment Framework (IWESAF) for Water-Energy Sustainability and Resilience

2016-152-NO

Eugene Yan, Getnet Betrie, Corrie Clark, Mi-Ae Ha, Vladimir Koritarov, Mattew Mahalik, Vinod Mahat, Leslie Poch, Feng Qiu, Thomas Veselka, Jianhui Wang, May Wu, and Zhi Zhou

## PROJECT DESCRIPTION

Energy and water systems are intrinsically interconnected. The future growth in population and energy-water demand, climate change, increasing hydrologic and climate extremes, and rapidly evolving technologies and policy in energy and water spaces increase the complexity and uncertainty of energy-water systems interactions. The goal of this project is to develop an integrated regional modeling framework (IWESAF) that provides flexible and extensible energy-water system assessment tools and advanced system optimization models to evaluate and enhance the sustainability, reliability, and resilience of energy-water systems. The technical objectives include the following:

1. Developing an energy-water modeling framework that incorporates existing and new tools that represent major energy sectors; physical, chemical, and thermal processes related to hydrologic cycles; and management practices and human activities relevant to energy and water systems;
2. Creating an IWESAF coupling process that provides temporal and spatial coupling, allows for automatic aggregation and disaggregation of system components, and facilitates simulation of cross-domain feedback among systems;
3. Formulating data-modeling processes that characterize intensity, duration, and frequency of hydrologic responses to extreme weather events; provide hydrologic forecasting; and optimize electricity generation, power grid operation, and planning in response to extreme events, water forecasting, and market values; and
4. Validating IWESAF's functionality and capability for various applications such as identifying/quantifying spatial and temporal dynamic interactions among all energy-water systems components and evaluating climate change, demand growth, and adaptation/optimization strategies.

## MISSION RELEVANCE

This project supports the DOE's missions in energy security, science, and the environment. The integrated framework developed from this project will support the DOE's energy-water nexus (EWN) crosscut effort, especially in the area of EWN data, modeling, and analysis. The IWESAF framework will make it possible to (1) investigate complex, dynamic interactions of energy and water systems under various scenarios; (2) improve our understanding of these interactions, which will lead to more resilient, robust and reliable energy-water systems; and (3) provide a basis for identifying regionally appropriate technologies and energy-water infrastructures.

## RESULTS AND ACCOMPLISHMENTS

We have completed the initial data exchange and storage design, which can facilitate data exchange among all tools via a common database that considers various spatial and temporal scopes and foci. We have also made significant progress on the following key system models, including process models and sector models:

*Regional Hydrologic Modeling.* The regional hydrologic system model is mainly developed for coupling energy system models. We use the Upper Mississippi River Basin (UMRB) as a test basin for the framework testing. The hydrologic modeling tool includes hydrologic modeling, stream water temperature modeling, and water management modeling. The simulated results will be used as an input to power plants for evaluating the impact of water on thermal and hydropower generation. We utilized the previously developed hydrologic model for the UMRB and added a new module for simulating stream water temperature regimes.

*Climate and Hydrologic Extreme Event Generator.* The objective of the climate and hydrologic extreme event generator is to identify and generate climate and hydrologic extreme events for evaluating the effects of extremes on the water-energy nexus and system response as well as the resilience of the power grid system. We characterize the extremes on the basis of duration and frequency to determine the corresponding intensity (Intensity-Duration-Frequency, or IDF). We have identified an approach and developed a methodology to determine IDF and sets of extremes for each area which can provide extreme climate and hydrologic intensity maps based on duration and frequency to water and energy system models for further evaluation (Figure 1).

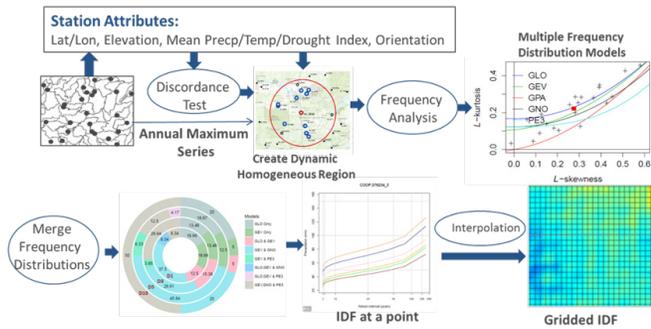


Figure 1. Process used by climate and hydrologic extreme event generator.

**Thermal Power Plant Simulator.** Thermal power plants are major water users in power generation. The majority of the existing power plants in Illinois require high water-use intensity for system cooling. In this task, we evaluated more than 2000 thermoelectricity plants on the basis of fuel source and cooling technology and developed a power plant model to predict electricity generation efficiency under water stress (water shortage and increased water temperature). Figure 2 shows predicted reduction of thermoelectricity generation at major power plants in Illinois during a 100-year heat-wave event of seven days' duration.

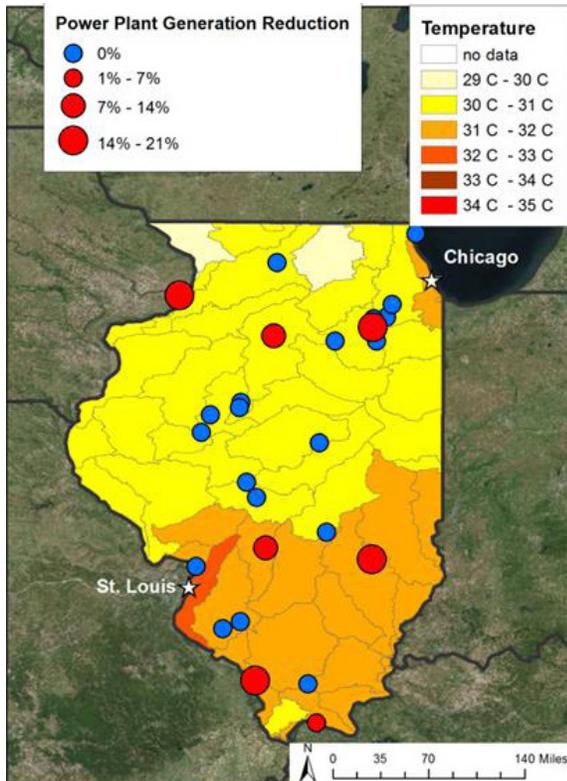


Figure 2. The water temperature distribution and generation reduction of power plants in Illinois resulting from a 100-year heat-wave event.

**Power Grid System Model.** The main objective of this task is to integrate the grid system model with hydropower and thermal power generation models that incorporate interactions between energy and water systems. We tested the power grid using the IEEE 118-bus system, which includes 54 thermal generators (21 gas/oil and 33 coal units) and three hydropower plants. The system coordination is shown in Figure 3.

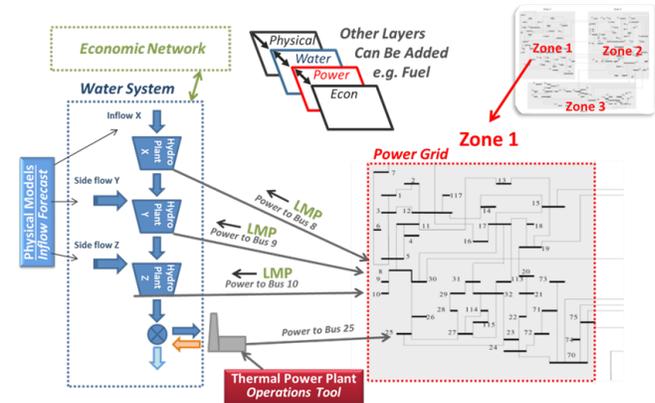


Figure 3. Integration testing with IEEE 118-bus system (grid system model, hydropower operation model, and thermal power plant simulator).

The water use intensity from thermal power units was input from the thermal power plant simulator on the basis of two types of cooling systems (once-through and recirculation). The three cascaded hydropower plants were operated considering reservoir operations, water delivery obligations/targets, and maximum power outputs and turbine release, as well as service obligations. A loose coupling between the grid system model and the hydropower plant operation model was tested to identify the future approach for improvement of the framework integration. An interactive process was performed on the basis of the Locational Marginal Price reaction function. The hydropower output was optimized considering several metrics: financial revenues, service obligations, reservoir storage and elevation, and water delivery obligations.

The integrated grid system model can be used to evaluate impacts of water shortages and heat waves on potential curtailment, optimal dispatch, and associated cost. The testing results indicated that severe load curtailment could occur with restricted water supply, resulting in higher total system cost due to more expensive generation dispatch and penalties from load curtailment.

## PROPOSED FUTURE WORK

In the second year of the project, we will complete development of all individual system component models and improve the integration of the power grid model with the thermal power plant simulator, hydropower model, and hydrologic system model on the basis of the gaps, missing features and functionalities identified in the first year. A framework application and test case will be performed in the third year to (1) demonstrate model integration, (2) identify system response and assess resilience, and (3) evaluate adaptation/optimization strategies.

## VERIFI 2.0: Next Generation Engine/Fuel Simulation Codes

2016-175-NO

Douglas Longman, Paul Fischer, Yuri Georgievski, Stephen Klippenstein, Janardhan Kodavasal, Misun Min, Sibendu Som, Ananias Tomboulides, and Albert Wagner

### PROJECT DESCRIPTION

VERIFI 2.0 undertakes the development of a well-integrated suite of massively parallel simulation codes for engines and/or fuels that (1) provides a substantial improvement in computational combustion and predictive engine and/or fuel simulation, (2) is well tuned for computer architectures of the upcoming decade, and (3) is capable of greatly accelerating the design of future engines and/or fuels. This major advance in the existing Virtual Engine Research Institute and Fuels Initiative (VERIFI) effort will yield a unique capability that will be used in DOE national labs and academia to understand the science required to enhance engine efficiency, and in industry to engineer the engine-fuel combustion concepts of the future. It will also help establish at Argonne ongoing development and support of these codes and their underlying science into the future, including development support for the EStokTP code (in collaboration with researchers from Politecnico di Milano, Italy) and direct numerical simulation (DNS) work (in collaboration with researchers from ETH Zurich, Switzerland).

### MISSION RELEVANCE

This program is relevant to DOE's energy security mission. New DOE programs, such as the Office of Energy Efficiency and Renewable Energy's (EERE's) Co-Optimization of Fuels and Engines (Co-Optima), which began in FY 2016, would be a prime beneficiary of the VERIFI simulation capability. The VERIFI 2.0 program could likely be the launching pad for a new DOE Office of Science Basic Energy Sciences (BES)-sponsored

Energy Frontier Research Center (EFRC). We will actively pursue engagement with DOE programs like the existing Advanced Scientific Computing Research (ASCR) co-design centers. U.S. Department of Defense (DoD) agencies have long wanted a single fuel in the field for all of their combustion devices. The power of VERIFI 2.0's NEK5000, together with predictive fuel chemistry mechanisms could enable the development of combustion concepts in devices that are more fuel agnostic. Engine manufacturers will also benefit from these Argonne-developed codes as they will enable predictive engine and combustion simulations with new fuels of interest.

### RESULTS AND ACCOMPLISHMENTS

A 60-million core-hour ASCR Leadership Computing Challenge (ALCC) award on Mira was used to perform thousands of gasoline compression ignition (GCI) engine computational fluid dynamics (CFD) simulations with the commercial code CONVERGE. The data generated from these simulations was used to perform a global sensitivity analysis (GSA) on the relative impact of uncertainties in various model inputs on combustion and emissions predictions from the model. The GSA picked out key inputs that were shown to be important to key engine performance targets such as combustion phasing and hydrocarbon and nitrogen oxide (NO<sub>x</sub>) emissions.

Enhancement of Argonne's open source CFD software NEK5000 to add features required for internal combustion engine simulation continued with progress on the ease of mesh generation and study of fluid flow through real engine intake valve geometry (see Figure 1). Our effort involved implementation of a moving mesh approach for the simulation of flow and combustion in internal combustion (IC) engines. We implemented and validated an approach that allowed us to take a time step that was five times larger in size, reducing the overall computational time by a factor of three.

Our fuel chemistry efforts focused on the development of a code (EStokTP) for automatically predicting the chemical kinetics of single-channel reactions. The code for this has been tested on a large number of reactions and is now being used to provide high-quality results for interesting abstraction reactions. Recently, we have expanded the EStokTP code to include more or less arbitrary isomerization reactions, which now allows us to explore the majority of combustion reactions.

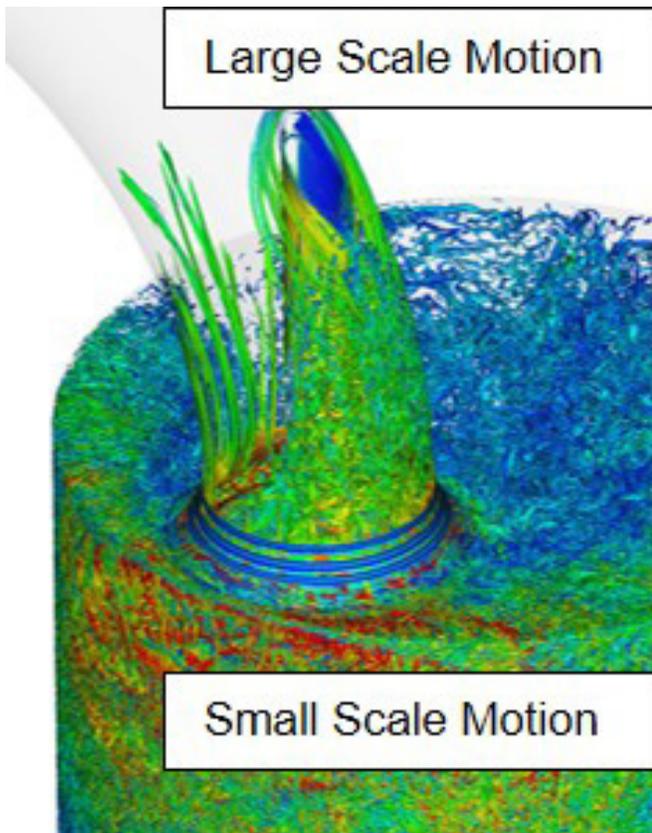


Figure 1. Performed DNS of flow inside the intake pipe of the Transparent Combustion Chamber engine with ETH Zurich. The results demonstrate the significant impact on the scales of motion with the cases of multiple Reynolds numbers for the geometry involving the valve and valve stem.

### PROPOSED FUTURE WORK

The milestones for FY 2017 include efforts to:

1. Produce parallel and scalable automatic reaction mechanism generation software;
2. Demonstrate ensemble engine simulations for GSA studies through an existing ALCC award (CONVERGE) and renew the FY 2016 ALCC award;
3. Extend the engine simulation capabilities of the NEK5000 code, including resolved meshing; and
4. Apply for a 2018 INCITE Award.

Using NEK5000, we will work on the coupling of the valve(s) and piston motion for the Transparent Combustion Chamber (TCC) engine geometries. The next stage of EStokTP development will involve coupling this code with other electronic structure codes such as NWChem and our Variable Reaction Coordinate Flux (VaReCoF) kinetics code for treating barrierless reactions. We will also write driver programs to sample over the relevant combustion reactions for a specified fuel. This activity will lead us to start interacting with WorkFlow software such as SWIFT, which is being used with the engine CFD work.



# **LDRD PRIME – BIOLOGICAL AND ENVIRONMENTAL SCIENCE CAPABILITY DEVELOPMENT**

# Identifying Patterns and Associations among Hyperspectral Data and Meteorological and Biological Measurements for Investigating Near-Surface Atmosphere-Biosphere Interactions

2014-132-R2

Yuki Hamada, David Cook, Nicola Ferrier, and Roser Matamala Paradedá

## PROJECT DESCRIPTION

Atmosphere, plants, and soils control terrestrial carbon and water cycles. To enable more accurate climate forecasting, researchers need to gain a better understanding of ecosystem dynamics at the biosphere-atmosphere interface. The goal of this project is to explore analytics for investigating temporal patterns and associations between optical measurements and meteorological and biological measurements by using high-temporal-frequency, hyperspectral reflectance measurements of the land surface. These analytics will demonstrate the power of hyperspectral reflectance measurements to predict the carbon and water exchange fluxes between the atmosphere and the biosphere. These predictions will improve climate modeling by facilitating parameterization of land surface models and by providing data for model output evaluation and benchmarking. The objectives are to (1) construct a rugged optical tower system capable of enduring all weather conditions and supporting the collection of land surface measurements autonomously; (2) collect high-temporal-frequency, hyperspectral reflectance measurements of plants and soil; (3) investigate associations and temporal patterns between hyperspectral measurements and meteorological/biological measurements; and (4) determine the effectiveness and limitations of hyperspectral measurements in estimating ecosystem processes, such as carbon and water fluxes.

## MISSION RELEVANCE

This project is relevant to DOE's environmental quality mission and, in particular, to the Office of Biological and Environmental Research (BER), because it addresses current roadblocks to collecting and analyzing high-temporal-frequency hyperspectral data for developing and improving land surface models. Outcomes of this

project will benefit DOE BER Terrestrial Ecosystem Science and Earth System Modeling programs by contributing new enabling technologies to the Atmospheric Radiation Measurement (ARM) baseline measurements and the AmeriFlux network. It will also benefit DOE-BER Systems Biology Knowledgebase by integrating hyperspectral data into cloud computing to study plant/ecosystem activities.

## RESULTS AND ACCOMPLISHMENTS

In FY 2014, we completed the rugged and robustly equipped tower that supports the EcoSpec optical sensor system and Linux-based software that enables the autonomous collection of hyperspectral reflectance data and associated measurements in a synchronized manner. In FYs 2015 and 2016, we deployed the EcoSpec system at the AmeriFlux Site (US-IB1) located at Fermilab. We collected hyperspectral reflectance measurements and other optical and infrared data approximately every minute from dawn to dusk through the growing seasons of 2015 and 2016. Simultaneously, we collected carbon dioxide (CO<sub>2</sub>), water, and energy measurements using the Eddyflux tower at the site. During the 2016 season, we conducted intensive biological measurements in order to determine the indicative power of hyperspectral remote sensing for plant functions and their mechanisms. We took weekly leaf sampling and measurements of plant height, chlorophyll content, leaf count, and canopy cover in our aim to understand plant growth and biogeochemistry (e.g., carbon and nitrogen) flow across the growing season. Our two-day diurnal leaf tissue sampling was accompanied by leaf-scale hyperspectral reflectance and leaf-surface temperature measurements to understand the physiological responses of plants to light, temperature, and moisture (i.e., shifts of pigment ratios related to plants' photosynthetic capacities and their defense mechanisms).

A preliminary analysis showed that the Red-Edge Normalized Difference Vegetation Index (RENDVI) calculated from the hyperspectral reflectance data corresponded well with estimates of gross primary production (GPP), a measure of carbon assimilation through plant photosynthesis obtained at the site ( $R^2 = 0.85$ , where  $R^2$  is a statistical measure of how close the data are to the fitted regression line). However, subsequent analysis indicated that the temporal dynamic of the limiting factors influencing GPP throughout the plant growth stages and environmental conditions had the result that no single index reliably estimated GPP throughout the year. To overcome this obstacle, we developed a Bayesian model that integrates multiple functions and an autoregressive component for

simulating temporally varying limiting factors influencing photosynthesis. The model, called the NDVI\_PRI model, uses two narrow-band spectral vegetation indices to predict GPP across the growing season: the Normalized Difference Vegetation Index (NDVI) indicates plant architecture and the amount of photosynthetic biomass, and the Photochemical Reflectance Index (PRI) indicates the light-use efficiency of plants.

The NDVI\_PRI model strongly correlates with GPP measurements estimated using the eddy covariance method ( $R^2 = 0.95$ ) (Figure 1), which is currently the most prevalent method for obtaining GPP. The NDVI\_PRI model significantly improved GPP prediction from a previous single-index model based on RENDVI, with ( $R^2 = 0.85$ ). GPP estimates using the NDVI\_PRI model resulted in minimal bias (slope = 0.96) and great consistency (intercept = 1.12) as shown by the linear fit to the data in the figure. Further, the NDVI\_PRI model GPP estimates closely matched the reference GPP across the season (Figure 2) by predicting the steady increase in the early season and the sharp decline in the late season. The model also captured the fluctuations of GPP that were likely associated with drought and high temperature during the mid-season. We expect this model to be of great interest to the scientific community because it provides a new understanding of optical data analysis and an innovative way for measuring ecosystem fluxes.

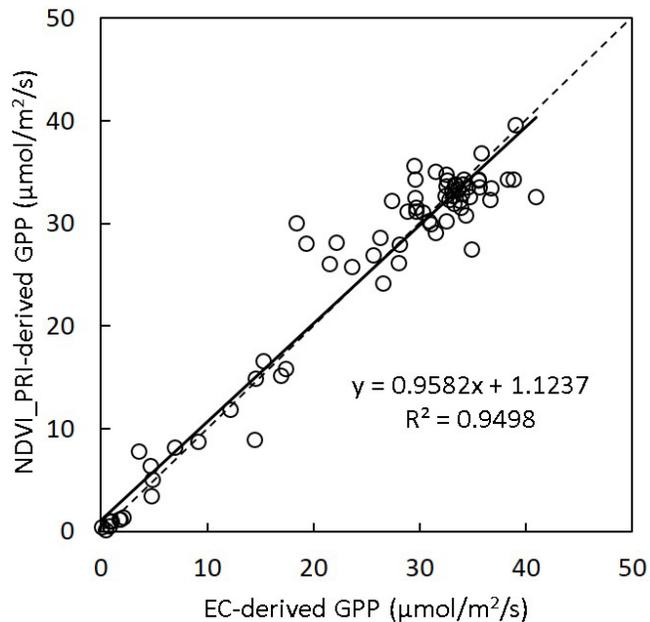


Figure 1. Scatter plot of gross primary production (GPP) predicted by our model (NDVI\_PRI) and estimated using the eddy covariance (EC) method.

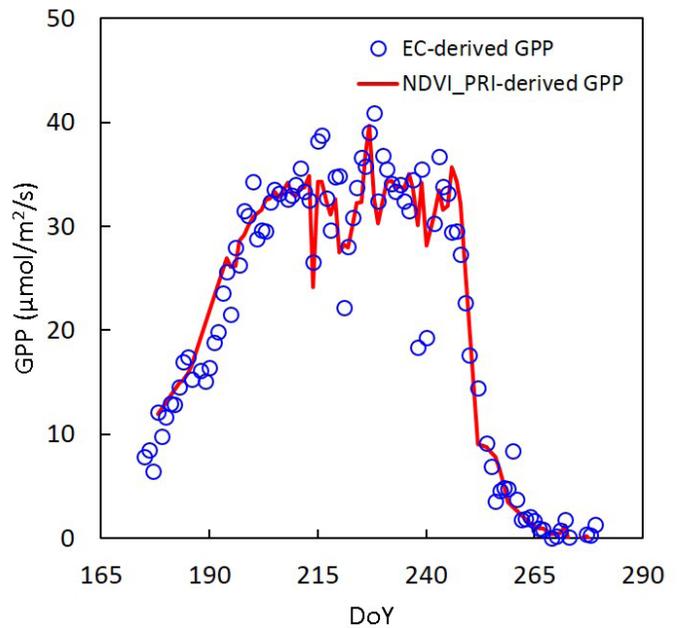


Figure 2. Seasonal courses of GPP predicted by our model (NDVI\_PRI) and estimated using the eddy covariance (EC) method. (DoY=Day of Year)

#### PROPOSED FUTURE WORK

FY 2016 was the final year of the LDRD project. The NDVI\_PRI model could be further improved in the future by training it to (1) depict distinct GPP patterns associated with sudden shifts in moisture availability that may occur in the early season, (2) constrain overestimation that may occur during drought and high-temperature conditions in the mid-season, and (3) better capture the onset of senescence. We are confident that consistent hyperspectral data collection throughout the growing season and the integration of spectral information about pigment ratios and leaf moisture will further improve the accuracy of GPP prediction by the model. These tasks will be supported by the Lillie Research Innovation Award (Marine Biological Laboratory). We are currently working on characterizing these properties using hyperspectral data. In addition, we plan to extend model development into predicting ecosystem respiration and transpiration fluxes for coming years. Our plan is to submit a proposal for a field campaign at the DOE's ARM Southern Great Plains Climate Research Facility for measuring and monitoring ecosystem fluxes during the summer of 2017.

## Minimizing Environmental Microbial Community Complexity at the Bench: Isolating and Characterizing Minimal Stable Communities (MSCs) Over Time

2014-141-R2

Dionysios A. Antonopoulos, Theodore M. Flynn, and Folker Meyer

### PROJECT DESCRIPTION

Many natural environments (e.g., soil) exhibit ultrahigh levels of microbial community diversity, thereby obfuscating study of specific interactions between organisms and how these interactions contribute to a community's stability. This project is focused on uncovering components of microbial community stability by isolating and studying what we term "minimal stable communities" (MSCs) via a high-throughput screening, cultivation, and monitoring platform. For a given complex microbial community, we want to determine the microbial *interactions* that are the basis for stability—in other words, how community members respond to a disturbance.

### MISSION RELEVANCE

This project has direct relevance to development of the DOE Systems Biology Knowledgebase platform, as well as other components within the DOE Genomic Science program. Notably, the research described here would contribute to the development of -omics experimental capabilities and the enabling technologies needed to achieve dynamic, systems-level understanding of organism and/or community function.

### RESULTS AND ACCOMPLISHMENTS

*Initial Environmental Microbial Community Minimization Using Parallelized Substrate Arrays.* A primary challenge in microbial ecology is understanding how environmental forces shape the structure and function of microbial communities. While niche adaptation plays a strong role in determining what organisms are active in a given environment, stochastic factors such as dispersal limitation are significant factors as well. In this project, we utilized parallel bioreactors to examine the effect of nutrient amendment on microbial communities taken from six disparate environments (i.e., soil from a temperate prairie and forest, tropical forest soil, subalpine forest soil, and surface water and sediment from a palustrine emergent wetland) by enriching for "minimal

communities" in each bioreactor according to substrate and then coupling it with massively parallelized DNA (deoxyribonucleic acid) sequencing to compare the profiles of the enrichments *en masse*.

Dilute subsamples of material from each environment were used to inoculate 96-well microtiter plates amended with one of 31 carbon sources from six different classes of organic compounds (phenols, polymers, carbohydrates, carboxylic acids, amines, amino acids) in triplicate. DNA sequencing libraries were then generated to inventory the organisms present in each well by targeting a broadly occurring gene found in all microorganisms: the ribosomal RNA (rRNA) gene, which is critical to the synthesis of proteins. These were then sequenced using an Illumina MiSeq instrument at Argonne's Environmental Sample Preparation and Sequencing Facility (ESPSF) and then analyzed using Argonne-based cloud computing platforms (Magellan).

The results from these initial surveys indicated to us that the most abundant organisms in the enrichments were not the most abundant organisms in the sampled environments. Sequences classified in the genus *Pseudomonas* accounted for 36% of all sequences in the enrichments but had an average abundance of only  $0.26 \pm 0.17\%$  across all of the environmental samples used as inocula. In five of the six enrichment experiments, *Pseudomonas* was enriched on average 61- to 300-fold relative to the inoculum. Others, like *Ralstonia*, were considerably enriched in some environments (tropical and subalpine forest soil) but were either absent or depleted in the others. Overall, these data showed that the operational taxonomical units (OTUs) most abundant in the enrichments were largely members of the Proteobacteria and the Bacteroidetes, whereas OTUs classified in the Actinobacteria, Verrucomicrobia, and Acidobacteria phyla were considerably less abundant in the enrichments than they were in the original environments. However, each individual well was composed of multiple organisms supporting the concept of enriching "minimal communities" using this approach.

Global ANOSIM calculations were conducted to compare the similarity of microbial communities within each substrate category and within each individual substrate itself. Most significantly, comparing enrichments amended with a carbohydrate with those amended with a phenolic compound yielded statistically significant ANOSIM values ( $R_{\text{ANOSIM}} = 0.483$  to  $0.597$ ) in three of the six environmental enrichments: wetland water, temperate forest soil, and subalpine forest soil. None of the other within-environment comparisons yielded significant results for more than one of the six environmental sources.

That the initial abundance of an organism does not determine the extent to which it became enriched provides evidence for niche adaptation within the enrichments by organisms better adapted to the nutrient-rich conditions within the microtiter plate. Yet across all of the microtiter plate enrichments, we found that the environmental source used to inoculate the well, not the carbon source it was amended with, was the strongest factor influencing the overall structure of the community in each enrichment suggesting a long-term selection by the environmental source persisting.

*Enriched Microbial Community Subsets and Identification of Generalists in Substrate Arrays under Varying pH Conditions.* We then conducted a second study focused on studying natural complex microbial communities from the temperate and tropical forest soils by enriching in a high-throughput manner subsets of the environmental communities based on substrate utilization under varying pH conditions. For a given complex soil microbial community, we sought to determine the effect of acidic or basic conditions on the composition of communities with identical substrates at their disposal and whether different pH conditions (acidic, basic, and neutral) favor or inhibit the emergence of “generalist” organisms in these enrichments. Incubations were conducted using materials collected from forest soils obtained from the DOE Fermilab National Environmental Research Park (NERP) and a Caribbean lowland rainforest within the EARTH University Forest Reserve in Costa Rica (the aforementioned temperate forest and tropical forest soils).

As in the prior experiment using these types of enrichment conditions with the general substrate array, the consistent appearance of generalist organisms specific to each inoculum environmental site was noted. For the Fermilab Temperate Forest, this was a member of the *Pseudomonadaceae* (a member of the Gammaproteobacteria), whereas for the Costa Rica Tropical Forest site, a member of the *Brucelleacea* (Alphaproteobacteria) consistently appeared across the enrichments. These observations suggest that differences in pH conditions affect the composition of microbial communities having the same amino acids at their disposal. Furthermore, differences in pH conditions may favor the emergence of new generalist organisms within a microbial community given that the same generalist was not consistently found under both acidic and basic conditions in the Costa Rica and Fermi Lab forest samples.

*Summary.* Overall, this work lays the foundation for further research on elucidating the resistance and resilience properties of candidate minimal microbial communities with regard to the extent to which initial diversity level is

recapitulated within the microbial community following enrichments and pH perturbation.

This work has provided us with a set of parameters for implementing parallelized continuous culture systems to test the response of the “minimal communities” to a disturbance (i.e., changes in substrate and pH) over time that would be of relevance to DOE and industry.

## Developing Remote Automated Sensors to Direct Sampling of Aerobic-Anaerobic Switching in Floodplain Ecosystems to Characterize the Response of Microbial Carbon Metabolism at High Temporal Resolution

2014-145-R2

Jack A. Gilbert, Christopher Henry, Kenneth M. Kemner, Sarah O'Brien, and Edward J. O'Loughlin

### PROJECT DESCRIPTION

Variation in the localized concentration and availability of terminal electron acceptors such as iron and nitrate are likely to influence the abundance of anaerobic respiratory microorganisms that utilize the reduction of these compounds for energy. Thus, changes in the concentration and availability of terminal electron acceptors will alter the onset of methanogenesis and the flux of methane due to competition between methanogenic archaea and anaerobic respiratory bacteria for the same electron donors (e.g., hydrogen and acetate). In addition, terminal electron acceptors (e.g., iron and nitrate) are required for anaerobic methanotrophy that will also modulate methane flux to the atmosphere.

However, the genomic and regulatory responses to differences in starting concentrations of electron acceptors are poorly characterized, especially regarding their influence on time-to-onset and duration of methanogenesis, and the resultant flux of methane to the atmosphere. The impact of anaerobic respiration and methanotrophy on methanogenesis should be directly linked to the concentration of terminal electron acceptors and to the production of electron donors by microbial fermentation of organic matter; however, the genotypes and functional markers responsible for these processes are poorly characterized. We propose to capture the genomes of the key organisms involved in this process

and determine how they will respond to changing concentrations of terminal electron acceptors with regard to the development of methane.

### MISSION RELEVANCE

This project is relevant to DOE's mission in the environment. Methane cycling in soils is of direct relevance to the DOE Office of Biological and Environmental Research's mandate to explore terrestrial carbon turnover associated with climate change.

### RESULTS AND ACCOMPLISHMENTS

In FY 2014, we focused almost exclusively on study design. We developed a working group that brought together researchers as well as other interested scientists to determine the specific question we would ask in the field and lab experiments for FY 2015. In FY 2015, we implemented sediment sample collection at a designated field site in Holland, Michigan, which resulted in microbial community and biochemical analysis, the data of which was the focus of investigation in FY 2016. Data collected from the Holland, Michigan, floodplain field sites were analyzed. Results from the work indicate that mature floodplains largely serve as a carbon dioxide sink, but also as a source of methane; however, newly formed wetlands are a source of carbon dioxide while generating very little methane. Furthermore, the microbial community structure in the different floodplains was primarily governed by carbon-to-nitrogen ratios at a particular site and depth profiles. Several species, including key members of the nitrogen cycling clades, are indicator species for floodplain location and depth. This work will help determine nutrient limitations and greenhouse gas fluxes from nascent and mature wetlands. We have completed the analysis, however we judge that at this time, publication would be premature. We had planned to develop more detailed microcosms studies, and to begin historic remotely sensed data collection, processing, and analysis for extracting environmental/contextual information such as land-cover-land-use (including plant community composition and structure) and flood patterns. While we were able to start a reduced version of the microcosm research plan, the remote sensing analysis was cut, in part due to budget constraints. However, we fulfilled most of the milestones and have detailed the historic data collection to develop geographic information system frameworks for these sites.

The reduced series of microcosm studies that we did perform, did yield promising results. Microcosms were incubated with soil from the different sites and depths collected from the Holland, Michigan, floodplains. All microcosms developed a methanogenic population that was then subjected to oxygen to mimic flooding

periodicity and resulting oxygen exposure. The oxygen exposure significantly inhibited methanogenesis for several weeks to months, even after returning the microcosms to an anoxic state, although a recovery was eventually made.

### PROPOSED FUTURE WORK

Work continues under program support within the Argonne Bioscience Division, and it is expected that we will identify persistent methanogenic cultures that resist oxygen exposure and indicate wetland carbon degradation capabilities. For the microcosm work, high-resolution temporal samples had been taken for metabolites and microbial community structure. This work is being continued under an effort to develop a wetland microbial biogeochemistry program.

## Biology@Speed: D-Factory, A Novel Experimental Framework

### 2014-157-R2

Gyorgy Babnigg, Andrew Binkowski, Robert Jedrzejczak, Andrzej Joachimiak, Karolina Michalska, and Boguslaw Nocek

### PROJECT DESCRIPTION

Future gene sequencing and bioinformatics studies will require more automation, significantly higher throughput, and direct translation of *in silico* ideas to executable workflows on a highly modular platform. The aim of this project is to develop the technology to enable high-throughput (HTP) "biology at speed." This platform will consist of a hardware layer, including modular microfluidics core engines coupled with detectors, and an abstraction layer describing workflows coupled with an application programming interface. The platform will use off-the-shelf products, incorporate in-house technologies designed specifically for a given task, and involve the Center for Nanoscale Materials (CNM). The microfluidics-based HTP assay platform will be benchmarked against traditional assay setups.

### MISSION RELEVANCE

The project is relevant to DOE's mission in science. Biology@Speed will reduce current bottlenecks in experimental biology. The modular and reconfigurable design makes it compatible with current and future science needs. The project is, therefore, relevant to the DOE Systems Biology Knowledgebase (KBase) and other biology projects funded by DOE and the National Institutes of Health (NIH).

## RESULTS AND ACCOMPLISHMENTS

In FY 2014, we explored several avenues to establish the microfluidics infrastructure: (a) use of the CNM, (b) use of fabrication resources offered by universities and industry, and (c) testing of off-the-shelf microfluidics products. We set up a dedicated lab space for the microfluidics work at the Advanced Protein Characterization Facility (APCF). We also established techniques for the cultivation of anaerobic microbes, whole-genome amplification, and messenger ribonucleic acid (mRNA) isolation. We fabricated several expression vectors and miniaturized and optimized assays in the microfluidics setting for glycoside hydrolases and beta-lactamases.

In FY 2015, we designed new microfluidic HTP devices: a new droplet generator and sorting chips. We also started to fabricate a microchemostat and we acquired droplet mergers and double emulsion generators. We installed the dedicated confocal microscope for detecting fluorescent signals in microfluidic chips and developed electronic control mechanisms for droplet sorting.

We characterized several enzymes in 96-well plate assays. These included assays for beta lactamases and glycoside hydrolases. We showed that fluorocillin, a fluorescent beta-lactamase substrate, can be used in both cell-free and cell-based microfluidic assays. The microfluidic assay requires less than one-millionth of the volume of reagents used in traditional 96-well assays. We also tested the feasibility of using fluorocillin to measure enzyme activities indirectly against mixed-in beta-lactam antibiotics. We characterized several glycoside hydrolases via direct assays using fluorescent substrates or via coupled assays. We established a protocol to assay the activity of the heterologously expressed protein from a single cell encapsulated in an aqueous droplet in fluorinated oil (Figure 1). We identified several combinations of fluorinated oils, surfactants, and detergents and tailored them for a given single-cell biological assay. We also optimized conditions to culture single cells in microfluidic droplets and developed ways to monitor cellular activities and fitness.

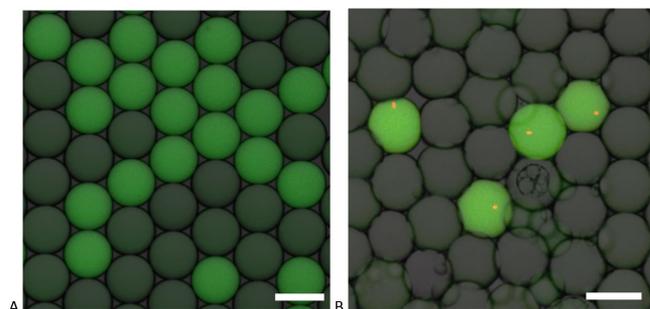


Figure 1. (A) Cell-free and (B) cell-based enzyme assays optimized for beta-lactamases and glycoside hydrolases. Bar length is 35  $\mu\text{m}$ .

In FY 2016, we tested several new designs for droplet generation. The droplet PCR requires the generation of small droplets (<30  $\mu\text{m}$ ), whereas those used for crystallography require larger stable droplets (>80  $\mu\text{m}$ ). We optimized fluidic chips to generate droplets for these scenarios. We also developed and tested a kinetic chip to characterize enzymes with fast kinetics.

We added several new anaerobic microbes to our repertoire. These include some species of *Bacteroides* (*acidifaciens*, *clarus*, *fluxus*, *massiliensis*, *oleiciplenus*, *xylanisolvens*), *Bifidobacterium* (*adolescentis*, *bifidum*, *breve*), and *Blautia* (*hansenii*, *hydrogenotrophica*). The genomic DNA was used to produce additional CAZymes and beta-lactamases for functional studies. Many of these targets were nominated to the structural genomics pipeline and resulted in several structures to date.

We generated DNA expression libraries from *Bacteroides intestinalis*, *Bacteroides cellulosilyticus*, and *Bacteroides salanitronis* using the MCSG expression vectors. The library from *Bacteroides intestinalis* expressed seven out of eight CAZyme genes tested via PCR. The library was tested in a droplet-based microfluidic enzymatic screen using a fluorogenic beta-glucosidase substrate. Four drops out of nearly 1 million droplets displayed activity against this substrate, providing evidence that the method works (Figure 2).

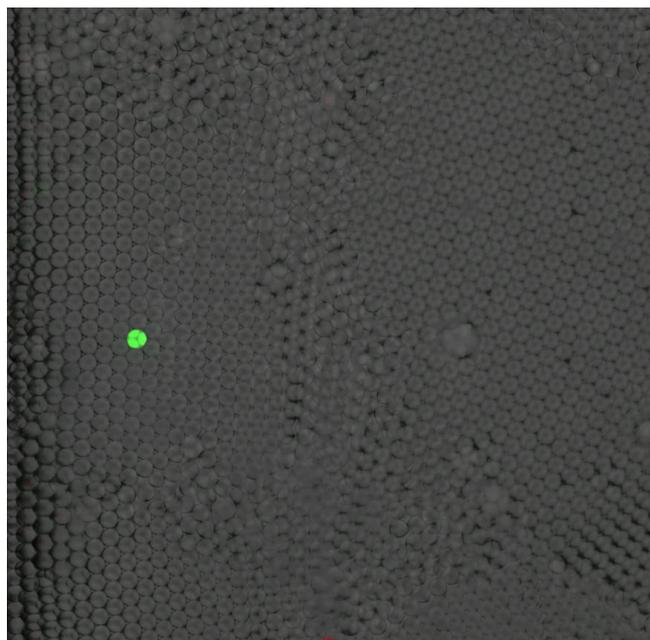


Figure 2. Screen of large expression library for beta-glucosidase activity.

Structural biology offers atomic-level insights into the function of proteins and their complexes. We tested the feasibility of using droplet-based microfluidics to generate crystals amenable for structural studies, tested the compatibility of several commercially available surfactant-containing fluorinated oils with our crystallization screens, and obtained diffraction-quality protein crystals for several CAZymes using this technique (Figure 3).

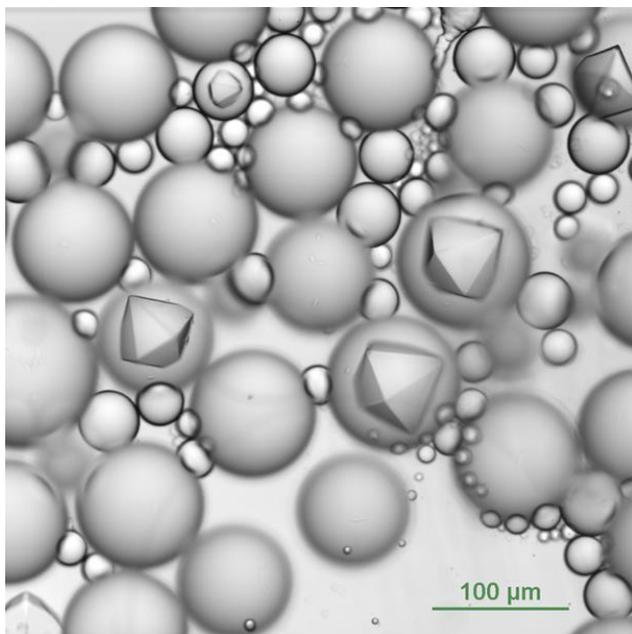


Figure 3. Formation of protein crystals in aqueous droplets in fluorinated oil.

### PROPOSED FUTURE WORK

FY 2016 was the last year of this LDRD project. The application of the developed microfluidics framework is already part of several projects and will be integral to future applications. An Argonne initiative, Protein Function Discovery, utilizes droplet-based microfluidics for function discovery. The technology will be used for enzyme engineering for the U.S. Department of Energy's Bioenergy Technologies Office (BETO) Agile Biofoundry project funded at Argonne.

## Impact of Radiation and Surface Turbulent Fluxes on the Transition from Stratocumulus to Cumulus Cloud Regimes

2014-183-R2

Virendra P. Ghate, Rao Kotamarthi, and John Krummel

### PROJECT DESCRIPTION

Marine stratocumulus clouds cover vast areas of eastern subtropical oceans. These clouds reflect more solar (shortwave) radiation back to space than that reflected by the ocean's surface. They emit similar amounts of terrestrial (longwave) radiation—as does the ocean's surface—because of the low ( $\sim 1$  km) heights of their cloud tops. Hence, they are a significant component of the Earth's radiation budget and need to be represented accurately in the global climate models (GCMs) that are used to predict future energy needs and future climate. The overall goal of this project is to improve the representation of marine stratocumulus clouds in GCMs and, specifically, to understand the transition of the stratocumulus clouds to the cumulus cloud field in the context of changes in boundary layer radiation and surface energy fluxes.

### MISSION RELEVANCE

This project falls under DOE's energy, environment, and basic science missions. The research uses data collected at the Atmospheric Radiation Measurement Climate Research Facility to quantify the interactions among aerosols, clouds, precipitation, radiation, and the dynamics and thermodynamics of the processes involved. to improve our fundamental, process-level understanding. The ultimate goal is reducing uncertainty in global and regional climate simulations and projections.

### RESULTS AND ACCOMPLISHMENTS

The main factors that affect the lifetime of marine stratocumulus clouds and eventually cause their transition to cumulus clouds are (1) a reduction in boundary-layer radiative cooling, (2) an increase in surface buoyancy, (3) a decrease in lower tropospheric stability, and (4) an increase in precipitation-induced evaporative cooling. In previous years, we compared stratocumulus-topped boundary layers over three different oceanic regions and cumulus topped boundary layers over two oceanic regions, and chose the data collected during the MAGIC field campaign to gain insights into the relative

importance of different processes for causing decoupling. The data collected by a vertically pointing Doppler cloud radar and a vertically pointing light detection and ranging instrument were combined to calculate profiles of liquid water content for our case. These data were then used as an input for a one-dimensional radiative transfer model called a rapid radiative transfer model to calculate profiles of radiative fluxes and radiative cooling rates. Our analyses suggest the cooling due to drizzle evaporation to be significant and at times equal to the cloud-top radiative cooling. We also tested some of the criteria that are widely used to diagnose boundary layer decoupling and found that although useful, some of the criteria failed to accurately predict decoupling and cloud breakup, mainly under conditions of heavy precipitation.

Results from our analyses will be submitted for publication in a peer-reviewed journal.

## Biomimetic Approaches for Water-Smart Landscapes

2015-170-R1

M. Cristina Negri, Jeanelle Grosvenor, Jonathan Pekarek, Herbert Ssegane, and Colleen Zumpf

### PROJECT DESCRIPTION

This project, a joint effort with Israel's Ben Gurion University (BGU), aims at understanding how vegetation self-arranges in arid environments and how to mimic this strategy to develop vegetative systems that survive drought. We developed experimental data to study the spatial self-organization patterns of vegetation in green infrastructure (GI). The experimental data we are generating helps validate the models developed at BGU and provides guidance on how to develop more efficient GI systems for U.S. cities.

GI is vulnerable to drought even in temperate regions, as its shallow soil limits water storage and exposes vegetation to potentially long dry spells. It is important to develop efficient GI, as it is an energy-efficient, low-cost, resilient approach to managing storm water and reducing ambient temperature in cities. We will also use the insights from this work to improve agroforestry systems in arid regions and xeriscapes in arid cities, such as those in the western United States.

This project has four tasks:

- Define model case scenario (BGU and Argonne),
- Perform experimental studies at green infrastructure sites (Argonne),

- Perform mathematical model development (BGU), and
- Perform model testing and validation (BGU and Argonne).

### MISSION RELEVANCE

Adaptation to climate change is critical to the mission of DOE and other federal and local government organizations. Relevant DOE mission matches are found in DOE's Office of Energy Efficiency and Renewable Energy (EERE) programs in bioenergy and the Energy-Water Nexus. The development of energy- and water-efficient GI is critical to ensuring that cities will be (1) adaptable to changed storm patterns caused by climate change, and (2) energy efficient in cooling indoor and outdoor spaces. Results from this work will be of interest to a number of sectors. During the FY 2015 and FY 2016 years, we have used this fledgling effort to participate in a large City of Chicago proposal to the Department of Housing and Urban Development to develop resiliency to flooding. The results will also be of interest to the City of Detroit, with whom we have had exploratory discussions. This work is also relevant to National Science Foundation (NSF) work on landscape adaptation to climate change and biogeochemical cycles, U.S. Department of Agriculture (USDA) work on crop water efficiency and drought tolerance, and U.S. Environmental Protection Agency (EPA) work on storm water management. Internationally, this work has potential to help support efficient water management technology in developing countries, which is important for global security.

### RESULTS AND ACCOMPLISHMENTS

This project began in April 2015. After coordinating with collaborators, our initial work focused on finding a suitable and receptive test location, which was identified with the Chicago Botanic Garden in Glencoe, Illinois. We started instrumenting and monitoring their green roof, which is mainly used for display and to test floristic compositions, by June 2015.

In FY 2016, we continued to collect extensive experimental data over the summer, until the first hard frost in November 2016. We repeated the data collection performed in 2015 and added several additional parameters, coordinating with our colleagues at Ben Gurion University. Results confirm that the depth of the soil medium in a green roof influences the water storage capacity and ultimately plant survival. At the end of the summer of 2016, we collected end-of-season plant material and dug up its root system to assess its depth, extension, and form. In 2016, we also researched precipitation infiltration rates and wetting

fronts, and we collected extensive soil moisture data using automated probes. Finally, we set up a controlled experiment reproducing the growth of a commonly used green roof plant, *Sedum spp.*, a stress-resistant grass, big bluestem, and a mix of the two to find out whether the mixed planting would provide a benefit compared to the single planting.

### PROPOSED FUTURE WORK

In FY 2017, we have these objectives:

1. We will continue with the development of field data at the Chicago Botanic Garden site for the 2017 growing season.
2. Using the information generated in 2015 and 2016, we will develop an experiment in which we will create conditions that simulate a long-standing drought and evaluate plant performance and development.
3. We will continue working with other researchers at Argonne to connect part of our sensing apparatus with their Array of Things project, which involves a cloud-based network of nodes, so that we can improve our monitoring efficiency as well as use our field station as a test facility to develop next-generation monitoring networks.
4. We will evaluate the model developed by BGU and propose general guidelines for exporting the knowledge generated to relevant landscape scenarios identified at project onset.

We will also seek partnerships with businesses to adopt our recommendations and findings. And, we will pursue sponsors to scale up the improved designs in real-life translational demonstrations.

## Genome Engineering of Environmental *P. fluorescens* to Investigate Bacterial Interactions with Plant and Other Microbes

2015-171-R1

Philippe Noirot, Gyorgy Babnigg, and Christopher Henry

### PROJECT DESCRIPTION

This project aims to advance genome engineering approaches for environmental *Pseudomonas fluorescens* strains, which are bacteria that associate with fungi and roots and provide benefits to plants. As it is generally very difficult to modify the genome of environmental

bacteria, studies of the mechanisms by which these bacteria provide benefits to plants have been slow and labor intensive. The availability of the efficient genome engineering tools in *P. fluorescens* will help bolster our understanding of the molecular mechanisms underpinning plant growth promotion (PGP). Such tools are not currently available. The major tasks pursued are (1) genome engineering in *P. fluorescens* strains, (2) mapping of transcriptional responses of *P. fluorescens* to plant and/or fungus, (3) functional validation of PGP and development of specific reporters for cellular processes of microbe-plant interactions (MPIs), and (4) development of a *P. fluorescens* platform for MPI studies.

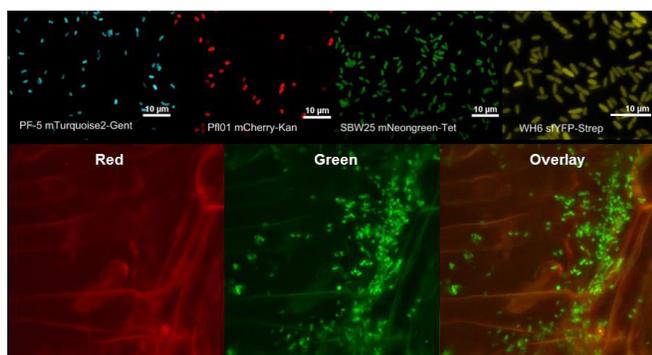
### MISSION RELEVANCE

The project has direct relevance to components of the DOE Genomic Science program, specifically by addressing the first objective, “[d]etermine the molecular mechanisms, regulatory elements, and integrated networks needed to understand genome-scale functional properties of biological systems.” In addition, it directly addresses two “Decadal Thrusts” from the DOE Office of Biological and Environmental Research’s (BER’s) Molecular Science Challenges (April 2015): “[e]lucidate mechanisms by which plants benefit from microbiomes” and “[c]haracterize signaling or communication pathways between microbiomes and plants.” BER has sponsored research in systems biology that includes MPIs. Thus, this project, which focuses on understanding the benefits plants receive from microbiomes, is relevant to the missions of BER.

### RESULTS AND ACCOMPLISHMENTS

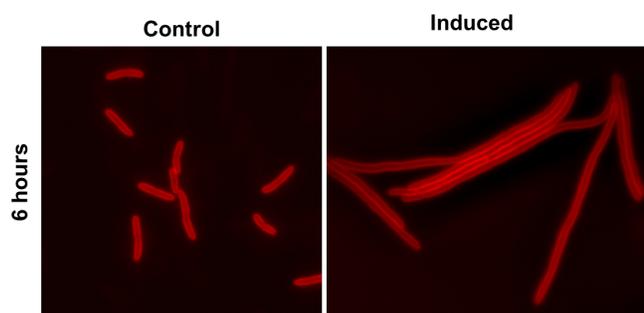
During the first year of the project, we identified and collected biological parts, assembled them to form a genome editing system, and obtained proof-of-concept of genome engineering. Specifically, biological parts included published plasmid vectors, selection markers, phage-encoded recombinases, and genes that we had identified as being endogenous in *P. fluorescens*.

*Genome Engineering in P. fluorescens Strains.* We selected four fully sequenced PGP strains that phylogenetically cover the diversity in the *P. fluorescens* group. Using the appropriate biological parts for each strain, we fabricated a suite of vectors expressing various recombinases and enabling genome engineering in *P. fluorescens*. We used these tools to integrate unique combinations of selection markers and fluorescent protein (FP) color variants in the chromosome of each *P. fluorescens* strain (Figure 1).



**Figure 1.** Recombinant fluorescent-labeled *Pseudomonas* strains. Unique combinations of fluorescent protein (FP) color variants and antibiotic resistance markers were integrated at specific loci in the genomes of four strains. These strains will be used in the context of the DOE Biological and Environmental Research-funded bacteria environmental sensing response (ESR) scientific focus area (SFA) to analyze root colonization using fluorescence microscopy.

Clustered regularly interspaced short palindromic repeats (CRISPRs) enable genome editing in a broad range of organisms. In addition, a derivative CRISPR interference (CRISPRi) system can be used to control gene expression. The adaptation of CRISPR and CRISPRi in *P. fluorescens* is synergistic with our genome engineering tools for future high-throughput interrogation of gene functions. We first adapted the CRISPRi system in *P. fluorescens*. CRISPRi uses a catalytically deficient Cas9 enzyme (dCas9) that will act as a transcriptional roadblock to silence genes. The reliability of our CRISPRi system has been validated by down-regulating the expression of genes involved in cell division that have detectable phenotypes (Figure 2).



**Figure 2.** CRISPRi-mediated gene expression interference in *P. fluorescens* SBW25. SBW25 cells expressing a guide ribonucleic acid (RNA) targeting the cell division *ftsZ* gene were stained with a membrane dye (red). Induction of dCas9 (right panel) for six hours resulted in a marked cell filamentation phenotype resulting from cell division arrest relative to control cells where dCas9 was not induced (left panel).

*Mapping of Transcriptional Responses of P. fluorescens to Plant and/or Fungus Communities.* We encountered the problem that bacterial ribonucleic acid (RNA)-sequence reads from plant and/or fungus and/or bacterial communities are not abundant enough to obtain reliable gene expression data. We are now leveraging the fluorescent protein (FP)-labeled strains to monitor, microscopically, the colonization of roots and fungal roots

by *Pseudomonas*. Results from this study will allow us to select the optimal time and condition where bacteria are abundant and active at the roots for further analysis of gene expression.

To understand the bacterial responses during root colonization, we fabricated a biosensor strain of *P. fluorescens* able to conditionally express FP upon sensing arabinose, a major component of root exudates. We found a dose-dependent response of this reporter strain to increasing amounts of root exudates. This experiment provides a proof-of-concept for visualization of bacterial cells that utilize arabinose in the rhizosphere. The same principle can now be adapted to other pathways to determine the *in situ* metabolic activity of *P. fluorescens* cells during the colonization of roots. These results lay the foundation for our future studies of bacteria environmental sensing and response (ESR) to plant and rhizosphere exudates in the context of our scientific focus area (SFA) program.

This work was performed with Dr. Marie-Francoise Gros of Argonne's Biosciences division.

### PROPOSED FUTURE WORK

We will combine our complementary genome engineering methods [i.e., deoxyribonucleic acid (DNA) recombineering, CRISPR] to create and combine various mutations in a single genome. Transcriptomic experiments involving bacteria growing on plant roots under optimal conditions will be initiated to measure bacterial responses to plant roots and fungus. The identified root-responsive bacterial promoters will be fused to green fluorescent protein (*gfp*) gene variants and will be integrated into the *P. fluorescens* chromosome, enabling the microscopic observation of how expression of a particular gene and/or its pathway is modulated in the bacterial population within the rhizosphere.

# Illuminating Linkages between Microbial Diversity and Biogeochemical Cycling in a Redox Dynamic Environment

2015-179-R1

Theodore M. Flynn

## PROJECT DESCRIPTION

Environments such as floodplains and wetlands, which exist at the terrestrial-aquatic interface, can be both major sources and sinks of greenhouse gases. To a large extent, the flux of methane from these environments is controlled by microbial metabolism. Both methane-producing and methane-consuming organisms inhabit the water and sediments there, although the extent to which the activity of each is controlled by environmental variables (e.g., pH, temperature) is poorly understood. In particular, the dynamic oxidation-reduction (redox) conditions of these environments are thought to cause large shifts in both the rates of greenhouse gas emissions and, concomitantly, the structure of microbial communities.

As a result, the flux of methane from periodically flooded environments such as wetlands is a significant source of uncertainty in global climate models. Our project seeks to understand the microbial processes that regulate greenhouse gas emissions in a wetland environment at spatial and temporal scales relevant to earth system modelers. We are leading a rigorous effort involving field sampling as well as laboratory microcosms to measure relevant biogeochemical parameters (e.g., concentrations of dissolved gases in water and sediment) and to determine the composition of the microbial community by using targeted gene sequencing and metagenomics. This effort will not only improve our understanding of the feedback between microbial metabolism and greenhouse gas emissions but will also provide us with a more quantitative understanding of microbial ecology by monitoring changes in native microbial communities over space and time.

## MISSION RELEVANCE

DOE's Genomic Science Program has five key objectives, three of which are addressed by this project:

1. "Determine the molecular mechanisms, regulatory elements, and integrated networks needed to understand genome-scale functional properties of biological systems,"
2. "Flexibly scale understanding of biological processes from defined subsystems to individual organisms, consortial assemblies of multiple organisms, or complex communities operating at ecosystem scales," and
3. "Understand the foundational rules and 'design principles' governing living systems and develop tools for more sophisticated biosystems design, enabling the targeted modification of functional properties at the genome scale."

In this study, we use omics-enabled techniques to uncover basic organizing principles of biological systems in a freshwater wetland and how these relate to the emission of greenhouse gases such as carbon dioxide and methane in this critical environment. Combining systems biology with detailed geochemical measurements will provide key variables to inform improved models of the critical biogeochemical processes that control the storage, release, and transport of carbon, nutrients, and contaminants in the critical zone, which are all critical mission challenges recently identified by DOE's Biological and Environmental Research (BER) program.

## RESULTS AND ACCOMPLISHMENTS

Following initial surveys of local wetlands in FY 2015, we chose a field site located near the Freund Lodge within the Argonne grounds for our sampling efforts. Initial characterization showed the presence of a diverse microbial community as well as reproducible results. Beginning in November 2015, we conducted weekly sampling of aqueous geochemistry, dissolved gases, and microbial community composition (water and sediment). We employed high-throughput DNA sequencing of a target gene to characterize the composition of the microbial community at each time point. Analysis of the initial results from November to May (Figure 1) indicates that the community in the water varies significantly more than the community in the sediment.

We also used water and sediment from this wetland to create microcosm experiments in the laboratory. We amended these microcosms with the iron oxide mineral goethite and quinone-based electron shuttles of varying redox potentials. Earlier work by others had suggested a link between the availability of electron shuttles and both the rate and extent of ferric iron reduction as well as the release of the greenhouse gas methane. Our initial results indicate that some electron shuttles (AQC) inhibit methanogenesis almost entirely. Furthermore, the addition of these shuttles has a substantial impact on the diversity of the microbial community in the microcosm (Figure 2). This finding suggests that electron shuttles of a particular redox potential may select for specific members of the microbial community.

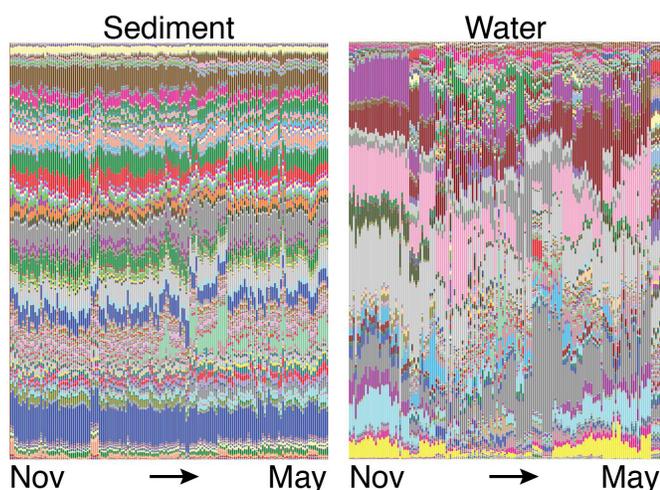


Figure 1. Change in the relative abundance of specific microbial taxa in the sediment (left) and water (right) of a freshwater wetland during a six-month period. The community composition in the sediment remained relatively consistent over this time period, whereas the planktonic community changed substantially. Each color represents the relative abundance (comprising 100% in total) of a particular genus of bacteria.

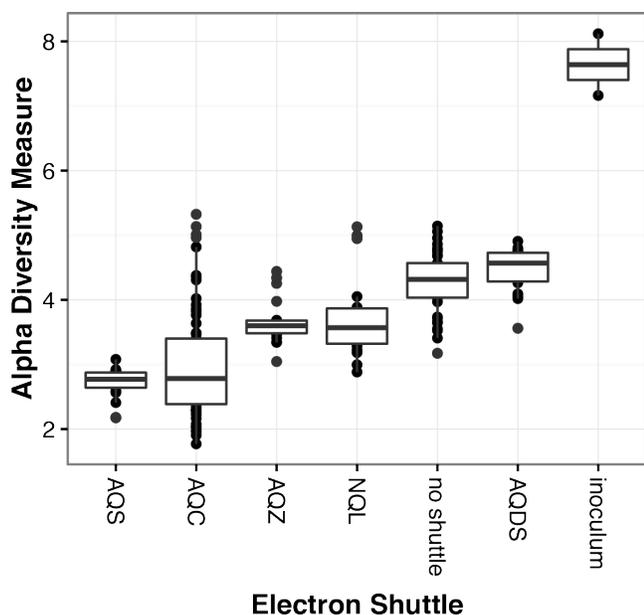


Figure 2. Box-and-whisker diagram illustrating changes in the alpha diversity (total number of bacterial taxa) in wetland sediment microcosms amended with the ferric iron mineral goethite and quinone-based electron shuttles (AQS, AQC, AQZ, NQL, and AQDS) of varying redox potentials. The addition of certain shuttles, such as AQS, caused the microcosms to become highly enriched for specific taxa (e.g., *Pelobacter*, *Shewanella*) relative to unamended controls, while others (AQDS) caused a similar degree of diversity to unamended controls. Each box represents the range of the first and third quartiles of the Shannon alpha diversity metrics calculated for each sample group, and the line within each box represents the median. Data points outside these boxes show the spread of values for each sample group.

## PROPOSED FUTURE WORK

Weekly sampling events are ongoing for at least a full 12 months to capture the degree of variability over a full growing season. Upon completion, we will move sampling operations to a different wetland on the Argonne site that experiences more variable flooding to better understand the impact of periodic inundation on greenhouse gas emissions and microbial community function. We will also employ whole-genome shotgun metagenomics to look at the genomic composition of uncultivated microbes in this wetland. Additional laboratory incubations will also be conducted to further explore the link between iron-reduction bacteria and methanogenic archaea.

## Functional Analysis of Proteins from a Key Signaling Network Involved in Plant-Growth-Promoting Bacteria

2015-180-R1

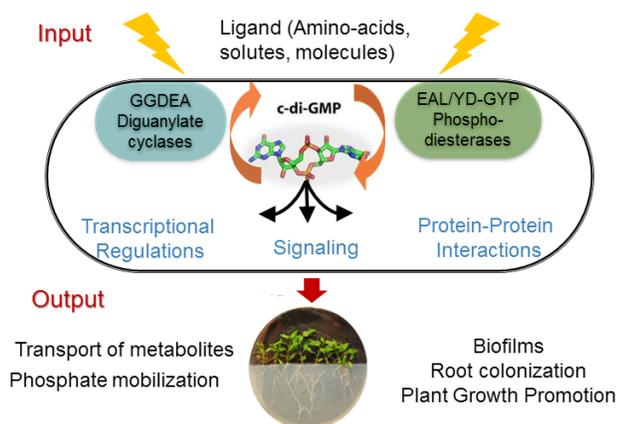
Marie-Francoise Gros

### PROJECT DESCRIPTION

Plant-growth-promoting (PGP) rhizobacteria exert their beneficial effects—including mobilizing soil nutrients, producing antibiotics, and eliciting plant defense mechanisms—through direct and indirect interactions with plant roots. However, while PGP activities have been extensively characterized at a physiological level, the underlying molecular mechanisms remain poorly characterized. This project addresses this knowledge gap by identifying protein complexes that decipher environmental stimuli and initiate signal transduction pathways in rhizobacteria to trigger PGP effects. In many bacterial species, the second messenger cyclic diguanylate (c-di-GMP) has emerged as a ubiquitous regulator of bacterial physiological functions, such as biofilm formation, developmental transition, production of exopolysaccharides, and control of virulence. The object of this project is to characterize the protein-protein network underpinning the bacterial response to c-di-GMP in a PGP bacterial strain of *Pseudomonas fluorescens* SBW25.

In bacterial cells, intracellular levels of c-di-GMP result from the balance between synthesis by diguanylate cyclases (DGCs) and degradation by phosphodiesterases (PDEs). Upon binding c-di-GMP, these proteins can exert a regulatory action on gene expression at transcriptional, post-transcriptional, or post-translational levels, either directly or through interactions with other

proteins (Figure 1). To fully understand the molecular logic underlying c-di-GMP circuitry in PGP bacteria, a comprehensive inventory of all the players (DGCs, PDEs, and c-di-GMP-binding regulators); their regulatory interplay; and their targeted processes is necessary. This study combines interactomic approaches to identify protein complexes involved in c-di-GMP regulatory pathways with the analysis of their cellular function to provide mechanistic insight into the basic principles of plant growth promotion mediated by rhizobacteria.



**Figure 1. Schematic of c-di-GMP signaling in PGP bacteria. Regulation of c-di-GMP homeostasis is carried out by diguanylate cyclases (DGCs) and phosphodiesterases (PDEs) upon receiving environmental signals.**

Biologically validated interactions will be used to benchmark the development of a microfluidic-based approach to identify protein complexes at high throughput. By leveraging recent developments in microfluidic capability, we aim at establishing a proof-of-concept in collaboration with Argonne’s Biosciences Division for a high-throughput microfluidic methodology based on fluorescence detection of transient protein-protein interactions (PPIs) involved in signaling. This approach is expected to provide a leading-edge methodology to map PPIs on a genomic scale.

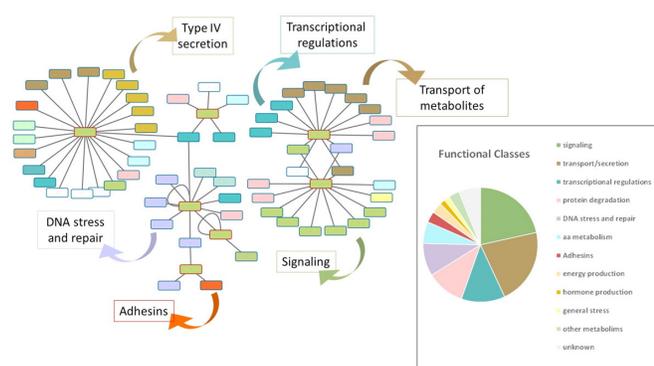
## MISSION RELEVANCE

This project is relevant to the DOE missions in transformative science and the environment. The determination of the molecular mechanisms, regulatory elements, and integrated networks needed to understand the functional properties of microbes and their interactions with plants is one important aspect of the search for sustainable bioenergy that is promoted by the DOE Office of Science through the Office of Biological and Environmental Research. Within this framework, understanding the c-di-GMP signaling cascade of *P. fluorescens* will prove invaluable in learning how to design plant-microbe communities with more efficient

PGP properties. Our exploration of the development of microfluidic-based interactomics is also fully consistent with the objectives of the genomic science program to develop omics capabilities to achieve a system-level understanding of living organisms.

## RESULTS AND ACCOMPLISHMENTS

The genome of *P. fluorescens* SBW25 encodes for 48 predicted c-di-GMP-associated signaling proteins (Protein Supercluster SC\_37130). To identify the main players in the c-di-GMP signaling pathway involved in PGP and related phenotypes, we leveraged the available transcriptomic data on plant-root-colonizing versus non-colonizing bacteria in the aspen/*P. fluorescens* model system generated in the framework of the Environmental Sensing and Response-Scientific Focus Area (ESR-SFA, Argonne’s BIO science division). The analysis of the variation of gene expressions enabled the identification of seven candidates among the gene-encoding proteins of the SC\_37130 supercluster. These candidates were used as baits to identify their protein partners by screening a *P. fluorescens* genomic library (from Hybrigenics Services). Anticipating potential cross-talks, these c-di-GMP binding proteins were tested for their ability to cross-interact as well as to self-interact. A high-quality binary protein-interaction map centered on c-di-GMP signaling in *P. fluorescens* was built from very high-confidence interactions (Figure 2). This PPI network was composed of 72 interactions involving 68 different proteins clustered in two connected modules. It exhibited a remarkable structural organization which revealed functional associations connecting the c-di-GMP binding proteins to particular metabolic pathways and cellular machineries. This network was of high biological significance and provided a wealth of hypotheses for further deciphering the relationships between c-di-GMP signaling and plant (aspen)-root colonization by *P. fluorescens*.



**Figure 2.** PPI network centered on c-di-GMP binding proteins involved in bacteria-plant root association. Proteins are nodes and interactions are symbolized by edges. The c-di-GMP bait proteins are outlined in red. Colors illustrate functional categories.

### PROPOSED FUTURE WORK

Work in FY 2017 will focus on exploring the role of c-di-GMP in plant growth promotion in *P. fluorescens*. We will use our PPI network to drive functional studies on a selected number of protein complexes, aimed at validating the role of c-di-GMP signaling in PGP and colonization of roots. Knockout (KO) mutants, which are characterized by silencing of individual genes encoding c-di-GMP-binding proteins, will be generated using chromosome engineering methods based on our recent development of Clustered Regularly Interspaced Short Palindromic Repeats (CRISPR)-based recombineering and expression-interference genetic tools in *P. fluorescens* (in collaboration with the LDRD project “Genome Engineering of Environmental *P. fluorescens*”). The effect of the c-di-GMP-mediated signaling mutants on the spatio-temporal dynamic of aspen-root colonization will be assayed by live-cell fluorescent microscopy. The fitness of the KO (or silenced) mutant strains will be assessed by evaluating their ability to promote the growth of aspen seedlings in a vertical plate assay. The c-di-GMP gene sensors exhibiting the strongest PGP-related phenotypes will be selected for further functional studies.

During FY 2017, these functionally validated PPIs will be leveraged to establish proof-of-concept for a high-throughput microfluidic methodology based on fluorescence detection of transient PPIs involved in signaling.

## Models to Observations, a Digital Atmospheric Library (MODAL)

2016-139-NO

Scott Collis, Yan Feng, Virendra P. Ghate, Nicki Hickmon, and Robert Jacob

### PROJECT DESCRIPTION

The goal of developing Models to Observations, a Digital Atmospheric Library (MODAL) is to enable researchers to sufficiently sample a particular phenomenon to build new climate parameterizations in support of DOE missions. Despite efforts like those made in the Atmospheric Radiation Measurement (ARM) program, supported by the DOE Office of Biological and Environmental Research, comparisons of data collected in the field with numerically simulated atmospheric phenomena have been disjointed. Now that ARM uses very-high-resolution models as a framework for process-level understanding of climate-pertinent processes, a unique opportunity exists to build a well-engineered, lasting infrastructure around a digital library of atmospheric scenes. This digital atmospheric library (DAL) will become MODAL when coupled with a framework supported by an architecture that is driven by a community open-source data model for simulating observations. Argonne manages the Southern Great Plains ARM site, coordinates all instruments across ARM, leads retrieval efforts from the scanning radars, and has a stake in how observations are used to understand nonprecipitating clouds and aerosol processes. MODAL's unique ability to fuse instrument simulators and atmospheric models will be used for fundamental research in sub-grid-scale processes and large-eddy-scale (LES) models and cloud-resolving models (CRMs). Good results have come from using instrument simulators, especially for space-borne platforms. When coupled with a retrieval framework, the simulators can be used to observe system simulation experiments.

### MISSION RELEVANCE

MODAL is aligned with the mission of the Department of Energy's Atmospheric Radiation Measurement (ARM) program in improving the understanding of aerosols and clouds. However its applications are wide-ranging for existing and future climate efforts. Most importantly, MODAL is a tangible, well-engineered asset comprising version-controlled community software plus open data. As an engine for the dynamical downscaling of rainfall data for the Department of Defense, the Department of Housing and Urban Development, and the Department of Homeland Security, MODAL would

return not only rain fields, but also simulated sensor output that would support planning of future networks. MODAL can be used in university classrooms to allow students to study atmospheric processes and how remote sensors sample the environment. Laboratory, intergovernmental, and university collaborators can all use MODAL to design future field campaigns and instrument deployments. Consequently, MODAL would become a vital piece of infrastructure of interest to the National Aeronautics and Space Administration, and the National Science Foundation.

**RESULTS AND ACCOMPLISHMENTS**

During the first year of work, we have made substantial progress on MODAL. Foremost is the establishment of LES capability on Argonne computational assets, primarily the Laboratory Computing Resource Center (LCRC) Blues (the newest addition to the computational power of LCRC). LES modeling, which explicitly resolves vertical motion in clouds and storms and statistically represents the eddy scale (think of an eddy as gusts of wind), is run at resolutions ranging from hundreds to tens of meters. Our first LES simulations focused on open oceans and used forcing data from the earlier “Rain In Cumulus over the Ocean” field campaign. This campaign involved conditions very similar to those over the DOE ARM site in the Azores. We read these data into a common data model in Python and coupled a newly developed scanning cloud radar instrument simulator that mimicked the behavior of one of the ARM cloud-sensitive radars. We then used existing retrieval techniques to build a three-dimensional picture of clouds’ liquid water content from scanning radar data. Figure 1 shows modeled cloud liquid-water content from Weather Research and Forecasting Model (WRF)-LES on the left and a retrieved cloud field from a conically scanning cloud radar on the right. The figure shows “smearing” of the clouds, which is due to the gridding techniques and sub-optimal sampling. While the sampling method has a small impact in the horizontal direction, its impact is much greater in the vertical because of the nature of the instrument’s scanning (sampling) pattern. The radar maps a volume of space using a number of concentric cones. Figure 2 shows the increasing error in retrieved cloud fraction (the fraction of the area covered by cloud liquid water content (CLWC) > 0) as a function of height and the number of cones used to map out the three-dimensional space. These results show that for clouds at low levels, there are diminishing gains after 15 scans, while high-level clouds still retain a high level of error and may require different scanning strategies.

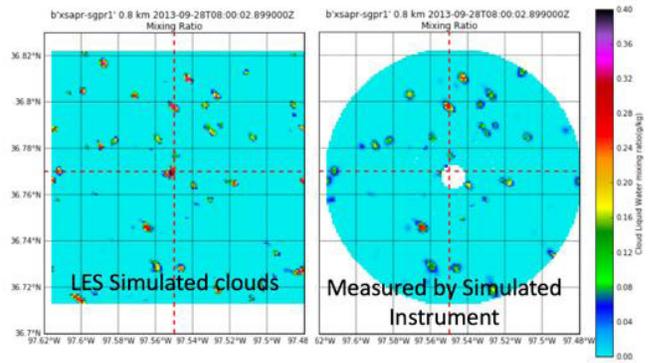


Figure 1. Example of LES simulated clouds (left) and clouds that have been radar-sampled and then re-gridded (right).

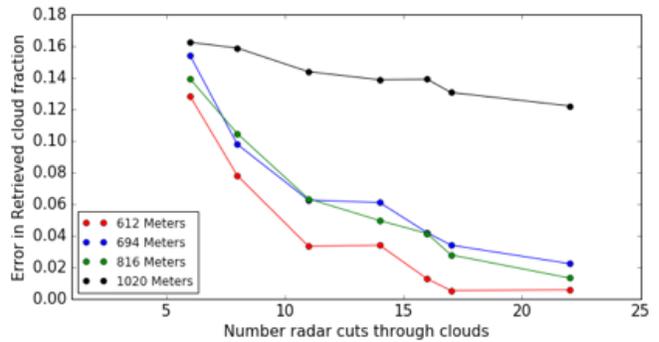


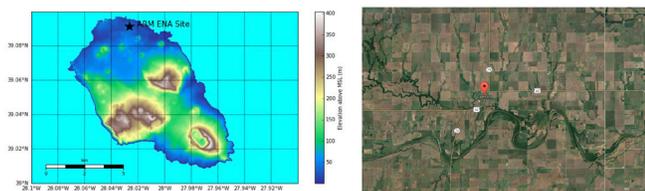
Figure 2. Error in cloud fraction as a function of height in the model domain and number of elevation angles in a conical scanning pattern.

**PROPOSED FUTURE WORK**

In FY 2017, we will expand the number of instruments simulated. We will slightly reduce the number of planned instruments to ensure success with the suite of instruments that support ARM’s Actively Remotely Sensed Cloud Layers (ARSCl) program. This suite consists of the vertically pointing cloud radar, microwave radiometer, and micropulse laser imaging detection and ranging, the last two of which are managed by Argonne scientists. We will engineer these simulators and couple them to the model data so that they are reusable and become a strategic asset.

Because many papers develop cloud climatologies from ARSCl, we can use MODAL to investigate the impact of the local environment on clouds retrieved using the simulator. Using a model to generate our cloud scenes allows us to turn the local environment on and off. We will explore two specific examples:

1. The impact of flow over terrain on radar cloud climatologies. We will model open-ocean clouds near ARM’s Eastern North Atlantic site, with and without the island on which it is located (see Figure 3, left), to see whether the clouds measured are truly representative of the open ocean.



**Figure 3. Left: Terrain of Graciosa Island in the Azores, Eastern North Atlantic. Note the small size of the island. Right: Aerial image of the landscape around the ARM Southern Great Plains Site. Note the patchwork of crops, which leads to differing moisture fluxes that generate clouds.**

2. The impact of surface heterogeneity in the southern Great Plains. We will download data from the LES ARM Symbiotic Simulation and Observation (LASSO) project and use them to force LESs using observations with and without the effect of land surface heterogeneity (i.e., the patchwork of crops around the site, as shown in Figure 3, right).

## Resolving Land-Atmosphere Interactions at Kilometer Scales: Model and Measurement Needs for Next-Generation Earth System Models

2016-164-NO

Nicki Hickmon, YoungSoo Chang, Julie Jastrow, and Roser Matamala Paradeda

### PROJECT DESCRIPTION

We will examine currently used sensors and field instrumentation intended to provide scientific measurements in support of characterizing climate relevant phenomena in the subsurface, surface, and atmosphere. Specifically, we will explore how the Atmospheric Radiation Measurement (ARM) Climate Research Facility, the Critical Zone Observatory (CZO), and the National Ecological Observatory Network (NEON) deploy these instruments. Analysis of these instruments and their deployments will result in information about their potential to be integrated into an Integrated Field Laboratory (IFL) concept. We propose to bridge climate model analysis and terrestrial ecology areas of interest, where Argonne has particular expertise, as we develop the concept for an IFL.

### MISSION RELEVANCE

This work supports the DOE mission in environmental quality by addressing environmental observation infrastructure and the science informed by that infrastructure. ARM is a DOE Office of Science user facility. DOE Climate and Environmental Sciences Division (CESD) programs will benefit from this work. Also benefitting will be the CZO and NEON programs of the National Science Foundation (NSF). Climate science work is growing throughout the federal enterprise, and this initiative will assist in defining options going forward for those programs.

### RESULTS AND ACCOMPLISHMENTS

Initial data acquisition, which consisted of gathering factual information about sensors and field instrument capabilities, is essentially complete. Instrumentation types, measurement abilities, and deployment specifications have been captured for ARM and NEON. The deployment specifications determine if the instrumentation could be cross-utilized between programs. These data are the basis for our analysis.

### PROPOSED FUTURE WORK

This was a one-year exploratory effort. Future efforts, including the addition of CZO's instrumentation information, should involve cross-referencing the technical capabilities, analyzing efficiencies and identifying overlapping capabilities with an eye toward formulating the synergistic concept of an IFL.

## Establishing a Proof-of-Concept for Protein Function Discovery Initiative

2016-165-NO

Philippe Noirot, Dionysios A. Antonopoulos, Gyorgy Babnigg, Christopher Henry, Kenneth M. Kemner, Philip D. Laible, Peter Larsen, Tijana Rajh, and Rosemarie Wilton

### PROJECT DESCRIPTION

Protein function discovery is a scientific problem of enormous scale that can only be tackled by a multidisciplinary strategy that integrates experimental and computational approaches, as well as new technological developments to ensure that the strategy can be applied at large scale. Our current capabilities in protein production and characterization at Argonne's Advanced Protein Characterization Facility (APCF), capabilities in computation and gene annotation (KBase), and recent

developments in microfluidics and nanomaterial science at the Center for Nanoscale Materials (CNM) place us in a favorable position to develop a global strategy for protein function discovery. This project aims at establishing a proof-of-concept for an integrated experimental and/or computational approach for the functional characterization of proteins. Our integrated approach will be applied to gain insight into plant-microbe interactions within a tripartite symbiotic system composed of a tree, an ectomycorrhizal fungus, and a bacterium. The three organisms are fully sequenced, which enables a graded application. Our proof-of-concept will be established using the bacterium and will be further developed for discovery of the functions of fungal and plant proteins.

### MISSION RELEVANCE

The project is directly relevant to DOE's mission in science and the environment and, in particular, to two scientific themes in the DOE Office of Science, Office of Biological and Environmental Research (OBER), Biological Systems Science Division strategic plan. Under the BER Biosystems Design theme, this plan addresses the goal of developing “*the fundamental understanding of genome biology needed to design, modify and optimize plants, microbes, and biomes for beneficial purposes.*” Under the Environmental Research theme, it addresses the goal of advancing “*systems biology studies on microbes, microbial consortia, and microbe-plant interactions involved in large-scale terrestrial carbon cycling.*” To reach these goals, we will leverage (i) our core capabilities in computation (KBase), protein science (APCF), and imaging and nanomaterials (CNM). For this reason, Protein Function Discovery is part of the Argonne's strategic plan.

### RESULTS AND ACCOMPLISHMENTS

The project is divided into three interdependent tasks.

#### Task 1 — Metaboseq: An Approach Coupling Microfluidic Cell-Free Assays with Metabolic Profiling for Functional Analysis

This task focuses on the integration of a microfluidic chip with a mass spectrometer.

*Mass Spectrometer.* After evaluation of mass spectrometers, ionization methods, fluidic rates, and electronic interface with instruments, the Agilent Technologies 6150 Quadrupole liquid chromatography–mass spectrometer (LC/MS) with a nano-electrospray ionization source was purchased. The instrument was installed and tested with the installed JetStream electrospray interface. An additional analog input/output kit was installed, which will enable multiple reaction

monitoring of four ions in parallel. In addition, the Agilent 1200 HPLC (high performance liquid chromatography) was recertified and connected to the mass spectrometer. The LC/MS profiles of several substrate and/or product pairs will be tested in the coming months.

*Microfluidic Chip.* A chip containing a droplet splitter, a magnetic separator, a droplet sorter, a delay channel, and flow control sections using pneumatic valves was designed and fabricated. The flow control hardware and software components were installed on a dedicated laptop computer.

#### Task 2 — Apply Metaboseq Pipeline to Fill Gaps in Metabolic Pathways of *P. fluorescens*

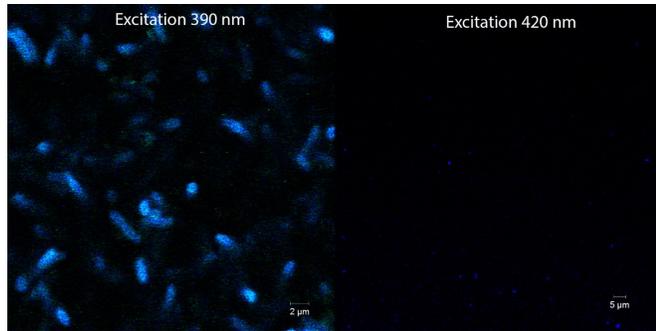
*Modeling and Cheminformatics.* We made progress in the following areas:

- Constructed draft metabolic models of four lab strains of *Pseudomonas fluorescens*, including Pf-5, Pf0-1, SBW25, and WH6;
- Gapfilled all draft models for growth on complete media, as well as several minimal media formulations with different sulfur substrates;
- Transitioned cheminformatics pipeline to RDKit to permit the generation of reactions that integrate into metabolic models; and
- Extended the reaction rules in the MINE database to handle new types of chemistry.

*Selection of Enzyme Targets.* Known glycolytic enzymes (and their complexes) were expressed from a number of microbial genomes. The glycolytic pathway enzymes consume cofactors (adenosine triphosphate or nicotinamide adenine dinucleotide) which can be monitored via fluorescence measurements, while product formation can be observed via MS in parallel. These properties will be used to optimize and validate the MetaboSeq technology. To validate predicted functions, *P. fluorescens* SBW25 genes encoding enzymes predicted to synthesize the plant-growth-promoting compound indole-acetate (IAA) from tryptophan were cloned and expressed in *E. coli*. Individual genes as well as protein complexes from two potential parallel pathways were expressed and the solubility of the products was evaluated. These IAA biosynthetic enzymes will be characterized with the corresponding substrates and the reaction monitored via MS. The reaction mixtures will be sent to the Northwestern University user facility for metabolite characterization.

### Task 3 — Whole-Cell Assays to Functionally Associate Nutrients With Transporters Using Nanoparticles as Tracers

**Uptake of Glycine-Conjugated Nanoparticles.** Uptake of glycine-modified quantum dots (QDs) was investigated using a laser confocal microscope equipped with a nonlinear module for two-photon light absorption. We found that *P. fluorescens* can be effectively visualized alive using time-lapse imaging with very short exposures using two-photon excitation wavelengths of 780 nm. QDs taken up by *P. fluorescens*, monitored by the same technique, were visible using a different excitation wavelength (840 nm), as shown in the Figure 1. However, as a single laser was used for imaging of both microbes and QDs, the time-lapses could not be overlaid to determine the parts of the microbes that contained QDs. In future experiments, we will use QDs with excitation in the range of 456 to 488 nm, which can be excited by other lasers, for simultaneous visualization of *P. fluorescens* and QDs. Also, 5-nm gold (Au) nanoparticles were synthesized and functionalized with (a) mercapto succinic acid that is covalently linked to glycine and (b) cysteine, which is a mercapto substituted glycine. These particles are ready to be supplied for uptake by *P. fluorescens*.



**Figure 1.** Two-photon laser confocal microscopy image of *P. fluorescens* obtained by autofluorescence (excitation 390 nm) of the free-floating bacteria in the medium (left), and image of the fluorescence of uptaken QDs obtained by imaging (excitation 420 nm) in the same solution (right).

**Uptake of QDs by Various Bacterial Species.** This work was performed to create multiple scenarios to further test cell-sorting approaches for bacteria. We tested numerous bacterial species for uptake of QDs conjugated to glycine, adenine, or glucosamine. These included three strains of *A. dehalogenans*, two strains of *B. subtilis*, two strains of *P. fluorescens*, two strains of *P. protogens*, and *S. oneidensis* MR1. Results yielded uptakes of conjugated QDs ranging from 1 to 15%, except for *B. subtilis* 3610, which exhibited more than 90% uptake after 4 hours under our conditions.

### PROPOSED FUTURE WORK

**Task 1.** We will establish MetaboSeq using known reactions and determine the limits of the technology using the current experimental setup. Experimentally determine the activity of enzymes predicted to be involved in IAA biosynthesis.

**Task 2.** We will refine models with existing transcriptome data sets and develop the global analysis of gaps in all reference genomes to identify high-priority targets for activity determination using MetaboSeq. Develop automated interfaces to predict suitability of substrates and products for MS analysis.

**Task 3.** Regarding uptake of nanoparticles, we will functionalize QDs and Au nanoparticles with the nutrients found to be necessary for rapid growth of the bacteria, such as arabinose, mannose, and galactose. The uptake of nanoparticles will be monitored using laser and Raman confocal microscopy as well as X-ray imaging. Uptake of QDs by *B. subtilis* 3610 will be optimized to enable the screening of mutants lacking the capacity to take up QDs, using a cell-sorting strategy.



# LDRD PRIME – HARD X-RAY SCIENCES

# Development of a Novel Analyzer System for Resonant Inelastic X-ray Scattering with Better Than 10-meV Resolution

2014-127-R2

Jung Ho Kim, Thomas Gog, and XianRong Huang

## PROJECT DESCRIPTION

State-of-the-art resonant inelastic X-ray scattering (RIXS) developments pioneered at the Advanced Photon Source (APS) are now at light sources worldwide. Maintaining scientific leadership in this field requires timely development of the next-generation analyzer system, which will pave the way to overcome the intrinsic energy resolution limit of conventional spherical analyzers. Specifically, the present project has focused on the development of an energy resolution smaller than 10 meV, which is more than three times better than the current best energy resolution using RIXS. The expected improved energy resolution of 10 meV will enable studies of a new class of emerging materials that have remained inaccessible because of the inherently small energy scales of their relevant elementary excitations. Furthermore, this new X-ray spectrometer will help mitigate the unavailability of large enough single crystalline samples required for inelastic neutron scattering.

## MISSION RELEVANCE

The project is relevant to DOE's science mission. The development of a novel analyzer system will have a large impact on RIXS instrumentation, and therefore on our understanding of correlated electron systems, when implemented at the APS and other synchrotron facilities. The project is well aligned with the Grand Challenge of understanding novel phenomena in condensed matter emerging from complex correlations of electronic constituents and the control of these properties. The new instrumentation, together with theoretical modeling, will benefit the APS as a user facility and contribute to the RIXS facilities in the context of the APS Upgrade.

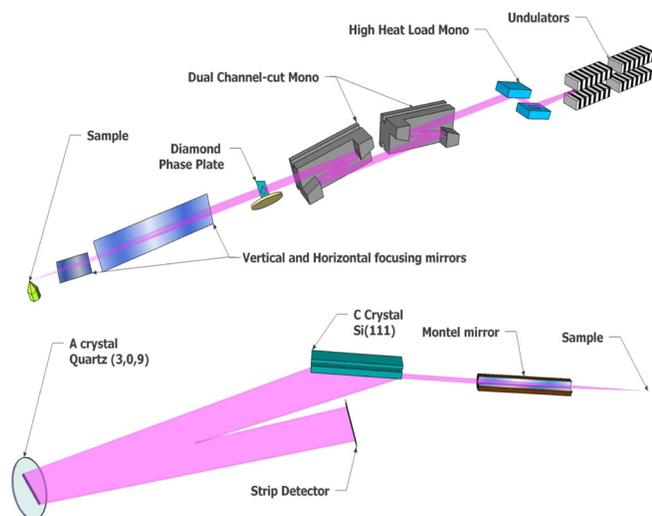
## RESULTS AND ACCOMPLISHMENTS

In the proposed novel analyzer system, a two-dimensional multilayer Montel mirror is placed between the sample and the proposed analyzer, collecting scattered X-rays and collimating the reflected beam to match the angular acceptance of the succeeding flat crystal optics. The first crystal collimates the scattered beam emerging from the Montel mirror, while subsequent crystals select a specific energy and transfer it to the detector.

In FY 2014, all essential optics and silicon (Si) crystals were designed and manufactured: the Montel mirror, all Si crystals of the new analyzer system, and the four-bounce 7-meV monochromator. The working principle and performance of the 7-meV monochromator was commissioned at the 9-ID beamline.

In FY 2015, the Montel mirror was successfully characterized at beamline 27-ID in terms of its angular acceptance and collimation. Comparing with X-ray tracing simulations, the measured X-ray divergence could be well understood, and it was found that the Montel mirror satisfies the required quality of X-ray collimation for use in an angular-dispersion multi-crystal RIXS analyzer system. A few different combinations of flat crystals were studied to find the optimum combination in terms of good energy resolution and reliable/easy operation. We found that the combination of the asymmetric Si(111) and the symmetric quartz(309) gave the best energy resolution of 11 meV with high efficiency.

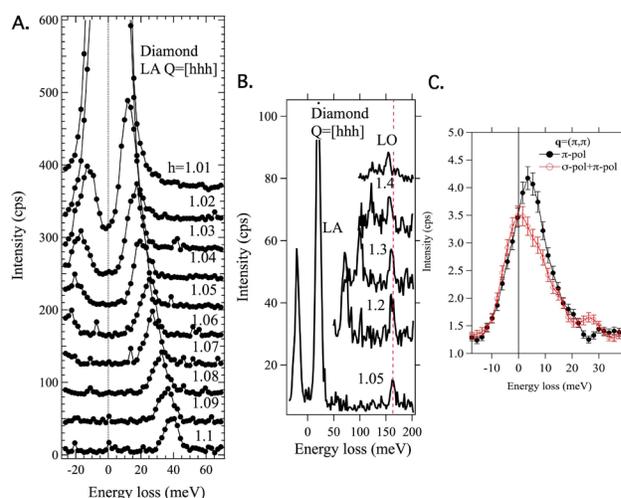
In FY 2016, the proposed multi-crystal RIXS analyzer system, shown in Figure 1, was fully tested. A highly monochromatized ( $\sim 8.5$  meV) beam, generated by two symmetric Si(844) monolithic channel-cut crystals, is incident on the sample. Scattered radiation is collected and collimated by a parabolic, graded multilayer Montel mirror. In the new RIXS analyzer system, a highly asymmetric Si(111) and a symmetric quartz(309) crystal operate in the collimating-dispersing mode. The total energy resolution was found to be 9.5 meV, indicating that the multi-crystal RIXS analyzer resolution is as good as 4 meV.



**Figure 1.** Schematic setup of the current RIXS analyzer system. A highly monochromatized and focused beam is incident on the sample, generated by a 4-bounce, double monolithic Si(844) channel-cut monochromator and a Kirkpatrick-Baez mirror system. Scattered radiation is collected and collimated by a parabolic, graded multi-layer Montel mirror. The reflected beam is further collimated by a highly asymmetric Si(111) crystal, and energy is analyzed by a symmetric quartz(309) crystal in near-backscattering geometry.

Longitudinal acoustic (LA) and optical (LO) phonons of a diamond crystal were successfully measured (Figure 2A and 2B). These diamond phonon energies, well known and tabulated in the literature, served as energy references for calibrating the new RIXS analyzer system. The measured LA phonon dispersion reproduces the literature values very well, while the energies of the optical phonons are consistent with the literature values and show a characteristic downturn, as the momentum transfer approaches the zone boundary. The strong signal intensity confirms the high efficiency of the new analyzer system.

The 4-meV RIXS spectrometer was then used to measure the spin-wave gap of the spin-orbit-coupled Mott insulator,  $\text{Sr}_2\text{IrO}_4$ . Because of its small energy, this electronic excitation could not be observed previously within the current best energy resolution of 25 meV provided by conventional spherical, diced Si analyzers (Figure 2C). A phase retarder was exploited to rotate the incident photon polarization and produce more elastic scattering to define the zero-energy loss. The magnon energy gap is found to be  $3.5 \pm 1$  meV, implying that there is a sizable anisotropy in  $\text{Sr}_2\text{IrO}_4$ .



**Figure 2.** (A) Longitudinal acoustic phonons of a diamond crystal. All phonon energies are consistent with values found in the literature. (B) Longitudinal optical phonons of a diamond crystal. Energies of these optical phonons are well matched with literature values and show a characteristic downturn as the momentum transfer approaches the zone boundary. The strong signal intensity confirms the high efficiency of the new analyzer system. (C) Red open circles show the elastic scattering peak, which was generated by the phase retarder and defines the zero-energy loss. Black-filled circles show the magnon peak at the magnetic zone center,  $(\pi, \pi)$ , which is the collective spin excitation of the antiferromagnetic lattice. The magnon peak energy is found to be  $3.5 \pm 1$  meV, implying that there is a sizable energy cost to rotate the spin, that is, a sizable spin anisotropy in  $\text{Sr}_2\text{IrO}_4$ .

## Three-Dimensional Coherent Diffraction Imaging Using Polychromatic Hard X-rays

2014-134-R2

Stephan O. Hruszkewycz, Wonsuk Cha, Paul H. Fuoss, Ross J. Harder, Matthew J. Highland, Wenjun Liu, and Jörg Maser

### PROJECT DESCRIPTION

In this project, we are developing a three-dimensional coherent X-ray diffraction imaging (3D-CDI) technique that uses the energy spectrum and integrated flux delivered by an Advanced Photon Source (APS) undulator to rapidly measure volumetric coherent diffraction and provide about a 100-fold reduction in data acquisition time. The central concept of the technique is to scatter a range of X-ray energies from a sample and use a series of very thin analyzer crystals to extract simultaneous slices of coherent scattering. This imaging technique has implications beyond the coherent diffraction imaging and materials communities, including incoherent ultrafast time-resolved measurements at dedicated timing instruments and certain ultrafast pump-probe experiments, especially “one-shot” pump-probe studies.

## MISSION RELEVANCE

This project is relevant to DOE's mission in science. Polychromatic coherent diffraction methods will provide a fundamentally new capacity for the study of novel nanoscale materials and will address outstanding challenges in the field of 3D-CDI, making advances toward *in situ*, real-time materials studies. Polychromatic 3D-CDI will be useful at DOE light sources that emphasize both coherent imaging and time-resolved physics, including the new National Synchrotron Light Source and potential diffraction-limited synchrotron facilities.

## RESULTS AND ACCOMPLISHMENTS

In FY 2014, we designed and commissioned an initial model of the instrument to develop the basic principles of the pink beam analyzer system. We demonstrated that a single-crystal silicon (Si) membrane can be used as an analyzer, and we performed preliminary tests on X-ray scattering from a ferroelectric thin film.

In FY 2015, we built and commissioned a second dispersive pink beam analyzer system in the beamline 34-ID-E endstation, improving significantly on the original system built in FY 2014. The underlying design of the new system is shown in Figure 1. A critical design element for this instrument was the compact five-analyzer Laue system that offsets the angle of each Si membrane by one degree. This diffractometer system successfully demonstrated the multi-analyzer approach by resolving the twin domain peaks of a ferroelectric lead titanate (PbTiO<sub>3</sub>) thin film grown coherently on a DyScO<sub>3</sub> single-crystal perovskite substrate at elevated temperatures.

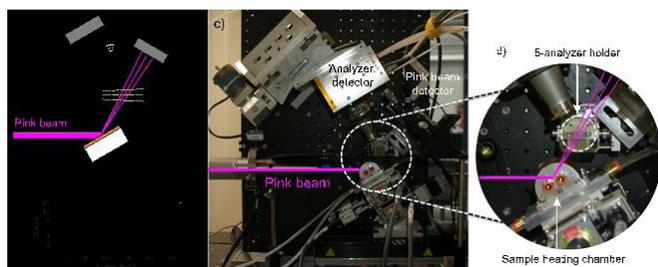
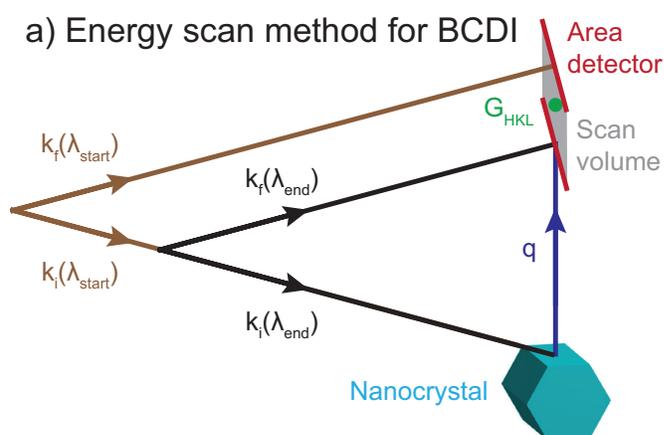


Figure 1. (a) Schematic of analyzers arranged in Laue diffraction geometry. (b) Typical tapered undulator spectrum. (c) Completed diffractometer system. (d) Closeup of the sample chamber and 5-analyzer holder.

In FY 2016, we developed and demonstrated a new image reconstruction technique, which we named variable-wavelength Bragg coherent diffraction imaging (vwBCDI) and which is based on scanning the energy of a coherent X-ray beam, thus leveraging the broadband X-ray spectrum of the APS for 3D coherent imaging. This capability is made possible by manipulating the wavelength of a coherent hard X-ray beam incident on the sample instead of scanning the beam angle (Figure 2).

To reconstruct a 3D image of a diffracting crystal, our approach utilizes a new phase retrieval concept that accounts for variable X-ray wavelength. This method enables new *in situ* studies of materials in environments where sample manipulation is difficult and the details of nanoscale strain evolution remain elusive—for example, during high-temperature crystal synthesis or the deformation of individual grains in a polycrystalline material under applied stress. We demonstrated the approach by imaging a gold nanocrystal with vwBCDI, and we found that image fidelity is preserved compared to current BCDI methods in resolving lattice strain at the nanoscale near facets of the crystal.



## b) Reconstruction of Au nanocrystal

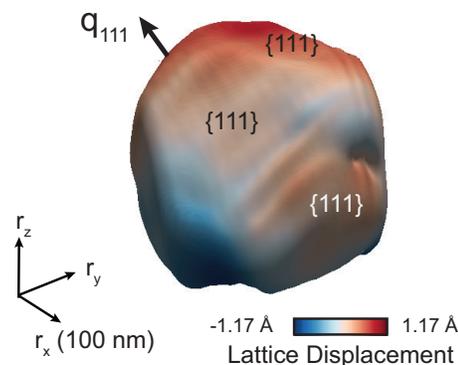


Figure 2. Panel (a) shows a schematic of the vwBCDI data collection concepts. By changing the wavelength of the X-rays incident on the sample, an X-ray area detector moves in reciprocal space but is fixed in real space. Thus, a reciprocal space volume about a Bragg peak can be measured with no sample motion. The challenge in inverting such data lies in accounting for the wavelength-dependent scaling of reciprocal space at each energy step of the scan. vwBCDI addresses this challenge, and we demonstrated the approach by reconstructing a 3D image of lattice displacement in a gold nanocrystal (shown in [b]).

## PROPOSED FUTURE WORK

This LDRD project has been completed. The next steps will be to integrate the multi-analyzer data collection

approach demonstrated in FY 2014/2015 with the new phase retrieval concept developed in FY 2016. This way, three-dimensional imaging can be implemented with the rapid multiplexed data collection, a capability that will potentially enable new scientific discoveries at the upgraded APS.

Continued development of the test-bed multi-analyzer instrument and phase retrieval approaches developed over the course of this LDRD and integrating them more permanently into the beamline will be pursued. An APS Partner User Proposal (PUP) with Los Alamos National Laboratory will be supporting this work.

## YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> High-Temperature Superconducting Prototype Undulator

2014-137-R2

Ulrich Welp and Yuri Ivanyushenkov

### PROJECT DESCRIPTION

The goal of this project is to develop a short superconducting undulator by using yttrium barium copper oxide (YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> [YBCO])-coated conductors for the magnet coils. Undulators are at the heart of X-ray synchrotron storage rings as well as free-electron laser-based light sources. Advances in brilliance and tunability in next-generation light sources are, therefore, intimately tied to progress in undulator technology. Current superconducting undulators are fabricated with niobium-titanium (NbTi) superconducting wire, which is a mature technology. However, NbTi has nearly reached the limits of its performance in terms of critical current and critical field. In recent years, tremendous progress has been made in high-temperature superconductors (HTSs), in particular YBCO-coated conductors (YCCs). The YBCO tapes currently under development meet or exceed the performance of NbTi under operating conditions typical for undulators, which would enable a higher on-axis field and, therefore, a higher undulator strength. Furthermore, NbTi undulators operate at liquid helium temperature, which requires complicated and expensive cryogenic installations. In contrast, HTS undulators could equal the performance of NbTi while running at a higher temperature, about 10 K, thereby enabling simpler and cheaper cooling systems.

### MISSION RELEVANCE

This project addresses novel insertion devices within advanced light sources and is related to DOE's mission

in science and innovation. In this mission, user facilities such as the Advanced Photon Source play a central role, since they provide new knowledge about the structure and function of new materials for innovative devices. Our project will establish the technology for a new generation of HTS undulators with enhanced X-ray brilliance and tunability.

### RESULTS AND ACCOMPLISHMENTS

In the previous years, we designed magnet cores and developed winding technologies that allowed us to fabricate magnet structures consisting of alternately polarized magnets using tape-shaped commercially available YCCs. Such structures generate a spatially periodic magnetic field in the undulator, which induces an oscillatory motion of relativistic electrons and results in the emission of high-energy photons. In FY 2015, we successfully implemented the fabrication and winding of U-slit YCCs. The U-slit wires were fabricated by SuperPower, Inc., by slicing a commercial 7.5% Zr-doped 12-mm-wide YCC. A new magnetic core was designed and fabricated, and a test winding comprising four winding stacks with 55 layers each was produced. At 4.2 K, the windings reached a critical current of  $I_c = 545$  A, corresponding to an engineering critical current density  $J_e$  of 1,360 A/mm<sup>2</sup>. Magnetic field profile scans showed a peak field of 0.75 T for a complete undulator, thus matching the performance of NbTi devices. However, the sliced edges of the YCC in long wire lengths were found to be prone to delamination. We therefore devised an alternative wiring scheme that allows for the continuous winding of standard 4-mm YCCs without the need for resistive joints and wire slitting. By incorporating turnaround pieces into the structure of the magnetic core, the winding sense of neighboring stacks was reversed, yielding a “figure 8” wire pattern. A test device containing seven winding stacks with 30 layers each was wound using 4-mm YCCs. This coil reached a critical current of  $I_c = 660$  A at 4.2 K, corresponding to  $J_e = 1,646$  A/mm<sup>2</sup>. Magnetic field scans indicated an on-axis field of 0.8 T, surpassing the performance of the initial test device as well as NbTi devices.

In FY 2016, we optimized this winding technology and fabricated several 11-pole test magnets. In order to maximize the value of  $J_e$  and the cooling efficiency of the winding stacks, we initially employed the so-called non-insulation winding scheme, in which the HTS tape is wound onto itself without any interlayer insulation. However, these magnets displayed unacceptably long settling times originating from current sharing between windings. A successful resolution, which maintains as high a  $J_e$  as possible at the magnet side facing the beam

pipe and at the same time minimizes current sharing, was found in the form of partial interlayer insulation, in which 25- $\mu\text{m}$ -thick insulating Kapton strips are inserted between HTS layers only in those sections of the winding facing away from the beam pipe. With this approach, the magnetic field generated by the magnet settled essentially instantaneously. Figure 1 shows a picture of a partially insulated 11-pole HTS undulator magnet, and Figure 2 displays the coil voltage of this magnet together with the on-axis field measured at two locations as a function of the applied current. The magnet was charged to a current of 800 A, corresponding to a  $J_e$  of  $\sim 2,100 \text{ A/mm}^2$ . This  $J_e$  is the highest value that has been reported yet for an undulator magnet. It is  $\sim 40\%$  higher than that reached with NbTi superconducting wire. We thus demonstrated that HTS YCCs are suitable for winding into undulator magnets yielding significantly enhanced performance as compared to existing wire technologies.

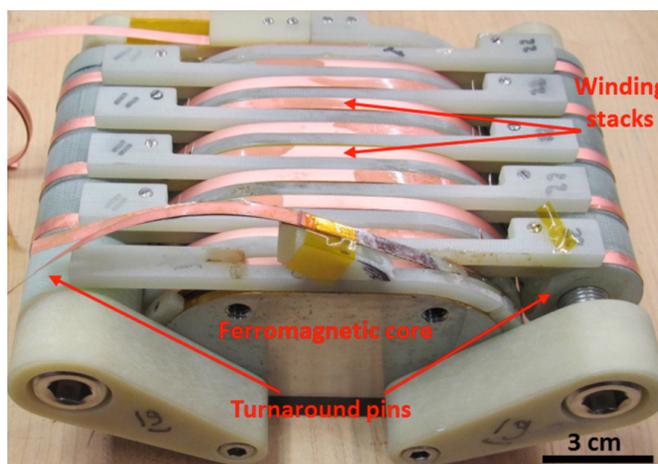


Figure 1. Photo of an 11-pole HTS undulator magnet. The beam pipe would be located underneath and parallel to the pictured device. The alternatingly poled HTS winding stacks are seen in brown color. The reversal of the winding polarity is achieved with the aid of turnaround pins running alongside the magnet core on either side.

We also performed extensive tests on epoxy impregnation of the HTS magnets. Since ultimately the undulator magnet will be operated in a conduction-cooled environment, epoxy impregnation is essential to achieving good heat transfer between the windings. Araldite filled with diamond nanoparticles ( $<100 \text{ nm}$ ) performs well and penetrates into the micron-sized gaps between the HTS tapes in a winding stack. Of particular concern is the free-standing HTS tape in the turnaround sections, as a thick epoxy coating is known to cause delamination and conductor degradation. We have found during our tests that covering the top and bottom of the HTS tape with protective layers in the form of adhesive-covered aluminum strips prevents degradation of the YCCs and, at the same time, is easily implemented in the winding process.

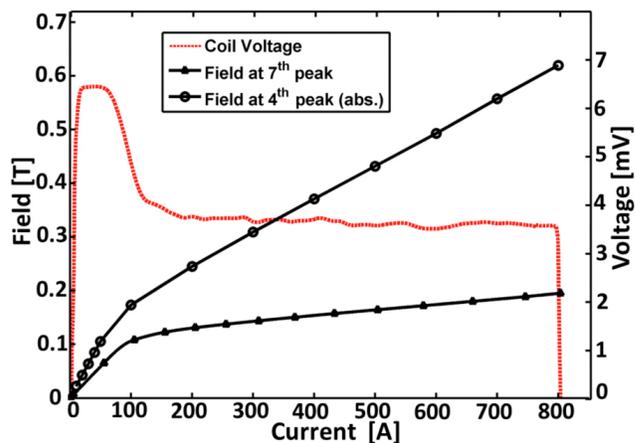


Figure 2. Dependence of the coil voltage and the generated magnetic field on the current applied to the device shown in Figure 1. This magnet reached a current of 800 A, corresponding to  $J_e = 2,100 \text{ A/mm}^2$ , which is the highest value achieved in any undulator magnet. The drop in coil voltage and the non-linearity in the field-current curves near a current of 100 A arise from the magnetic saturation of the ferromagnetic core.

## PROPOSED FUTURE WORK

FY 2016 was the final active year of this project. We expect further development of this technology will be pursued with support from the Scientific User Facilities Division.

## Automation of *in situ* Crystallization Plate Screening and Data Collection at Room Temperature

2014-175-R2

Craig M. Ogata and David J. Kissick

## PROJECT DESCRIPTION

Macromolecular crystallography has remained the method of choice in determining the structure of complex proteins and/or nucleic acids for several decades. The resultant structures have led to insights in understanding the functionality of these proteins and nucleic acids and have contributed, for example, to the development of pharmaceuticals and vaccines in the treatment of diseases. Part of the reason for the method's long-term success has been its ability to take advantage of developing technologies. One such technology was the use of synchrotron radiation. These stronger X-ray sources, such as the Advanced Photon Source (APS) at Argonne, have—by providing a higher X-ray dose to the sample—allowed the study of weakly

diffracting, biologically interesting molecules that were difficult to crystallize. In recent years, the development of the serial crystallographic, one-diffraction image per crystal, approach to collecting room-temperature data has been demonstrated at new X-ray free electron laser sources. The success of these experiments has prompted investigation of these applications at current synchrotron sources. The serial approach of using many samples circumvents the radiation damage that prevents complete data collection from a single room-temperature sample. Extending the application of serial data collection methods to sample crystals in their native, *in situ* growth conditions expands the opportunities for room-temperature data collection. This process allows data to be collected from samples prior to damage from mechanical extraction out of microliter drops, and prior to the contamination by chemical cryoprotectants used to freeze the samples to liquid nitrogen temperatures—both common procedures used in current conventional methods. This project focuses on providing a platform for X-ray diffraction characterization of biologically interesting macromolecular complexes and membrane protein crystals, in their native crystallization conditions. Identification of diffraction quality was combined with the exploration of serial crystallographic approaches adapted to the APS synchrotron source.

### MISSION RELEVANCE

This project is relevant to DOE's mission in science. It provides the capability for a significant subset of the APS user community, protein crystallographers, to characterize diffraction quality *in situ* for biologically important macromolecular crystal samples. This early characterization will guide investigators to crystallization experiments that lead to better diffraction and a high-resolution structure. In addition to screening, room-temperature serial crystallographic experiments are a way to study future data collection methods for improved, next-generation synchrotron sources such as the APS Upgrade. In addition to its relevance to DOE projects, it is supportive of National Institutes of Health (NIH) initiatives in structural biology. The tools developed for screening, data collection, and automation will be applicable and available to both academic and industrial scientists in the pharmaceutical industry.

### RESULTS AND ACCOMPLISHMENTS

The previous fiscal year (FY 2015) culminated with the completion of an experiment that encompassed the key aspects of this proposal. It used a prototype sample chip to deliver hundreds of crystals ranging in size from 10 to 15 microns to the X-ray beam. The serial crystallographic approach of collecting a single image per crystal was used to collect a complete room-temperature dataset that was used to solve the structure of a test lysozyme protein. Another example, completed in FY 2016, that demonstrated the scope of the project was the development and characterization of the Mylar *in situ* crystallization method. This setup was specifically developed for the crystallization of membrane proteins. The crystallization assembly and associated three-dimensional printed holders were used to solve the structure of a CO-myoglobin and the membrane protein, bacteriorhodopsin. The Mylar *in situ* crystallization drops have been used in attempts to automate the serial data collection process through the use of raster-style approaches that cover portions of the crystallization area combined with fast diffraction image analysis (Figure 1). Although this step automated the process, it pointed to the need for more intelligent search methods that could identify crystal locations to improve the efficiency of the data collection. One such approach that the team investigated, was the sparse supervised learning approach for dynamic sampling (SLADS), which reduces X-ray induced damage by probing the fewest possible points needed to reconstruct an image of the sample (Figure 2). This method is still in the early phases of development.

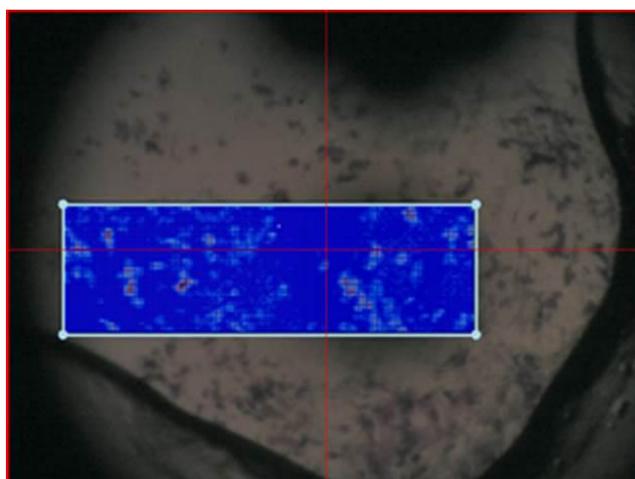
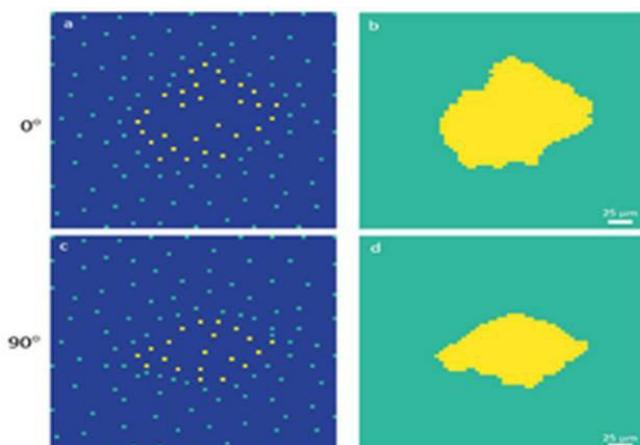


Figure 1. Automated rastering results (blue rectangle) superimposed on a section of an optical image of an *in situ* crystallization drop. An X-ray diffraction image is taken at each of the pixel locations. The pixel coloring is proportional to the number of diffraction spots recorded in the diffraction image (blue = low; red = high). The presence of diffraction spots corresponds to crystal locations.



**Figure 2.** SLADS implementation on a large lysozyme crystal. Measured locations for (a) the 0° rotation and (c) 90° rotation. The spots in the images of the column on the left correspond to sampling locations, the color coding, (green = background; yellow = crystal; blue = not probed), indicates the possible crystal location. The right column, (b) is the generated crystal reconstruction obtained from panel (a), and (d) is that generated from panel (c). As can be seen, a sparse number of probe locations can be used to outline the sample, resulting in reduced radiation damage prior to data collection.

Fiscal Year 2016 was the last year for this LDRD project. The results of this project demonstrated feasibility and interest for both *in situ* characterization and room-temperature data collection. Future development of the project will depend on support from our current NIH sponsors. The integration of other crystal identification techniques (e.g., offline ultraviolet fluorescence or second-order nonlinear imaging of chiral crystals [SONICC]) will be incorporated into more intelligent crystal identification methods for improved automated serial data collection. The current test setups will be further refined and integrated into the control programs for general use by the protein crystallography community.

## Using Hard X-rays to Accelerate the Synthesis of Materials

2015-141-R1

Peter Chupas, Karena Chapman, Gregory Halder, Guy Jennings, Charles Kurtz, Kenneth Poeppelmeier, and Xianbo Shi

### PROJECT DESCRIPTION

Our ability to deliver a battery with five times higher energy density, a catalyst with five times longer lifespan, or a material that is 30% more efficient at converting sunlight to electricity is predicated on our ability both to discover and, also, to synthesize the next-generation of functional materials. Computational approaches,

such as the Materials Genome and Inverse Design, have been successful in identifying an expanded library of potential materials with predicted stability and attractive functionality; however, few of these materials have been physically realized beyond the confines of a computer. The critical unresolved bottleneck in materials discovery is the synthesis and physical realization of these new predicted materials. Our goal is to eliminate this bottleneck and thereby accelerate the synthesis of new materials, by developing hard X-ray-based *in situ* characterization tools that will allow the rapid identification of new or metastable materials during the synthesis process.

### MISSION RELEVANCE

This project aligns with DOE mission to promote energy security. Materials discovery and synthesis science is critical to developing new energy technologies. It is a high priority within DOE and a traditional area of strength at Argonne, as well. Our project addresses this science area and provides a strategic path to accelerate discovery of new materials, changing the processes we use to search for new materials. This work complements existing programs at Argonne and it will have significant impact on the broader materials community (both industrial and academic) by providing an accessible platform for accelerated materials discovery at the Advanced Photon Source (APS) that is unique within the DOE complex.

### RESULTS AND ACCOMPLISHMENTS

Several research and development (R&D) activities have been ongoing in parallel with the expectation that they coalesce in the final year, consisting of both X-ray optics development and high-temperature sample environment development, where simulation and design activities were largely the focus of year one and device development the focus of year two. A critical aspect of the R&D has been the development of a monochromator concept and design optimized for the energy range 30–55 keV that maintains the current flux and energy resolution required for quantitative powder diffraction on an APS bending-magnet source.

Simulations and optimization of various configurations were completed in the first year, and a complete functioning device was subsequently fabricated. This instrument has been completed, tested, installed, and is in use at the 17-BM beamline. A vertically focusing bent Bragg and horizontally focusing bent Laue configuration monochromator has been built and demonstrated to provide the necessary focusing and flux while eliminating the need for additional optical components (i.e., mirrors).

The second R&D activity has been the development of experimental equipment (i.e., sample-environments) that allows materials reactions to be probed by hard X-rays during the synthesis process. Standard environments have been designed to accept the standard reaction vessels and volumes used in lab-based synthesis (e.g., sealed quartz and/or tantalum tubes) so that insights will be directly transferable to subsequent lab efforts. The device is a compact furnace designed around sample vessels—with suitable apertures for the incident and scattered X-rays.

The furnace can accommodate multiple reaction tubes to enable more efficient, parallel reaction studies. Test measurements have demonstrated data acquisition timescales of a few seconds, which allows multiple samples to be studied in parallel and at fine reaction intervals (e.g., 10 data points for each of 10 reactions for a 10-min synthesis). The furnace model has been refined to allow continuous use up to 750°C through the application of advanced corrosion-resistant alloys. The demonstrated concept of rapid screening of synthesis reactions coupled with concomitant *in-situ* characterization can be extended to other common synthesis routes, including high-pressure and hydrothermal methods.

## Development of a Compact 352-MHz/12-kW CW Solid State RF Power Amplifier System for Accelerators

2015-147-R1

Alireza Nassiri, David Bromberek, Aditya Goel, Douglas Horan, and Geoff Waldschmidt

### PROJECT DESCRIPTION

This project focuses on developing trial designs for high-power radio frequency (RF) amplifiers operated at 352 megahertz (MHz) and employing highly efficient and compact solid-state power amplifier technology. This technology's advantages over conventional electronic tube technology include system compactness, higher power efficiency, and ease of operation and maintenance.

### MISSION RELEVANCE

DOE has committed to meeting sustainability goals by, among other initiatives, improving energy efficiency at DOE laboratories. Among the systems with high energy consumption at DOE laboratories are the RF sources that power accelerators. Significant energy savings can be realized if high-efficiency alternatives are installed

as existing RF sources reach end-of-life or as new facilities are brought on-line. This project aims to address these issues.

### RESULTS AND ACCOMPLISHMENTS

In FY 2015, we accomplished three key tasks:

1. We completed the RF simulation of the power devices design for 2-kW power output at 352 MHz.
2. We completed the thermal and mechanical design of the power amplifier cooling system.
3. We initiated the design of the compact radio-frequency high-power combining cavity for a 12kW output demonstration.

In FY 2016, the design of the 2-kW amplifier module was completed. The first design achieved a sustained output power of 1.87-kW using a single LDMOS (laterally diffused metal oxide semiconductor) output device at 71% DC-to-RF efficiency. A second amplifier of identical design was assembled, and it achieved equivalent performance. Sustained operation of these amplifiers validated the high-efficiency cooling system design, consisting of a water-cooled cold plate and a carrier for the amplifier printed circuit board (see Figure 1).

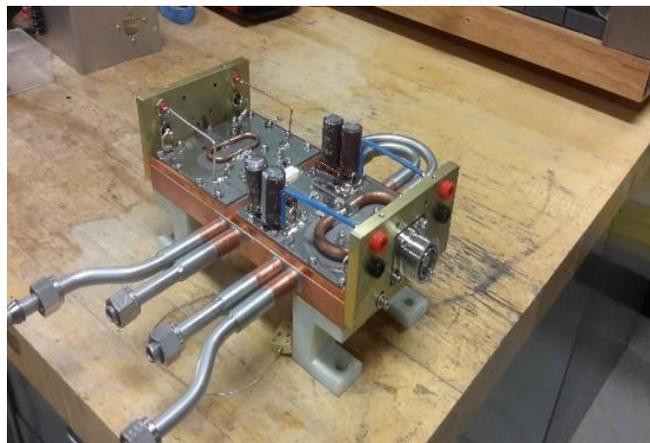


Figure 1. The 2-kW amplifier module design (dimensions: 4 inches wide by 7 inches long by 1.5 inches high).

The design of a 108-input, manually tuned resonant combining cavity (see Figure 2) was also completed, including thermal and electrical simulation analysis. The design includes adjustable input coupling loops for match optimization, a piston tuner for resonance control, an adjustable cavity output coupler, and water-cooling circuits on the output coupler and waveguide T-bar transition. Simulation results indicate very low stored energy in the cavity, which significantly reduces cooling requirements. Achieving 2 kW of output power from a single LDMOS output device requires very efficient

removal of heat from the device. Tests were performed with a 500-watt ceramic heater to validate thermal simulations of both the cold-plate/carrier and alternative vapor-chamber and heat-pipe cooling systems. Data from these tests indicate that the cold-plate/carrier configuration outperforms the present iteration of heat-pipe technology in this application. Nano-bonding was explored as an alternative to conventional soldering to address thermal stresses on components during amplifier assembly. The nano-bonding technique was evaluated for both thermal and electrical performance in two areas, transistor and circuit board attachment to the carrier. An amplifier was fabricated using the nano-bonding process; however, initial tests indicate insufficient thermal contact between the transistor and carrier due to voids in the nanobond. This work is ongoing with different geometries and processes.

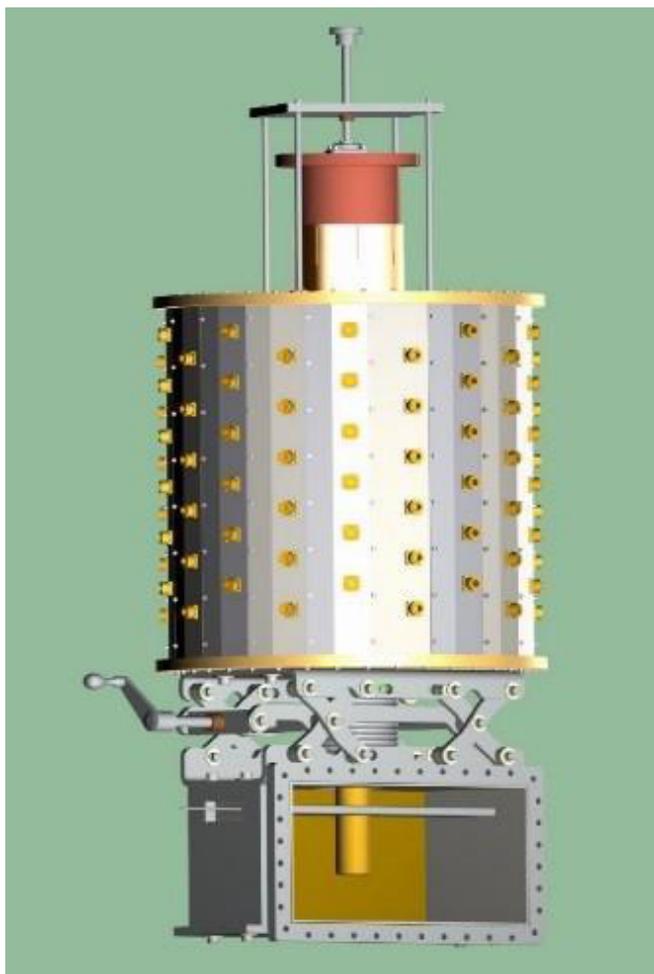


Figure 2. Resonant combining cavity with multiple coaxial inputs and single waveguide output (dimensions: 2.5 feet in diameter and 6 feet high).

### PROPOSED FUTURE WORK

In the third and final year of the project, we will complete the fabrication of the resonant combining cavity with six 2-kW inputs for the 12-kW test. We will seek an alternative sponsor for the building of a 352 MHz/150kW unit employing the cavity combiner system developed in house. Once completed, we will test and characterize its performance powering a single-cell resonator using the Advanced Photon Source 352 MHz high-power test stand. We will also explore potential technology transfer to industry for the production of high-power CW RF power with solid-state power amplifiers employing the high-power combining cavity system concept.

## Unraveling Mesoscale Spatial-Temporal Correlations in Materials Using Coherent X-ray Probes

2015-150-R1

Alec Sandy, Rebecca Bradford, Anthony DiChiara, Eric Dufresne, Paul H. Fuoss, Zhang Jiang, Alan Kastengren, Meimei Li, Xiao-Min Lin, Timothy Madden, Antonino Miceli, Suresh Narayanan, Paul F. Nealey, Nicholas Schwarz, Joseph Strzalka, Donald Walko, Jin Wang, John Weizeorick, Haidan Wen, and Hoydoo You

### PROJECT DESCRIPTION

Our project focuses on (1) advancing X-ray photon correlation spectroscopy (XPCS) to very fast time scales, and (2) creating and deploying the infrastructure necessary to develop coherent surface scattering imaging (CSSI) beyond its current demonstration state. The overarching goal is to develop coherent X-ray scattering capabilities—aligned with the proposed Advanced Photon Source (APS) upgrade—that will enhance understanding of the structure and dynamics of condensed matter at the mesoscale.

### MISSION RELEVANCE

Our project is a first step in creating programs that will lead to full utilization of the increased coherent flux from the proposed APS multi-bend achromat upgrade. It will advance coherence-based techniques for surfaces and for measuring fast energy-dissipative dynamics. Our project supports the large investment that DOE-Basic Energy Sciences (BES) has begun making to upgrade the APS into a fourth-generation light source. In addition, our project greatly enhances basic science capabilities that DOE-BES already supports through programmatic funding at national laboratories and universities.

## RESULTS AND ACCOMPLISHMENTS

During the first year of our LDRD, our efforts were focused on, first, securing and characterizing the fast detector infrastructure required for the very short time delay measurements described below and, second, designing and procuring the necessary sample positioning assemblies for CSSI and performing demonstration lower dynamic range measurements.

During FY 2016, our two principal accomplishments were (1) performing X-ray area-detector measurements of spontaneous nanoscale fluctuations in a gelling suspension with markedly improved time resolution, and (2) obtaining CSSI data with sensitivity dramatically better than what has been realized previously.

Gelation measurements were performed using the so-called ultrafast X-ray camera (UFXC) provided by researchers at the AGH University of Science and Technology in Krakow, Poland. Initial tests of the detector were performed with an 11-kHz frame rate (90  $\mu$ s frame spacing) and resulted in a recent publication in the *Journal of Synchrotron Radiation*. On the basis of the success of these measurements, we worked with the team to successfully extend the frame rate to 50 kHz (20- $\mu$ s frame spacing). This frame rate is higher than any other XPCS-suitable detector in the world and 50 times faster than had previously been accomplished at the APS. We used this detector to study changes in the nanoscale structure and dynamics of a dense colloidal suspension as it was slowly heated from the gel to the fluid state and when it was quenched from the fluid to the gel state.

We also performed rheology measurements under the same conditions to correlate the macroscale viscoelastic response with changes at the nanoscale. Figure 1 shows both the observed time correlation functions and the time-averaged structure measurements (inset). When the temperature of the suspension is changed by only  $\sim 1^\circ\text{C}$ , the dynamic signature of the suspension changes by several orders of magnitude, but only modest changes are observed in the time-averaged structure. Analysis and interpretation of this data are ongoing, but the UFXC detector has provided an unprecedented view of short-time caged dynamics in gelling colloidal suspensions.

CSSI capabilities and results were advanced in two main directions. First, we have mostly reconfigured our experimental station to provide sufficient resolution and focusing for obtaining high-quality CSSI data. Second, during this reconfiguration, we created additional representative samples and measured CSSI patterns from them using the P10 beamline at Petra-III (at the Deutsches Elektronen-Synchrotron [DESY] in Germany). Figure 2

shows a schematic of one sample (top left inset) and the coherent scattering that has been measured (main figure and bottom left inset enlargement). The dynamic range that we have obtained is 10,000 times greater than has been measured previously. Although inversion of this coherent scattering pattern is in progress, other single-shot scattering patterns have been successfully inverted and indicate that it will be possible, with the increased coherent flux provided by the upgraded APS, to perform time-resolved CSSI measurements.

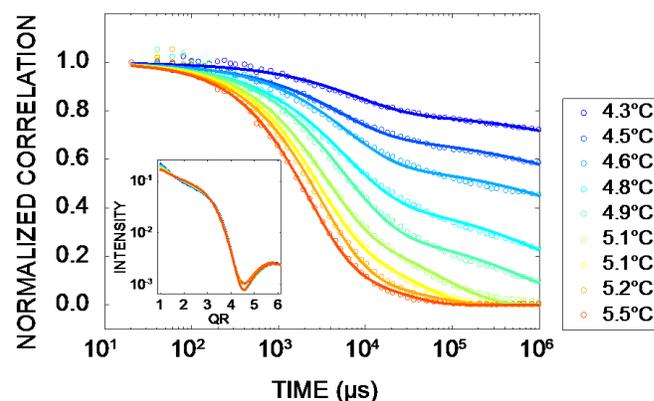


Figure 1. Time autocorrelation functions and time-averaged scattering (inset) from a 20% volume fraction suspension of 86-nm-diameter, octadecyl-coated silica nanoparticles suspended in decalin.

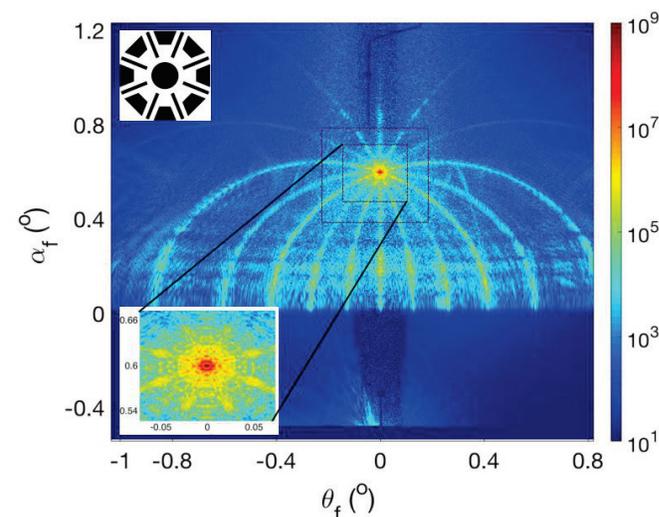


Figure 2. Coherent surface scattering image obtained from a sample (schematically illustrated at upper left). The lower-left inset is a closeup of the center of the coherent scattering pattern.

## PROPOSED FUTURE WORK

In FY 2017, we will perform high-flux XPCS experiments using broad bandpass undulator radiation as a proxy for the coherent flux that will be delivered by the proposed APS upgrade. We will accomplish this project goal by designing and installing enhanced detector flight path infrastructure that will provide fine resolution under these experiment conditions. We will use the broad bandpass X-ray beam to study the dynamics of colloidal suspensions under high pressures where anticipated novel liquid and solid phases of the suspending medium should modify the diffusion properties of the suspension. Other key goals are to increase the frame rate of the UFXC detector by a factor of two, so that the minimum frame spacing is 10  $\mu$ s, and increase the sparsification of the data produced by this detector so that it can run with a higher duty cycle. With respect to the coherent surface scattering imaging portion of our project, we plan to complete and publish work on angular and lateral ptychography in the CSSI geometry. We will also design and commission a vacuum environment for the fine lateral and angular positioning assembly that we have assembled as part of this project, and we will use this assembly to perform coherent scattering measurements at beamline 8-ID at the APS.

## The VelociProbe: Ultra-High-Resolution Ptychographic Hard X-ray Nanoprobe

2015-153-R1

Stefan Vogt, Junjing Deng, Chris Jacobsen, Barry Lai, Jörg Maser, Curt Preissner, Chris Roehrig, and Shane Sullivan

### PROJECT DESCRIPTION

The goal of the VelociProbe project is to design, build, and demonstrate a new type of X-ray microscope that can achieve sub-10-nanometer (nm) spatial resolution using ptychography and scan 1-square-micron areas in under 10 seconds so as to take advantage of the Advanced Photon Source Upgrade (APS-U). Currently, no instruments exist that can do this. Our novel approach employs new stage designs for accurate positioning, new positioner control designs, and new data acquisition (DAQ) strategies, including high-bandwidth interferometric positioning. The hardware design maximizes dynamic stability to enable high-speed scanning. The controller design will push the limits of the scanning bandwidth and enhanced disturbance rejection, also taking advantage of the high-frequency dynamics to employ scanning strategies other than the simple raster scan. The new DAQ strategies may relax constraints on the precision

of the hardware positioning while still allowing for the highest resolution.

The challenge of high-resolution and fast scanning will be met in two fundamental ways: (1) development of a nanopositioning system with high dynamics and low drift, and (2) control and metrology systems that offer scanning and disturbance rejection heretofore unavailable in the X-ray microscopy world. Our nanopositioning design incorporates a commercially available low-mass, high-dynamics scanner integrated into a novel and ultra-stable coarse positioning system. This hardware provides the necessary long travel ranges to accommodate real samples and variable-energy operation while remaining highly stable during scanning. Our advanced control design will take advantage of bandwidth-enhancing and disturbance-rejection schemes employed by scanning probe instruments (e.g., atomic force microscopes). It is the product of joint efforts with Professor Vasu Salapaka of the University of Illinois at Urbana-Champaign.

### MISSION RELEVANCE

The VelociProbe (an ultrahigh-resolution ptychographic hard X-ray nanoprobe) is being designed to enable science at DOE-SC's Multi-Bend Achromat (MBA) lattice upgrade of the APS—scientific investigations that have as yet never been performed. This upgrade represents a major improvement for nanofocusing experiments. Therefore, this project is relevant to DOE's science mission and to all other mission-related activities that rely on advanced high-resolution X-ray tests at DOE light sources.

### RESULTS AND ACCOMPLISHMENTS

The major accomplishments in FY 2015 were the design and procurement of the ultra-stable coarse-positioning system. In addition to the coarse-motion platform, the fast-scanning stage and one of the two three-axis interferometer systems have been acquired. The electronics to develop both our baseline controller and the advanced controls have been acquired, including those for one of the two three-axis interferometer systems (with 0.1-nm position accuracy). Testing of these components was carried out to verify that they meet specifications and develop the initial control setup.

Major accomplishments in FY 2016 included the final design of the coarse granite positioning system, integration of the coarse and fine motion systems, and initial testing of the system, in preparation for first beam early in 2017. This positioning system is the foundation of the new instrument design, leading to high stability to

allow for pushing the speed and dynamics of the rest of the system.

In parallel with finalizing the coarse-positioning system, all relevant subsystems were tested, including the interferometer, the sample stages, and the fine zone plate scanner. Significant progress was made on the so-called advanced scanning control. This advanced scanning system should provide better performance than the built-in controller for the scanner. Laboratory testing has already indicated that this will be the case. The advanced controls enable the motion system to better reject structure-borne disturbances, resulting in higher resolution. Scanning bandwidth can also be increased. The implication for the VelociProbe is that arbitrary scan trajectories will be followed to a high degree of accuracy. Figure 1 shows some resolution measurements for the Y (vertical) axis. In the current system, resolution is somewhat limited by the bandwidth of the digital input module acquiring the interferometer signal. Testing has determined that our piezo scanner can achieve sub-nanometer (0.3-nm) resolution by using a higher-bandwidth digital input module.

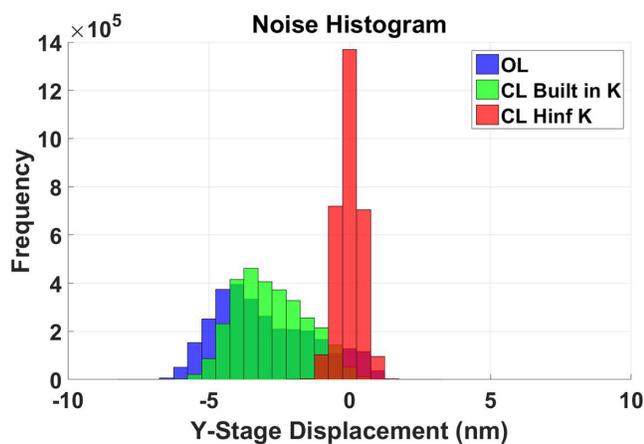


Figure 1. Histogram chart comparing the open-loop system (OL – blue), built-in controller (CL – green), and the APS-developed controller (CL Hinf – red), where a narrower distribution is better. The APS-developed controller (red) in this case achieved a resolution of 1.3 nm, whereas the built-in controller and open-loop controllers only achieved 3.0-nm and 5.3 nm-resolution, respectively.

### PROPOSED FUTURE WORK

The VelociProbe is scheduled to be moved into beamline 2-ID-D and assembled in the hutch in January 2017. The control system and motion programs will be tested first without X-ray beam during the APS shutdown. In February, initial test scans for both fluorescence and ptychography images will be conducted to assess the reliability and stability of the whole instrument. A resolution test pattern will be used for this purpose and for the assessment of the achieved spatial resolution.

More complicated samples (e.g., integrated circuits) will be used for further demonstration of fast scans.

Future work in FY 2017 will include realizing tomographic and ptychographic capabilities. We will also conduct X-ray experiments to demonstrate the upper limits of both speed and resolution. We expect development of the advanced scanning control to continue. Experience and knowledge gained through this testing will enable us to begin conceptualizing how this capability will inform the development of the ptychoprobe and other APS-U X-ray microscopes, for which the VelociProbe serves as a testbed. In addition, we will use the instrument to begin developing the user science that requires the spatial resolution and scan speeds the VelociProbe can provide.

## Ion Beam Figuring with *in situ* Metrology: Diffraction Limited X-ray Optics and Dynamic Aperture for Three-Dimensional Control of Thin-Film Deposition and Ion-Beam Erosion

2015-161-R1

Raymond Conley, Lahsen Assoufid, Mark Erdmann, Kurt Goetze, Elina Kasman, Tim Mooney, Jun Qian, and Bing Shi

### PROJECT DESCRIPTION

This project has two goals, with the first to combine ion-beam figuring (IBF) with *in situ* metrology, and the second to design a dynamic aperture. At present, mirror substrates are fabricated by cycling between individual figuring and metrology instruments. Joining figuring with metrology may improve performance by reducing errors and shorten production time. These capabilities will be integrated into the Modular Deposition System (MDS) at the Advanced Photon Source (APS). The initial goal for the instrument, which is built around a precision in-vacuum brushless servo drive, is to produce advanced multilayer-based X-ray optical elements. However, the machine is also ideal to explore related figuring and metrology needs. By integrating this machine with an *in situ* Fizeau interferometer and ion-milling equipment, the APS may be able to fabricate mirrors in-house that can take advantage of the improved coherence beams from the planned Multi-Bend Achromat (MBA) lattice. The combination of ion milling, deposition and *in situ* metrology has the potential

for rapid turnaround on mirrors with the figure errors appropriate for the MBA lattice.

The second goal of this project is to develop dynamically actuated baffle arrays, comprising multiple, identical actuated baffle modules, for real-time control of thin-film deposition and/or ion-beam erosion in three dimensions. We wish to develop a modular actuated baffle mechanism that can be easily adapted to a variety of similarly sized planar, rectangular magnetron cathodes and rectangular ion sources, regardless of their specific dimensions. There are potentially three different applications of actuated baffles: (1) deposition of X-ray multilayer films having arbitrary lateral thickness gradients in one dimension onto flat or figured substrates; (2) deposition of X-ray multilayer films having arbitrary lateral thickness gradients in two dimensions onto flat or figured substrates; and (3) differential deposition and/or differential erosion (i.e., ion-beam figuring) to correct surface figure errors in flat or figured substrates, including cylindrical thin-shell glass X-ray mirror substrates.

By integrating the dynamic aperture into this machine, we hope to produce true three-dimensional thin-film gradients. This capability could be used for creating single-bounce collimating or focusing reflective X-ray optics. It could also be used for dynamic figure correction via material deposition. Such films would be especially useful as a phase-correction layer deposited on the top surface of a nanofocusing multilayer mirror. A phase correction layer compensates for errors in both the multilayer stack as well as the substrate and, depending on the aperture, requires a three-dimensional thickness profile.

### MISSION RELEVANCE

This work is relevant to all DOE missions to which studies at the Advanced Photon Source contribute (i.e., national security, energy, environment, and basic science) by increasing the performance of optics deployed at many beamlines there. This work is also relevant to the National Aeronautics and Space Administration's space-based X-ray telescope programs because the dynamic aperture can be used to correct the figure error of slumped-glass substrates used in Wolter geometry telescopes.

### RESULTS AND ACCOMPLISHMENTS

Dynamic aperture milestones by year include efforts to:

- Demonstrate a low-cost encoder that is ultra-high vacuum (UHV) compatible (FY 2015, postponed because of a design change).
- Develop a motor-bearing design that meets the 5-mm pitch requirement (FY 2015, completed).
- Demonstrate 75-mm motion with one dynamic aperture element in the atmosphere (FY 2016, completed).
- Design dynamic aperture using radial bearings (FY 2016, completed).
- Demonstrate use in a thin-film deposition environment (FY 2016, delayed to FY 2017 because of MDS installation).

Ion beam figuring and *in situ* metrology milestones by year include efforts to:

- Demonstrate a reliable method for measuring a flat mirror that is within a vacuum system while the interferometer is isolated from the UHV environment (FY 2015, completed).
- Using the existing WYKO interferometer, utilize a reference flat to examine methods for measurement of single apertures (mirror sizes 4" or less) through a UHV-atmosphere interface (FY 2015, completed).
- Fabricate the UHV iris for transmission flat protection. Expect that as of January 2017, the iris will be ready and will await MDS availability for integration.
- Fabricate the UHV gimbal with tip/tilt and rotate for transmission-flat alignment (FY 2016, completed).
- Integrate the interferometer, tilt stage, and ion milling apparatus into the MDS (FY 2016, in progress).
- Demonstrate accurate single-aperture measurement of flat mirrors in the UHV environment (FY 2016, completed).
- Demonstrate sub-aperture stitching of flat mirrors in the UHV environment (planned for FY 2017).
- Deploy focused mill apparatus to work on figure correction of higher-spatial-resolution mirror errors planned for (FY 2017).

### PROPOSED FUTURE WORK

In FY 2017, we will integrate all of the subsystems into the MDS and begin initial IBF trials. This effort will include significant controls and software development to merge the equipment. The dynamic aperture will be tested within a UHV environment.

## Next Generation Mössbauer Spectroscopy

2015-164-R1

Thomas S. Toellner, Ahmet Alatas, E. Ercan Alp, Michael Hu, and Jiyong Zhao

### PROJECT DESCRIPTION

Using synchrotron radiation as a radiation source to perform Mössbauer Spectroscopy (MS) offers many advantages for materials research. The inherent small beam size and excellent collimation, which do not exist for traditional MS, allow researchers to probe samples from a wide range of scientific disciplines on a microscopic scale. Currently, MS is performed at beamline 3-ID of the Advanced Photon Source (APS); however, the data collection rates are limited. This project aims to improve the data collection rates significantly, as well as to expand this measurement technique to include simultaneous X-ray diffraction. The project involves building a novel Mössbauer spectrometer at beamline 3-ID at the APS that will operate during the “hybrid-fill mode” by combining micro-focusing with high-speed shutters that will significantly improve data collection rates and allow simultaneous X-ray diffraction to be collected on samples containing Mössbauer isotopes.

### MISSION RELEVANCE

This project is carried out in support of a DOE synchrotron user facility by using a novel approach that provides improved measurement capability with higher data collection rates. This project is also relevant to the APS’s proposed multi-bend achromat (MBA) upgrade, which involves reducing the emittance of the source and offers a number of benefits for X-ray measurements, including the potential for a significantly higher spectral intensity. The proposed MBA upgrade entails a time structure for the delivery of X-ray pulses that reduces the time between pulses from what is currently provided at the APS. This reduction, however, is detrimental to some X-ray measurements that rely on longer times between X-ray pulses. Exploring the viability of high-speed shutters to perform X-ray pulse selection and isolation offers a potential means of providing a longer time between pulses for some measurements, while maintaining the benefits of a lower emittance source.

### RESULTS AND ACCOMPLISHMENTS

In FY 2015, the project team:

- Demonstrated a method for producing a pure, 10-neV gamma-ray source of 14.4 keV synchrotron radiation ( $\Delta E/E = 7 \times 10^{-13}$ ) using orthogonal linear polarization

filters and either a stainless steel absorber or a single crystal of potassium ferricyanide.

- Designed more efficient, in-line X-ray linear polarization filters for 14.4-keV synchrotron radiation.
- Designed both vertical and horizontal focusing systems for use with high-speed shutters.
- Designed a platform for the sample environment and high-speed shutters.

In FY 2016, the project team:

- Commissioned a vertical focusing system composed of one-dimensional beryllium refractive lenses and demonstrated 0.020-mm line focus (at 14.4 keV) at beamline 3-ID of the APS.
- Installed and commissioned a horizontal focusing system composed of an 830-mm bendable reflecting mirror at the same beamline and demonstrated a 0.011-mm line focus (at 14.4 keV).
- Installed and commissioned a platform for high-speed shutters and a sample environment.

### PROPOSED FUTURE WORK

In FY 2017, the project team will seek to:

- Complete the upgrade of the water-cooled diamond monochromator to a liquid-nitrogen-cooled silicon monochromator.
- Commission the high-speed shutters at beamline 3-ID of the APS and demonstrate the ability to measure Mössbauer time spectra and energy spectra with the completed instrument.

## Isotope Geochemistry via Sn Isotope Fractionation Using Inelastic X-ray Scattering of Synchrotron Radiation

2015-173-R1

E. Ercan Alp and Michael Hu

### PROJECT DESCRIPTION

Siderophilic (iron [Fe]-loving) elements provide clues to the conditions under which terrestrial planets differentiated into metallic cores and silicate mantles. The concentrations of such elements (e.g., nickel [Ni], cobalt, tungsten, and tin [Sn]) in the Earth’s mantle were set by metal-silicate equilibrium in an early magma ocean. The thermodynamic conditions that prevailed

during this differentiation (pressure, temperature, and  $fO_2$  [fugacity or effective partial pressure of oxygen]), however, are a matter of intense debate. The dependence of the partitioning of these siderophilic elements on these parameters is an important constraint on better understanding planetary core formation.

Tin is generally classified as a chalcophilic (sulfur-loving) element; however, classification as siderophilic or chalcophilic strongly depends on the nature of the host matrix. For example, there is a large variation in the thermochemical behavior of Ni-Sn and Ni-Fe alloys. Very large changes occur in the activity coefficient of Sn in Fe-Ni alloys as a function of composition. Furthermore, the behavior of two stable oxidation states of Sn as  $Sn^{+2}$  and  $Sn^{+4}$  creates a further complication in interpreting oxygen fugacity data. For example, it is reported that the Ni-rich phases (teanite) contain up to 100 parts per million (ppm) Sn, while the Ni-poor phases only contain 0.2 to 7 ppm Sn. Thus, the variation in the Sn content in rocks and meteorites undoubtedly points to the siderophilic nature of Sn.

One new approach for addressing the issue of core formation and obtaining independent information on the intensive parameters that controlled this differentiation is based on the isotopic composition of siderophilic elements (mainly silicon [Si] and Fe). It is quite valuable to develop a new proxy for isotope geochemistry studies that will indicate redox conditions at the time of formation.

The next geologically relevant and experimentally practical isotopic system to develop and exploit is Sn. Only the lack of fractionation factors limits its use in planetology. Here, we exploit a new capability at Beamline 30-ID-B of APS in terms of Sn-specific spectroscopy for isotope geochemistry work. We extract the required fractionation factors to make Sn isotopes a new probe of the early evolution of the Moon, the Earth, and Mars. The behavior of Sn oxides in glassy and crystalline silicates, Fe-based alloys, and sulfides of geochemical interest has yet to be studied.

We are collaborating in this work with Mathieu Roskosz (Museum Nationale d'histoire Naturelle, Paris), and Carolyn Fitoussi (Laboratoire de Géologie de Lyon–Ecole Normal Supérieure de Lyon, France). This project is part of FACCTS: France and Chicago Collaborating in the Sciences.

## MISSION RELEVANCE

DOE Chemical Sciences, Geosciences, & Biosciences (CSGB) Division has the geosciences program, which supports basic research in geology, geochemistry, and geophysics. Geochemical research emphasizes fundamental molecular-level understanding of geochemical reactions and phase equilibria in earth materials. Application of X-ray and neutron scattering using BES facilities plays a key role in these research areas. Our work in isotope fractionation already has encouraged many other researchers to carry out research programs funded by NSF, and others.

## RESULTS AND ACCOMPLISHMENTS

In the first year of the project, we synthesized five compounds of Fe-Ni-Sn, isotopically enriched with  $^{119}Sn$  and  $^{57}Fe$ :  $Fe_{0.995}Sn_{0.005}$ ,  $Fe_{0.99}Sn_{0.01}$ ,  $Fe_{0.97}Sn_{0.03}$ ,  $Fe_{0.96}Ni_{0.03}Sn_{0.01}$ , and  $Fe_{0.93}Ni_{0.04}Sn_{0.03}$ . We measured the pDOS and determined the force constants of these five compounds. It is now clear that we can measure the Sn pDOS even if Sn is a small fraction of the total alloy, as low as one atomic percent. It is also clear that Sn does not precipitate out, and that it remains in the solid as part of the body-centered-cubic Fe lattice.

In the second year of the project, we have performed a new set of measurements. We aimed to demonstrate the difference between mafic and felsic melts, which represent two end members of Earth's molten silicates. Basalt was chosen to represent the former, and rhyolite for the latter. Four silicate glasses were prepared for this study. Two basalts containing about 45%  $SiO_2$ , rich in alkaline-Earth cations and poor in alkalis were first studied because they reflect the dominant liquid extracted from the Earth's mantle. Two rhyolites, containing about 70%  $SiO_2$ , rich in alkalis and poor in alkaline-earth cations were also studied. They correspond to another end member of Earth's molten silicates. The strong compositional differences between rhyolites and basalts are known to be responsible for very different structural and vibrational properties of these glasses, including a large difference in the Fe force constants between these two glasses.

The results of these measurements in terms of data reduction and analysis are complete. Figures 1, 2 and 3 summarize the results of measurements on these four glasses and metals. There are obviously strong differences as a function of the glass matrix and for a given matrix as a function of the redox network (Figure 2) and there are no precipitates as crystalline compounds that would show in the density of states (DOS) as sharp peaks.

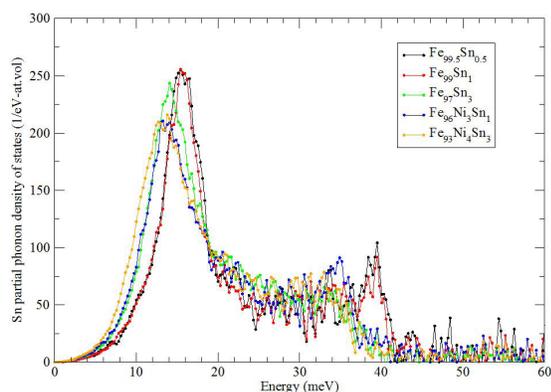


Figure 1. Sn partial phonon density of states for FeSn and FeNiSn alloys of different compositions. The high-quality data obtained from these measurements will enable the extraction of isotope fractionation, which will help us develop  $^{119}\text{Sn}$  as a new proxy for studying the partial pressure of oxygen (fugacity) as the Earth was forming.

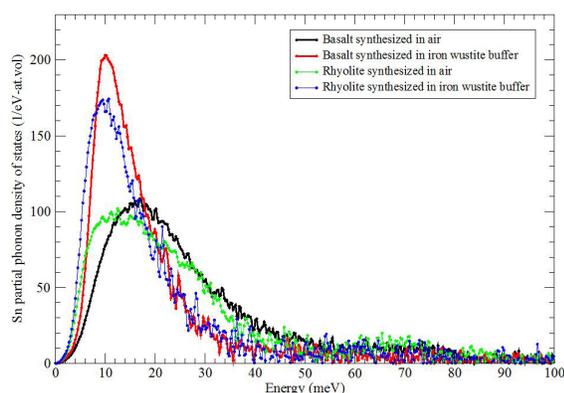


Figure 2. Partial phonon density of states of Sn in basalt and rhyolite, prepared under different redox conditions in air or in a FeO (wustite) buffer.

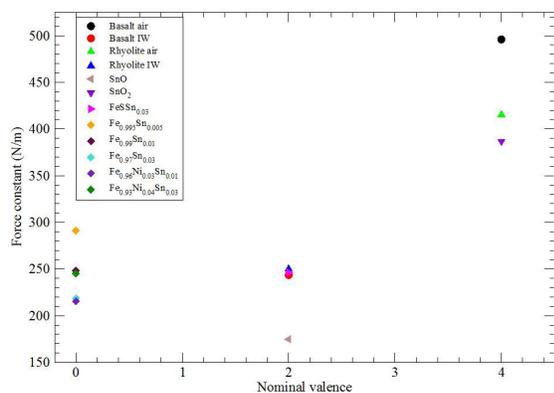


Figure 3. Force constant versus Sn valence derived from the phonon measurements in Fe-Sn alloys as a function of Sn content and in basalt and rhyolite prepared under different redox conditions.

## PROPOSED FUTURE WORK

In the coming months, we will propose an interpretation of the few isotopic data collected on natural samples by our colleagues from Lyon. This will require full data processing and a better characterization of the sample microstructure that will be performed in France. The next major step will be to synthesize different Sn-bearing sulfides. A preliminary test shows promising results, but the structure and the redox state and homogeneity of the Sn incorporation are very uncertain thus far. Our next beam-time allocation on Sector 30 will be devoted to sulfides.

## Developing New Schemes for Nuclear Resonant Scattering Measurements at an Upgraded APS

2015-182-R1

Bogdan Leu

### PROJECT DESCRIPTION

Soon after the discovery of the Mössbauer effect (ME) in 1958—which holds that a nucleus bound in a solid has a large probability of no recoil when absorbing or emitting a photon that will therefore have the precise energy of the nuclear excited state involved—theorists predicted the existence of energy shifts on the order of tens of milli-electron volts (meV) attributable to lattice vibrations (phonons) in the system. However, these shifts were beyond what conventional ME experiments could detect. Third-generation synchrotron sources circumvented the technical limitations and were able to measure phonon densities of states and to expand Mössbauer spectroscopy into the time domain. Sub-meV-resolution monochromators have been developed for energies near particular nuclear resonances. Owing to the sub-nanosecond duration of synchrotron pulses, fast detectors, and time discrimination techniques, a nuclear resonance signal can be observed.

Nuclear resonance scattering (NRS) is a relatively new, isotope-sensitive, synchrotron-based technique that provides information about the local atomic environment, vibrational dynamics, and electronic and magnetic states. The iron isotope  $^{57}\text{Fe}$  is the isotope studied most often with NRS because it possesses an appropriate nuclear excited state and iron is an important element in biology and geophysics systems. However, use of other isotopes, such as the tin isotope  $^{119}\text{Sn}$ —tin playing important roles, such as in thermoelectric materials, nanomaterials, and

geophysical applications—will substantially broaden the applicability and usefulness of the NRS method. The aim of this project is to develop a Sn-based NRS capability at beamline 30-ID of the Advanced Photon Source (APS), home of the high-energy resolution inelastic X-ray scattering (IXS) technique, by taking full advantage of the technical and scientific synergies between the NRS and IXS methods. The APS is perfectly suited for timing experiments such as NRS due to its characteristic electron bunch filling. The working energy for Sn-based NRS (23.88 kilo-electron volts [keV]) is generally outside the optimum performance of most undulators. Beamline 30-ID, however, has a new undulator that provides peak flux in the first harmonic at this particular energy. In addition, detectors and associated electronics with nanosecond time resolutions are available at the beamline.

Synchrotron Mössbauer spectroscopy (SMS) has several distinct advantages over conventional ME experiments: (1) it can excite isotopes for which there are no good radioactive parent nuclei; (2) the signal-to-noise ratio is on the order of  $10^6$  times better, so monolayers, dilute samples, etc., can be measured; (3) small samples under extreme conditions can be studied (high pressure, thin layers, buried layers, interfaces) with a synchrotron beam whose brightness is  $10^7$  times more intense; and (4) the time domain measurements make extremely small nuclear state energy splitting observable.

### MISSION RELEVANCE

The project supports DOE's science mission by enabling new areas of fundamental research on the atomic and electronic structures of materials relevant to a host of energy and environmental systems. It is applicable to Sn-containing anodes for battery research and thermoelectric materials to capture lost heat. These and many other applications will contribute to programs under the DOE Office of Science.

### RESULTS AND ACCOMPLISHMENTS

In FY 2015, we investigated two promising thermoelectric materials. Also, preliminary result on new tetra-nuclear antitumor drug entity, Sn(IV)-oxo-(di-o-vanillin) dimethyl dichloride, were successful. The main rationale for developing this program at beamline 30-ID is the six-bounce, cryogenically cooled monochromator. It yields a flux of  $4 \times 10^9$  photons/second at the sample with an energy resolution of 1 meV. The high flux not only shortens the duration of experiments, but also makes certain experiments possible that could not be performed in the past. Experiments on SnI<sub>4</sub> at high pressures demonstrated

that. The high flux becomes even more important for materials that are not enriched with the NRS-suitable <sup>119</sup>Sn isotope (natural abundance of about 9%).

In FY 2016, we moved the NRS program to the C-station at the APS to take advantage of the focusing capabilities and other equipment used by herix (e.g., zoom camera, 4-circle diffractometer, and cryostat). This relocation enabled us to study thin films and even monolayers of nanomaterials. Research into high pressures and biophysics continued. The Sector 30 NRS program has been established as a General User Program (GUP) accepting GUP proposals at APS. NRIXS study of SnI<sub>4</sub> under up to over 90 GPa pressure was done to investigate pressure induced amorphization (PIA) and recrystallization. In combination with density functional theory (DFT) calculations, it helps to elucidate the mechanism of these transformations. Sn nano wires were studied to understand superconductivity of nano-scale materials. SnSe at various temperatures was measured using the NRIXS method to reveal the anharmonicity and its effect on its low thermal conductivity.

### PROPOSED FUTURE WORK

Future work will be supported by APS operations and upgrade, and other DOE research funds if possible.

## Implementing New Microscopy Capabilities at the APS

2015-183-R1

Lydia Finney

### PROJECT DESCRIPTION

The overall goal of this project was to develop capabilities for multiscale and multimodal imaging across different Advanced Photon Source (APS) beamlines and instruments. In this project, we implemented and enhanced three new microscopy techniques in preparation for the APS Upgrade. First, a commercial transmission X-ray microscope (TXM) recently relocated from the National Synchrotron Light Source (NSLS) was commissioned on beamline 8-BM. This system provides full-field imaging capabilities with ~30-nanometer (nm) resolution in either the 2D or 3D mode. This system can be used for *in operando* imaging of the microstructure of materials such as battery electrodes, solid oxide fuel cells, and microelectronics, to name a few. Second, a synchrotron X-ray scanning tunneling microscope (SX-STM) system jointly developed by the APS and

Argonne's Center for Nanoscale Materials was installed and commissioned in an experimental station on 8-BM. This combination will provide truly transformational capabilities for understanding surfaces and/or nanostructured systems. Third, a system for wide-field fluorescence analysis with moderate [ $\sim 10$ -micrometer ( $\mu\text{m}$ )] spatial resolution was developed. This system enables rapid fluorescence measurements for statistical analysis studies of a large number of samples or sample screening prior to higher-spatial-resolution measurements on an optimized insertion device beamline.

### MISSION RELEVANCE

As part of DOE's mission to address America's energy, environmental, and nuclear security challenges through transformative science and technology solutions, the Office of Basic Energy Sciences supports world-class, open-access, and complementary scientific user facilities such as intense X-ray sources, neutron scattering facilities, electron beam characterization centers, and research centers for nanoscale science. The instruments developed under this proposal will benefit those members of the U.S. scientific user community who use X-ray spectro-microscopy for their research. This community is extremely large and varied, given that spectro-microscopy can be used to address a wide range of problems such as cellular function, medical drug delivery, energy conversion in catalysts, carbon sequestration, complex materials manufacturing, microelectronics failure, and the structure and composition of cultural heritage items. Enhancement of the capabilities of the APS will benefit DOE by enabling science that furthers the DOE mission, by keeping the APS at the forefront of the world's most advanced X-ray user facilities, and by replacing capabilities lost as a result of the closure of the NSLS at Brookhaven National Laboratory.

### RESULTS AND ACCOMPLISHMENTS

This project started in late 2015 and concluded in mid 2016. We initiated the installation of the TXM at beamline 8-BM and began preparing the instrument to accommodate users. This instrument will provide additional full-field imaging capacity in the United States, thereby accommodating displaced NSLS users until the corresponding instrumentation becomes available at NSLS II.

A double multilayer monochromator (DMM) was also installed. While use of this monochromator leads to a slight loss in spatial resolution because of chromatic aberrations, it can create 100 times more incident flux on the sample, allowing users to study dynamic processes that are otherwise not possible today.

Also, a trace-element large field-of-view fluorescence microscope for high-throughput sample screening or examining samples not suitable for current insertion device beamlines at the APS was developed. This will enable rapid fluorescence measurements for statistical analysis studies of a large number of samples or sample screening prior to higher spatial resolution measurements on an optimized insertion device beamline.

Because of the aberrations introduced by the DMM, and because of the greater divergence of the beam at beamline 8-BM relative to the beams where these instruments were piloted, additional development work is required for all three instruments—the wide-field fluorescence instrument, the TXM, and the XS-STM—to make them operational at 8-BM. Some examples include the development of slits, filters, and collimators as additional components of the system.

## Development of Novel X-ray Tools for Understanding Extreme-Pressure Magnetism and Electronic Ordering at Fourth-Generation Synchrotron Storage Rings

2015-184-R1

Yejun Feng

### PROJECT DESCRIPTION

We seek to develop the capability of resonant X-ray magnetic diffraction at high pressure at the Advanced Photon Source (APS). This effort seeks to address the properties of both magnetic and charge order, generally referred to here as electronic ordering, which are the results of materials' electronic structure. These types of electronic ordering are key features of important classes of functional and energy materials, such as magnets, oxides, and superconductors. However, they are very weak in amplitude and thus very difficult to study, especially when a sample is held under pressure in a device where the available sample volume is severely limited. Non-resonant X-ray magnetic diffraction under pressure was developed in the past decade at the APS. However, the capability for resonant X-ray magnetic diffraction under pressure does not yet exist, and the goal of this project is to develop it. The sample environment needs a different design, mainly because one needs a varying X-ray energy for different elements in various samples. We plan to build a capability for resonant X-ray magnetic diffraction in the transmission geometry at

the APS Sector 4-ID-D beamline, and possibly also at Sector 6-ID-B, if the X-ray focusing capability is improved.

### MISSION RELEVANCE

This project is relevant to DOE's mission in basic science. Through this project, we are attempting to develop a fundamental technique that would benefit research on magnetism—especially research on magnetism emerging near 0 K and on the competition between magnetism and other types of collective electronic phenomena such as superconductivity.

### RESULTS AND ACCOMPLISHMENTS

This project began late in FY 2015. We studied the efficacies of different scattering geometries and types of diamond anvil cells (DAC). These included reflection geometry coupled to panoramic type DAC and transmission geometry coupled to Merrill-Basset type DAC. It was determined that resonances up to 10 keV require a reflection geometry while those above this energy are best studied using a transmission geometry. The pros and cons of regular versus perforated diamond anvils were also evaluated. First experiments on an osmate oxide crystal ( $\text{Cd}_2\text{Os}_2\text{O}_7$ ) were planned.

We performed proof-of-principle experiments in FY 2016, with the pressure range pushed above 30 GPa and temperatures below 4.5 K (non-resonant magnetic scattering had only been previously done to 18 GPa). We explored the use of large perforations in partially perforated diamond anvils to reduce background scattering from the anvils. We carried out experiments at the osmium L-edge X-ray resonance of an osmate compound ( $\text{Cd}_2\text{Os}_2\text{O}_7$ ) using a transmission geometry through partially perforated diamond anvils and a polarization analyzer to further reduce charge scattering background in the X-ray magnetic scattering measurements. No magnetic field was applied. The pyrochlore osmate sample was chosen since it displays a metal-insulator transition coincident with onset of magnetic order, an unusual magnetic structure (all-in/all-out) bordering frustrated magnetism, and open questions as to the role of spin-orbit interactions in dictating the insulating ground state. We found that pressure suppresses magnetic ordering continuously, with pressures of about 30 GPa required to destroy magnetic order. Independent measurements of electrical resistance will be needed to see if the disappearance of magnetic order is accompanied by an insulator-metal transition. The measurements represent a breakthrough in pushing the state of the art in resonant magnetic scattering at high pressures.

### PROPOSED FUTURE WORK

FY 2016 was this project's final year. Staff at beamline 4-ID-D continue development work in this area and is making this capability available to general users. The first general user experiment was carried out successfully in December 2016 on a honeycomb iridate magnet,  $\text{Li}_2\text{IrO}_3$ . Beamline 4-ID-D will be upgraded as part of the baseline scope of the APS-Upgrade project and these measurements are expected to be greatly enhanced as a result of the increased brilliance and related increases in flux density of X-ray beams.

## A Conveyor Belt of Nanoliter to Picoliter Droplets for Hard X-ray Pump-Probe Experiments

2016-150-NO

Anthony DiChiara, Chris Benmore, Bin Hu, and Kamlesh Suthar

### PROJECT DESCRIPTION

We have begun designing a sample management system (SMS) that will provide a high degree of control for extremely small quantities of aqueous/liquid systems that are difficult or impossible to synthesize in appreciable (greater than several hundred microliter) amounts such as nanoparticles, biomolecules, fuels, and photocatalytic compounds. The SMS will target two critical areas in sample management that impose significant challenges to current experimental efforts using a combination of lasers and hard X-ray probes: (1) sample consumption and (2) on-demand sample renewal for systems that are permanently altered or damaged from radiation exposure. By performing an experiment on a single droplet, discarding it immediately after X-ray exposure, and then replacing it with a fresh droplet, one can obviate sample damage in an extremely efficient manner.

Our approach is to move from established techniques using ultrasonic acoustic levitation of millimeter-sized objects to acoustic *trapping* of submillimeter objects. This result can be achieved by using focused acoustic waves and moving toward higher-frequency sound sources. Implementation of a device that can create and hold on the order of 100-micron-size droplets on demand will allow a controlled amount of sample to be delivered into the interaction region with nearly perfect utilization efficiency.

## MISSION RELEVANCE

The instrumentation pursued here will have a lasting impact on multiple subdisciplines critical to DOE's missions in both energy and basic science. The Advanced Photon Source (APS) is unique among third-generation light sources in that it provides extremely bright, roughly 100-picosecond X-ray pulses, and therefore enables subnanosecond time-resolved science using stroboscopic laser/X-ray pump-probe techniques. Ultra-precise sample control is required as the types of systems being explored become both smaller and more exotic. The SMS described here is unique in that it allows unprecedented control of samples in a completely contact-free and containerless environment.

The device developed in this project will impact multiple disciplines within the APS user community and provide an alternative SMS for laboratory and industrial applications.

## RESULTS AND ACCOMPLISHMENTS

An acoustic trap functions by exerting a restorative force on an object through the object's interaction with an intense sound field. The strength of that force and, consequently, the stability of the trap are determined by both the intensity of the sound field and, critically, the shape of the field. The latter point has been a significant focus for our efforts in FY 2016. By controlling the shape of the acoustic field, we can build more stable acoustic traps capable of precisely holding objects smaller than one millimeter. Figure 1 shows a visual representation of the sound field produced by a single ultrasonic transducer as measured and as simulated. By verifying our ability to accurately simulate the sound field, we were able to design an efficient device using a single transducer-reflector geometry to trap particles. Figure 2a shows a particle-trapping dispersion curve demonstrating both the stability and residual force acting on water droplets of decreasing size.

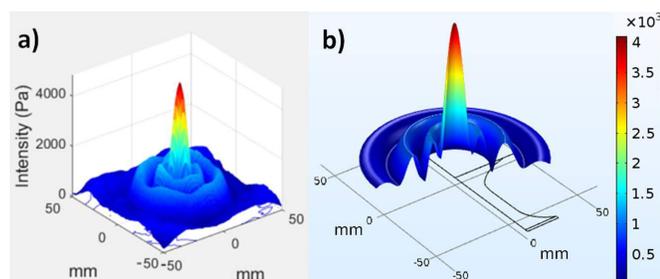


Figure 1. (a) Measured sound intensity profile from a 22-kHz acoustic transducer. (b) A multiphysics simulation that matches the experimental conditions in panel (a).

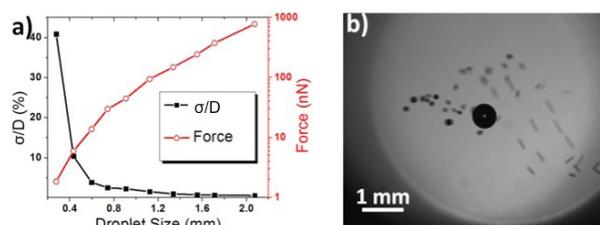


Figure 2. (a) The root mean squared (RMS) excursion amplitude ( $\sigma$ ) divided by the droplet diameter ( $D$ ) ( $\sigma/D$  – black curve) and the residual RMS force, Force (red curve), as a function of droplet size. Horizontal direction only. (b) A train of microdroplets agglomerating into the acoustic trap.

We have commercially obtained a modified levitator, using two transducers, which is now capable of translating droplets along its longitudinal axis. Further development is required for full implementation of this feature, but the hardware modifications and preliminary tests have been successful.

To enhance the experimental capacity of an acoustic trap, we have developed a method to remotely load the trap with droplets of a user-defined volume by using a piezo-driven microdispenser to fire a train of microdroplets at near-kilohertz (kHz) repetition rates into a trapping node. The acoustic trapping force then agglomerates the microdroplets with near-unity efficiency into a larger volume (Figure 2b).

We have also begun preliminary experiments that use ultrafast laser pulses to heat acoustically trapped droplets of nanoparticle solutions. The thermal expansion of the nanoparticles was then monitored using a combination of X-ray scattering techniques. These are prototype experiments of relatively well-understood systems that demonstrate the integrity of the SMS.

## PROPOSED FUTURE WORK

In FY 2017, we will continue our instrumentation development for a levitator that uses two transducers and two focusing elements in a single-axis configuration. This configuration will allow a single device to function with optimized stability while providing sample translation and automated injection, thus achieving project goals. We are also developing a system that can produce higher-frequency sound waves, and, consequently, sharper, more stable acoustic fields than those shown in Figure 1. Proof of concept laser pump- X-ray probe experiments in gold nanoparticles are near completion. We are moving towards investigating alloy formation and atomic diffusion in nanoparticle ensembles.

## Exploring Next Generation Coherent X-ray Science

2016-191-N0

Linda Young

### PROJECT DESCRIPTION

Next-generation light sources based on advanced accelerator and magnet technology aim toward complete coherence for short-wavelength X-ray radiation pulses in both longitudinal and transverse dimensions. This project explores scientific applications that require high-pulse-energy, temporally coherent X-ray pulses. These are not available from compact tabletop X-ray sources that utilize, for example, high harmonic generation. The typical coherent pulse energy available from accelerator-based free-electron laser sources exceeds that from tabletop sources by six orders of magnitude. The increased pulse energy from accelerator-based facilities enables use of single-shot coherent imaging and spectroscopic methods.

### MISSION RELEVANCE

This project supports DOE's basic science mission. Expanding the available scientific application portfolio for next-generation coherent X-ray light sources and facilities will provide input for future accelerator-based facilities situated at DOE national laboratories. These scientific applications are enabled not only by brighter, faster coherent light sources but also by improved detector technology.

### RESULTS AND ACCOMPLISHMENTS

In the past months, a worldwide network (comprising the United States, Germany, Sweden, and Singapore) has been formed to study electronic coherence and elementary electron, hole, and ion dynamics in a condensed-phase system of universal importance: liquid water. An experimentally verified first-principles understanding of ionization dynamics in water will enable a predictive understanding of its behavior in increasingly complex systems, eventually employing large scale simulation methods. Earlier work with an ultrafast optical probe has demonstrated coherence in the polarization of the hydrated electron following impulsive strong-field ionization. Optical probes are predominantly sensitive to the hydrated electron species, and do not detect the transient ionic species that evolve on a femtosecond time scale. Consequently, their correlations with the observed coherences are unobserved. We have proposed a scheme to track transient species following prompt ionization in liquid water using an X-ray free electron laser

to probe occupied and unoccupied valence orbitals with polarization-sensitive, core-level absorption and emission spectroscopy in the "water window." We note that the feasibility of single-shot emission spectra is dependent upon high pulse energy in the soft X-ray regime.

### PROPOSED FUTURE WORK

Theoretical work is planned to support the experiments with calculations of the X-ray spectra of the various transient ionic and radical species in water. We expect to have an opportunity to conduct a first experiment in FY 2017 if we are granted beam time at the Linac Coherent Light Source at Stanford University. The beam time would test the concept of simultaneous ultrafast time-resolved emission and absorption on a single-shot basis. The data could then be used to improve the precision of the single-shot time stamps using a newly developed data-analytical approach. We will pursue a sponsor of experiments to develop this scheme of polarization-sensitive, core-level ultrafast spectroscopy in the "water window" at a DOE light source facility.



# LDRD PRIME – MATERIALS AND MOLECULES TO MANUFACTURING

# Hierarchical Modeling of Self-Assembly in Nanostructured Soft Materials at Equilibrium and Far from Equilibrium

2013-184-R3

Juan J. de Pablo

## PROJECT DESCRIPTION

This project seeks to develop multiscale simulation algorithms that will enable design of self-assembled functional materials and will facilitate development of processes to prepare such materials. The particular focus of the project is in soft matter, including polymers, colloids, and liquid crystals.

## MISSION RELEVANCE

This project addresses DOE missions in fundamental science and energy security. It has important potential applications in energy research, including the development of energy storage systems, light harvesting systems, and separations media for a wide array of applications, ranging from water purification to gas concentration. Beyond the missions of DOE, the research is of interest to industry (semiconductor, battery, and polymers) and to other federal agencies, including the U.S. Department of Defense (DoD), the National Institutes of Health (NIH), and the National Science Foundation (NSF). Private sector companies, particularly those in semiconductor manufacturing would also be interested in this work.

## RESULTS AND ACCOMPLISHMENTS

We developed a multiscale formalism for simulating nanostructured polymeric materials. That formalism, called the theoretically informed coarse-grained (TICG) simulation approach, relies on Hamiltonians for the materials of interest. Hamiltonians were traditionally solved using self-consistent field theory. The TICG approach uses stochastic simulations of particle-based representations for the systems of interest to arrive at more realistic, and more efficient, representations of materials. Since its inception, TICG methods have gained considerable attention and have been adopted by dozens of research groups around the world, both from academia and industry. In FYs 2014 and 2015, we finalized the originally proposed work on the theory and simulation of macromolecular self-assembly, where we made progress on multiple materials platforms amenable to directed assembly, including proteins, deoxyribonucleic

acid (DNA) -based complexes, liquid crystals, and block copolymers. In each, we developed models and methods to probe emergent assembly processes and materials characteristics.

For protein assembly, we focused on two aspects for modeling unstructured polypeptides. Such molecules are of scientific interest (for applications) and also of medical importance. In FY 2015, we focused on islet amyloid polypeptide (amylin), a molecule implicated in the onset of type 2 diabetes. We also completed a study of dimerization of amylin and another study of the misfolding of amylin fragments and mutants in the vicinity of bilayer membranes.

We made significant advances in developing coarse-grained models of DNA. We completed a study of systematic coarse-graining for explicit ions in the vicinity of DNA, and a study of the mechanical properties of DNA-based nanomaterials. We also completed a study of nucleosome unfolding, which forms the basis for later studies of chromatin structure and properties.

For liquid-crystalline-based materials, we demonstrated that nanoparticles can be controllably assembled at the interface of liquid crystal droplets. We also demonstrated that the morphology of liquid crystals can be manipulated by confinement in droplets, thereby enabling applications in biosensing.

For directed assembly of block polymers, we published a comprehensive study of the pathways for defect annihilation in block-copolymer directed assembly. A significant accomplishment of this work was to demonstrate conclusively that the defects encountered in directed assembly of block copolymers by chemoepitaxy represent metastable states, as opposed to equilibrium configurations. By relying on string-method simulations, we were able to explain that such metastable states are kept in place by large, free energy barriers that, at low temperatures, are difficult to overcome. We identified the minimum free energy pathways that molecules must follow to climb such barriers, and we proposed processing strategies designed to traverse such pathways. Experimentally characterizing thin self-assembled films using three-dimensional transmission electron microscopy (TEM) tomography confirmed our predictions.

Figure 1 shows a representative result from our simulations, where the free energy along the reaction pathway is plotted in units of kT. As the figure shows, the free energy of the defective state is higher than that of the defect-free state by several hundred kT. The figure also shows that multiple barriers must be crossed for the system to eliminate its defects. The first, and

most important of these barriers, corresponds to the formation of a *bridge*, consisting of just a handful of molecules, connecting different polymeric domains. Once a sufficiently large bridge forms (i.e., the transition state), annealing can continue in a downhill manner, until all defects disappear. Figure 2 shows simulated images and experimental TEM images of a defect at various positions along a film. Those images show that the agreement between predicted morphology and experimentally observed states is quantitative.

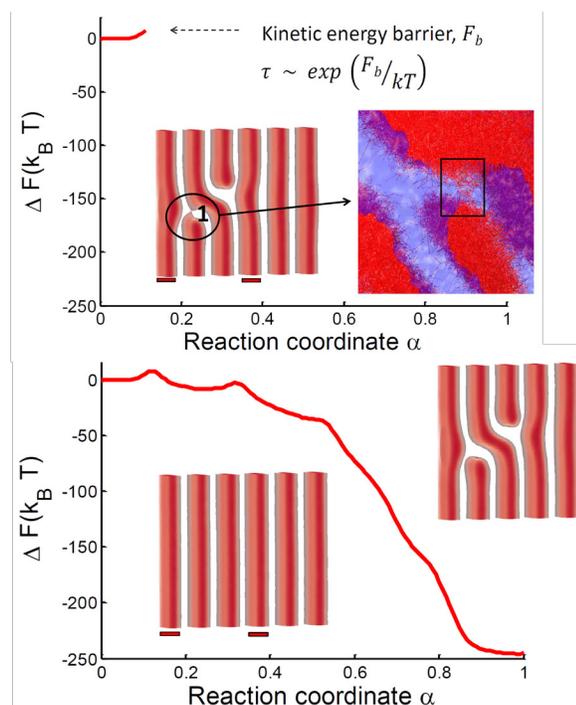


Figure 1. Free energy for defect annihilation in directed assembly. The red and white domains represent two blocks of a diblock copolymer. The inset in the top panel shows the transition state, with the formation of a molecular bridge. The insets in the bottom panel show the defective and defect-free states, along with the entire free energy profile.

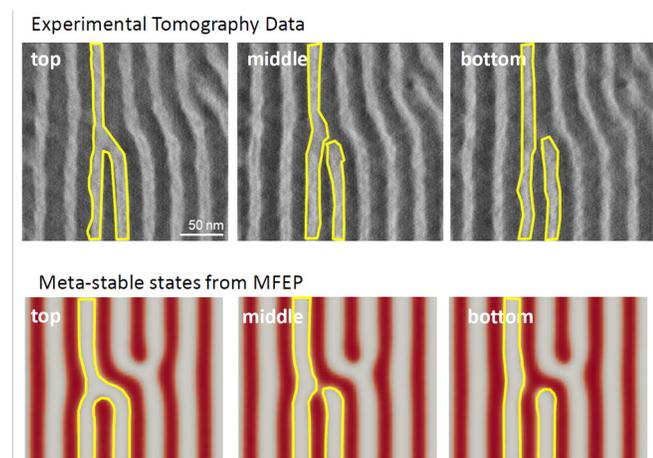


Figure 2. Experimental 3D TEM images and predicted configurations of defect in directed self-assembly of PS-PMA. The panels correspond to the top, middle, and bottom (near substrate) of thin films. The yellow line highlights the defective lamellae.

## PROPOSED FUTURE WORK

Although this project is complete, aspects of it continue in our laboratories. We have received new support from NIST, and have requested new support from DOE in our new FWP proposal, submitted in February of 2017. Additionally, support was received recently from DOE in the form of the MICCOM center for development of robust software using the methods developed in our LDRD project. Two directions, in particular, are worth emphasizing. First, we developed advanced modeling and optimization techniques to enable multimodal characterization of meso- and nanostructured materials (such as ordered block polymers) using evolutionary optimization. That led to important breakthroughs; much remains to be done by translating our findings and techniques to different types of materials and characterization techniques. Second, we created innovative inverse designs for developing materials, which offers considerable promise for advancing the design of hierarchically structured and functional materials systems. Such algorithms must be applied to broader classes of systems to realize their full potential.

## Directed Assembly and Three-Dimensional Characterization of Block Copolymers in Semi-Thick Films

2013-216-R3

Paul F. Nealey

## PROJECT DESCRIPTION

The central aim of this work is to advance the tools for characterizing the structures formed during directed copolymer assembly in semi-thick films. Inherently linked to the goal of the project is developing a fundamental understanding of the thermodynamic and kinetic factors controlling the assembly process. The project will form the basis for design rules to create equilibrium and non-equilibrium nanostructured materials with precisely controlled architectures, at a scale of 10 nanometers, in three dimensions. Characterizing the three-dimensional (3D) structures of the films and how they evolve requires advancing the capabilities of small-angle X-ray scattering (SAXS), grazing-incidence small-angle X-ray scattering (GISAXS), and resonant soft X-ray scattering, as well as using other complementary techniques, such as scanning transmission electron microscopy (STEM) tomography.

A unique aspect of the research relates to directly comparing dynamic experimental scattering data to

simulated scattering profiles generated from dynamic structures predicted by molecular simulations.

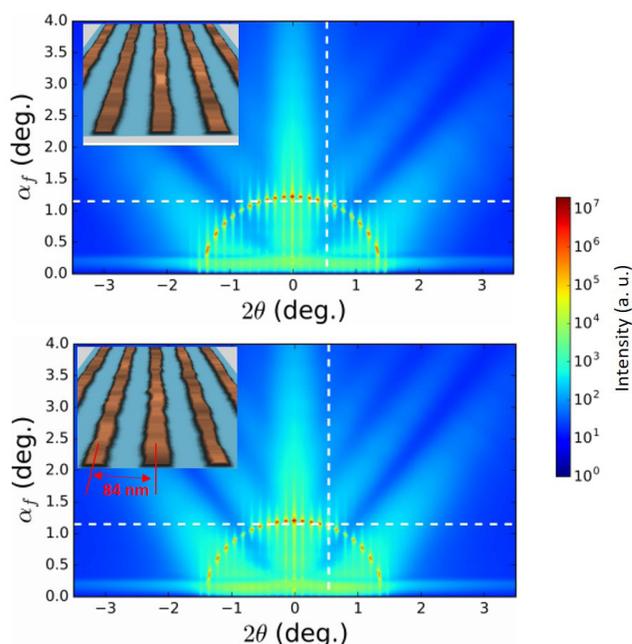
### MISSION RELEVANCE

The project is relevant to DOE's missions in science and energy. Beyond contributing new knowledge to the scientific community, this study of directed copolymer assembly will find a wide variety of possible applications relevant to DOE's missions. We also anticipate that the project will be the impetus for developing a suite of state-of-the-art 3D nanoscale characterization tools for soft materials at Argonne. The block copolymer systems we are developing, with their well-defined architectures, are ideal for developing such tools. Thus, the materials and tool development included in this project are broadly applicable in science-based research on structure-property relationships in nanoscale material architectures for energy transfer, chemical sensing, and information technology.

### RESULTS AND ACCOMPLISHMENTS

In FY 2013–2015, progress was made on both hardware and software for 3D characterization of nanostructures in polymer films. Newly installed sample environments at the GISAXS beamline 8-ID-E of the Advanced Photon Source and the transmission electron microscope (TEM) at Argonne's Electron Microscopy Center enabled us to collect high-quality data from nanostructured polymer films. Software to analyze the 3D structures from X-ray scattering and STEM data was also implemented, along with instrument upgrades.

During FY 2016, we verified our 3D nanoscale characterization tools by using lithographically defined nanoscale polymer grating samples with programmed roughness. Figure 1 shows 3D images and 2D GISAXS patterns from grating samples with different line-edge roughness, which were reconstructed by our 3D GISAXS analysis model. In contrast to traditional approaches that analyze a simplified data set (e.g., a 1D line cut from a 2D scattering image), our analysis model can capture a 2D data set recorded in a 2D detector. Access to extended dimensions in recorded scattering data allows us to quantitatively measure nanostructures in 3D spaces. This accomplishment represents substantial progress in X-ray scattering-based metrology, which typically interprets 3D structures as averaged 2D shapes.



**Figure 1.** Three-dimensional GISAXS analysis for polymer nano-grating samples with programmed line-edge roughness. Compared to GISAXS scattering pattern from smooth grating (top), the one from rough grating sample (bottom) shows weaker Bragg spot but stronger diffuse scattering in the background. Insets are 3D images of grating samples reconstructed by GISAXS analysis model. Newly developed methodology enables quantitative measurement of structures and fluctuations in polymer films.

Another milestone achieved during FY 2016 was to develop a new metrology technique, combining physics-based molecular simulation models and GISAXS, capable of probing the complex nanostructures in polymer films. We demonstrated this approach in the context of self-assembling polymeric materials, where theory and simulations provide the framework used to seamlessly mesh GISAXS data. As Figure 2 shows, the samples tested consisted of block copolymers that were self-assembled on chemically nano-patterned surfaces. The trajectories generated from simulations of physics-based models that impose a set of well-defined thermodynamic and boundary conditions were compared to GISAXS data. An optimal combination of model parameters was then identified by resorting to an evolutionary computational approach. Through this process, we examined the effect of polymer asymmetry, geometry, and surface chemical pattern on block copolymer morphology and the corresponding scattering intensity profiles. To validate the ideas tested, the outcomes of the analysis were compared to images generated by STEM tomography. The technique not only structurally characterizes the average morphology of a periodic directed self-assembled block copolymer film, but also furnishes, in a manner pertinent to our model, thermodynamic information that is otherwise unavailable. This thermodynamic information serves to clarify which of the numerous process conditions to adjust

to achieve a desired, defect-free morphology. Our belief is that such a method can advance our knowledge of these materials to the point of enabling significant progress in applying them to large-scale industrial processes.

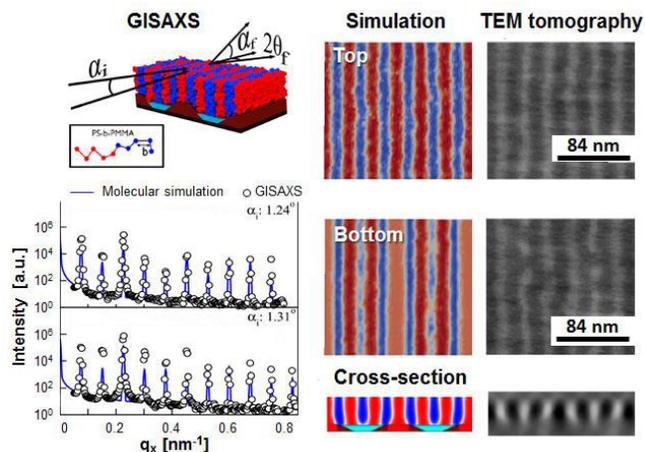


Figure 2. Combining physics-based molecular simulation modeling and GISAXS to develop 3D nanoscale metrology for soft materials. GISAXS scattering patterns are collected from the directed self-assembled block copolymer films using various incident angles. Black circles in the plots are GISAXS experimental data, while blue lines are predictions based on the molecular simulations. The validity of the structures determined from the technique is confirmed by direct comparison to results from 3D TEM tomography.

## Transition Edge Sensors for Fundamental Physics

2013-219-R3

Clarence Chang, Valentine Novosad, Gensheng Wang, and Volodymyr Yefremenko

### PROJECT DESCRIPTION

This project develops large arrays of superconducting transition edge sensors (TESs) for applications in fundamental physics. The TES is an ultra-sensitive thermal detector that exploits the sharp superconducting-to-normal transition of a superconducting film. Fabricating large TES detector arrays requires engineering material transport properties, tuning superconducting properties, and nano-machining superconducting circuitry and mechanical and thermal structures. This project involves studies of precision fabrication techniques and novel production processes, all with the goal of mass-producing large arrays of TES detectors. Developing this unique ability immediately opens up new opportunities. For example, our detector development program would enable fabrication of a 16,000-element TES detector array for the South Pole Telescope. Such an array would not only revolutionize our understanding of the Cosmic Microwave Background

(CMB) and cosmology, but would also put us in a position to address the technical challenges confronting future experiments that need large arrays of TES detectors. As examples, large TES arrays will detect long-wavelength photons and heavy particles, and perform X-ray and gamma ray spectroscopy.

### MISSION RELEVANCE

This project is directly relevant to DOE's science mission in its Office of Basic Energy Sciences. In particular, it develops the new technology needed to build large TES detector arrays, including the largest CMB focal plane in the world. This detector array will push the boundaries of CMB science, which explores the physics of our universe, the nature of cosmic inflation, and the mass of neutrinos. CMB measurement is a cornerstone of modern cosmology and a critical element of high energy physics in the United States. Being able to mass-produce large TES detector arrays not only sustains leadership in CMB science, but also lays the foundation for exploring new opportunities across a broad spectrum of applications. Potential future directions of interest to specific agencies include particle physics (DOE-Office of High Energy Physics [HEP]), nuclear physics (DOE-Office of Nuclear Physics) and astronomical instrumentation (National Aeronautics and Space Administration, National Science Foundation).

### RESULTS AND ACCOMPLISHMENTS

Over the past three years, we developed a process to fabricate CMB detector arrays consisting of 271 dual-polarization, multichroic pixels on a 150-mm substrate. These superconducting detectors are not commercially available, and reliable fabrication required developing new techniques for materials processing and nanofabrication to provide sufficient control of the underlying physical and functional properties. Our research and development over the past three years has substantially improved our understanding and control of relevant device properties, and we can now fabricate our detector arrays in batches of four, with each batch taking approximately three weeks of total fabrication time. By interleaving our fabrication, we can process multiple batches in parallel, yielding a fabrication throughput of about 12 wafers every four weeks.

We also initiated a new application of our technology: future experimental searches for neutrinoless double beta decay. Toward this end, we developed initial thin-film materials with transition temperatures in the desired range,  $\sim 30$  mK (see Figure 1), and started fabricating early detector layouts (see Figure 2).

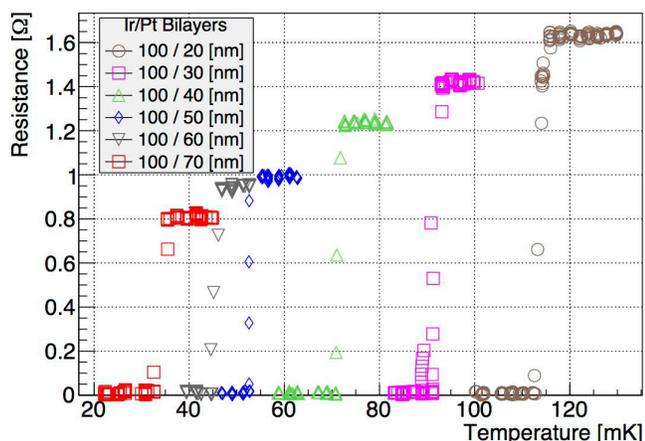


Figure 1. Plot of resistance vs. temperature for a number of iridium/platinum (Ir/Pt) films showing superconductive transitions in a temperature range relevant to future applications in neutrinoless double beta decay searches.

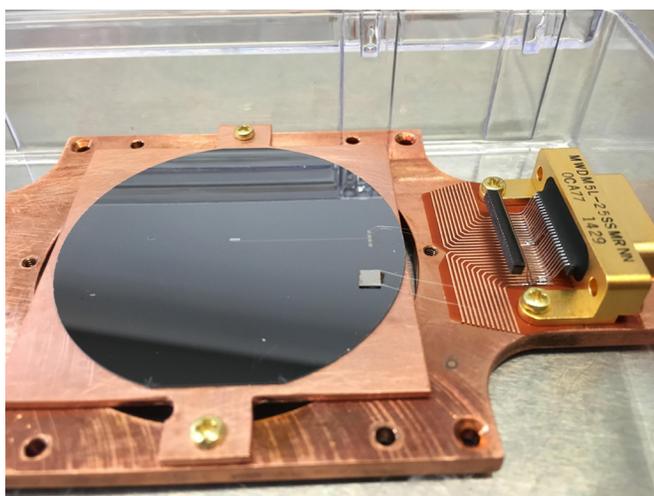


Figure 2. An initial detector fabricated for R&D in neutrinoless double beta decay searches.

Future work relevant to DOE-HEP will be supported through the DOE Office of Science; we are responding to a Funding Opportunity Announcement for neutrinoless double beta decay R&D.

## Length-Scale-Bridging Computational Scheme for Structure and Transport

2014-128-R2

Olle Heinonen, Dmitry Karpeyev, Nichols A. Romero, and Peter Zapol

### PROJECT DESCRIPTION

This project addresses the many-fold computational challenges encountered in systems in which a local domain has to be treated quantum mechanically but is interacting with and influenced by larger regions that cannot be treated quantum mechanically because of extremely high computational cost. Examples are metal/insulating-oxide/metal (MIM) heterostructures, where electrostatics and strain from the larger structure significantly influence the atomic structure and charge transport. Such structures are ubiquitous in resistive random access memories, battery electrodes, and catalysis systems. This project will develop a scalable computational framework that concurrently combines and merges first-principles quantum mechanical calculations for structure and transport with molecular dynamics and mesoscale calculations for quenched disorder at interfaces, including elastic strain and electrostatic fields on large irregular domains. The research will focus on MIM systems in which the insulating oxide is a transition metal oxide.

Aspects of the work are being conducted with colleagues at the U.K. National Physical Laboratory, Argonne's Mathematics and Computer Science Division, Argonne's Nanoscience and Technology Division, the Japan National Institute for Advanced Industrial Science and Technology, the Argonne Leadership Computing Facility (ALCF), Sandia National Laboratories (SNL), and Oak Ridge National Laboratory (ORNL), as well as the Institute for Molecular Engineering at the University of Chicago.

### MISSION RELEVANCE

The project is relevant to DOE's energy security mission. It supports the DOE Basic Energy Sciences (BES) mission to foster research in use-inspired R&D regarding new materials for information storage and the efficient use of energy. The general scientific community will also benefit from this project, as the developed codes will be made available to the public.

## RESULTS AND ACCOMPLISHMENTS

In the previous years, we focused on the electronic structure and properties of titanium (Ti) oxides and the effect on the electrical conductance of the so-called insertion layer of tantalum (Ta) in a titanium nitride-hafnium oxide-titanium nitride (TiN-HfO<sub>2</sub>-TiN) heterostructure for resistive switching (Figure 1). We showed that the insertion layer improved both the thermodynamic stability and the conducting properties of the conducting state. We also developed a computational method to efficiently evaluate the electrostatic or magnetostatic interactions between ferroelectric or ferromagnetic bodies, respectively.

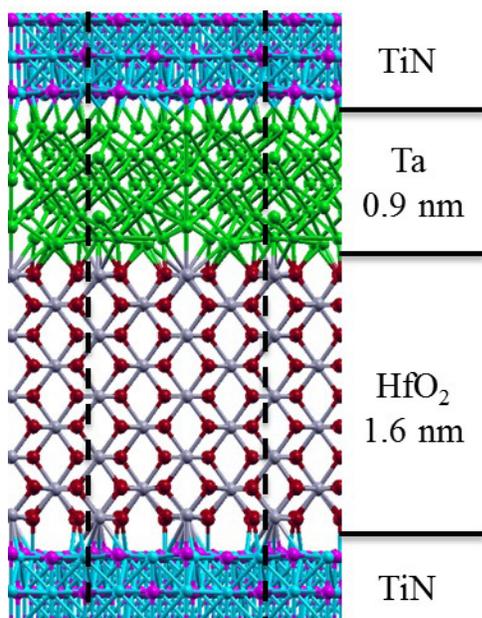


Figure 1. Relaxed atomic structure of the virgin TiN-HfO<sub>2</sub> device with tantalum layer insertion. The dashed lines show one unit cell containing 550 atoms used in the modeling. Color scheme: Ti in light blue, N in purple, Ta in green, Hf in grey, and O in red.

In FY 2016, we continued work on titanium oxides. Working with researchers at ALCF, SNL, and ORNL, we used highly accurate quantum Monte Carlo simulations to investigate the low-temperature magnetic states of the Magneli phase, Ti<sub>4</sub>O<sub>7</sub>. We showed that a less accurate (but much less expensive) density functional theory-based simulation gave the correct energetic ordering of the states, but the energy differences and magnetic moments were not quite correct. Our joint effort subsequently led to interactions with a BES-funded Computational Materials Science Center led by ORNL. We also continued the investigation of Hf oxides for resistive switching. Using density functional theory calculations, augmented to account for electronic interactions beyond classical Coulombic interactions, we showed how movement of a single oxygen atom by less than 1 nm (Figure 2) can increase the resistance by over three orders of magnitude

from the conducting state. We also showed that a single oxygen atom separates the conducting channel into two weakly coupled quantum wells, and that special bias voltages can induce resonances between the conducting states in the wells. We continued to investigate Ti oxides using quantum Monte Carlo simulations, and showed that the anatase phase has the lowest energy at 0 K, but at finite temperatures (~650 K), entropic contributions from lattice vibrations lower the energy of the rutile phase below that of the anatase phase, in agreement with observations. In parallel with this work, we continued to work on molecular dynamics simulations of quenched input structures for the density functional theory calculations.

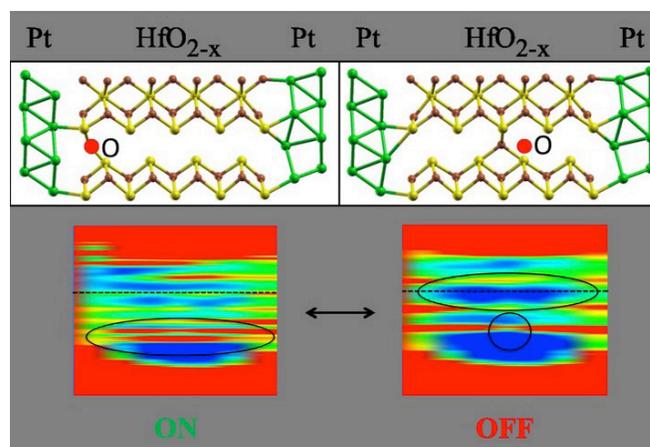


Figure 2. Top: Cross-section of Pt (green), Hf (yellow), and oxygen (red) in an oxygen-deficient Pt-HfO<sub>2</sub>-Pt structure. The left panel shows the On-state with an oxygen atom near Pt (indicated by the large red dot), and the right panel shows an Off-state with the oxygen atom near the center. Bottom: Depiction of available electronic states (along vertical, with number of available states in color going from blue, depicting zero, to red, depicting a high number of states) vs. position (along the horizontal) in the On-state (left panel) and Off-state (right panel). The dashed horizontal line indicates the Fermi level, chosen as zero energy. The oxygen atom at the center pinches off the electronic states, creating two quantum wells. The ellipse in the lower left panel indicates the two lowest states that extend across the system. In the lower right panel, the lower circle highlights how the quantum well state that extended across the system has been pinched off; the ellipse above highlights that the number of available states at the Fermi level is now very low (blue color, indicating no transport of electrons, and therefore high resistance).

While this LDRD completed at the end of FY 2016, various aspects of this work continue at two DOE-BES centers, the Center for Predictive Simulations of Functional Materials (ORNL) and the Midwest Integrated Center for Computational Materials (headquartered at Argonne).

# The Design and Synthesis of Novel Oxides: Coupling Materials Informatics with a Next Generation Deposition System Employing *in situ* X-ray Scattering and Photoemission Spectroscopy

2014-129-R2

Dillon D. Fong, Richard Rosenberg, and Jonathan Z. Tischler

## PROJECT DESCRIPTION

The primary goal of this project is to upgrade an existing diffractometer-mounted chamber and build the world's first *in situ* pulsed laser deposition (PLD) system with both surface X-ray diffraction (SXRD) and hard X-ray photoemission spectroscopy (HAXPES) capabilities at the Advanced Photon Source (APS). This new experimental capability is being combined with computational materials design focused on the development of novel  $A_2B_2O_5$  materials (so-called "225" compounds) displaying metal-insulator transition (MIT) behavior.

## MISSION RELEVANCE

This project is relevant to the DOE's mission in energy and the environment. A central goal of DOE-Basic Energy Sciences is to accelerate the design and discovery of materials capable of addressing the nation's energy and environmental challenges. The key strategy is to close the feedback loop between experimental synthesis and predictive materials theories. In this project, we address this challenge by focusing on complex oxide materials, an area with outstanding potential for meeting many of our technological needs.

## RESULTS AND ACCOMPLISHMENTS

During the first year of this project (FY 2014), we completed the redesign of the *in situ* PLD system at Sector 33 of the APS and received the mechanical components of the hemispherical electron analyzer (Scienta EW4000). The electron analyzer geometry permits easy control over the attenuation length by permitting variable X-ray incidence angles and energies, allowing variable depth profiles for HAXPES, protecting the HAXPES lens system from the deposition flux, and avoiding interference with the current scattering geometry. Before the availability of the *in situ* PLD-HAXPES system, we performed real-time growth studies of  $A_2B_2O_5$  materials, in this case  $Sr_2Co_2O_5$ , with *in situ* PLD-SXRD. We found that the successful growth

of this system is extremely sensitive to the strain state, temperature, and oxygen partial pressure.

In FY 2015, we received the electrical components of the electron analyzer and worked on upgrading the deposition facility into a hybrid PLD system (PLD + metal-organic chemical vapor deposition). This significantly expanded our synthesis capabilities by enabling the growth of layered oxides (e.g., Ruddlesden-Popper compounds) and the growth of 225 oxides and superlattices with controlled doping of the B-site; neither material would be possible without the hybrid capability. Furthermore, we studied the general properties of 225 superlattices.

In FY 2016, we installed a UV source (Specs model UVS300) and an electron flood gun (Specs FG22/35), and mounted a jib crane on the front end of the diffractometer table to provide counterbalancing for the goniometer. We conducted the first *in situ* SXRD and HAXPES study of PLD growth for lanthanum aluminate ( $LaAlO_3$ ) on strontium titanate, or  $SrTiO_3(001)$ , monitoring changes in the core level behavior and the valence band maximum (VBM) at  $700^\circ C$  and  $5 \times 10^{-6}$  Torr as a function of  $LaAlO_3$  thickness, from 0 to 4 nm (Figure 1). As the figure shows, the VBM and O 1s spectra continuously evolve as  $LaAlO_3$  grows, but the Ti 2p spectra shift only after the first  $LaAlO_3$  layer is deposited. These results describe the evolution of band bending at the  $LaAlO_3/SrTiO_3(001)$  interface and show how screening of the polar interface takes place at the Ti cations.

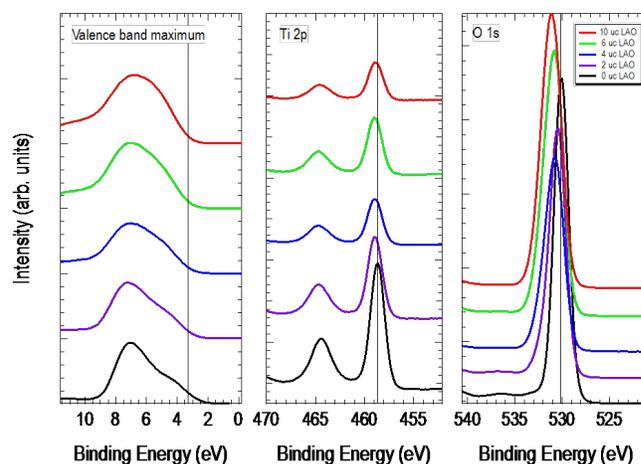


Figure 1. *In situ* HAXPES data taken at  $700^\circ C$  in  $5 \times 10^{-6}$  Torr of oxygen during growth of  $LaAlO_3$  on  $SrTiO_3(001)$ . The valence band maximum and the core levels of the Ti 2p and O 1s spectra are shown for different  $LaAlO_3$  film thicknesses, from 0 to 4 nm.

Our collaborators on this project have been J.M. Rondinelli of Northwestern University, G. Reyes and C.M. Rouleau of Oak Ridge National Laboratory, and R. Engel-Herbert (Penn State).

The DOE Office of Energy Efficiency and Renewable Energy (EERE) will be sponsoring utilization of this new SXR-D-HAXPES capability, and we are responding to calls from DOE in Energy Frontier Research Centers and from the Defense Advanced Research Projects Agency (DARPA), which has a stated aim of developing next-generation electronic devices.

## Fast Electronic Structure Methods for Rapid Reaction Screening for Inorganic Materials Synthesis and Particle Formation

2014-139-R2

Albert Wagner, David Dixon, Murat Keçeli, Álvaro A. Vazquez-Mayagoitia, and Peter Zapol

### PROJECT DESCRIPTION

If calculations and simulations are to assist experimental programs directed at the synthesis of new materials and chemicals, new electronic structure codes must be developed that are capable of studying experimental systems having very large numbers of atoms. We are developing highly parallelized codes to enable the discovery of new synthesis pathways via simulations involving molecules and solids having up to tens of thousands of atoms. One code involves semi-empirical molecular orbital (SEMO) theory, and the other involves tight binding based on density functional theory (TB-DFT). Two computational needs must be addressed:

- An efficient method to calculate the energy of molecular systems by the parallelization of available eigensolver methods for massively parallel computers.
- An improved training set for optimizing the “empirical” SEMO/TB-DFT parameters by supplementing scattering measurements of molecular energies with systematic and accurate *ab initio* electronic structure calculations on small molecular systems.

### MISSION RELEVANCE

The project is relevant to DOE’s missions in energy and science. Reliable computational methods that predict reaction mechanisms are needed for use in condensed-media synthesis planning and the management of particle growth in a broad variety of environments. The need for making and breaking chemical bonds means that electronic structure must be explicitly included in the simulation. At present, SEMO/TB-DFT electronic structure

methods are the fastest available. Success in developing efficient semi-empirical code will enable basic energy science studies in areas relevant to DOE’s mission, such as combustion (soot formation), heterogeneous catalysis, nuclear chemistry (aggregation phenomena), material phase changes, and multilayered materials.

### RESULTS AND ACCOMPLISHMENTS

*Parallelized Eigensolver.* In FY 2014, we developed a new, highly parallelized eigensolver called shift-and-invert parallel spectral transformations (SIPs). This method is especially applicable to local orbital electronic structure methods such as SEMO methods and TB- and SIESTA-type DFT methods. Local orbital methods produce eigenvalue-generating Hamiltonian matrices that are “sparse,” meaning that most of the matrix elements are zero. In FY 2015, we further developed this eigensolver and tested it relative to conventional parallelized eigensolver methods for *dense* matrices and two recent methods suitable for sparse matrices, namely, the 2013 “pole expansion and selected inversion” (PEXSI) method and the 2014 “multiple shift-and-invert Lanczos” (MSIL) method. These tests indicate that SIPs is a highly competitive method for sparse eigensolvers.

Much of FY 2016 was spent embedding our eigensolver in a highly parallelized code for constructing the Hamiltonian matrix. Initial efforts were directed at developing our own highly parallelized SEMO code. Although we were successful in developing a rudimentary code, developing a mature code with parallel gradients and efficient initial guesses at the wave function became too time consuming for the last year of the project. Instead, we decided to focus on including our eigensolver in the SIESTA software package. Like TB-DFT, SIESTA uses localized orbitals that guarantee the sparse matrices our method requires. Unlike many TB-DFT software packages, SIESTA is open source and well adapted to our eigensolver structure. The combined code we named SIESTA-QETSc is now installed on Vesta, Mira, and Blues at Argonne’s Advanced Leadership Computing Facility and on Cori at the National Energy Research Scientific Computing Center (NERSC). Our benchmark calculations (see Figure 1) for ~1,000-atom versions of polyethylene, a boron-nitride monolayer, and water clusters demonstrate that QETSc improves the performance more than 50% for lower-dimensional systems. We are in the process of using this code for science applications.

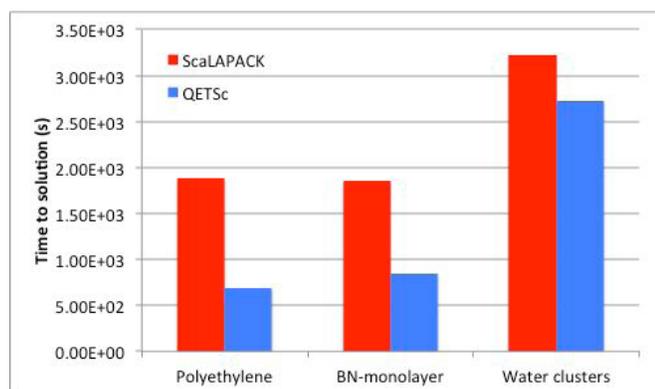


Figure 1. Time to solutions for DFT energy and gradient calculations with SIESTA using the default solver ScaLAPACK (in red) and our solver QETSsc (in blue) for three different applications.

Training Set Improvements. In FY 2014, we began extensive high-order *ab initio* and low-order DFT electronic structure calculations on metal oxide clusters of the transition metals titanium (Ti), zirconium (Zr), and hafnium (Hf) in Group 4 of the Periodic Table and chromium (Cr), molybdenum (Mo), and tungsten (W) in Group 6. In FY 2015, we extended those calculations to include up to four transition metals in a cluster. In FY 2016, we completed our study and published the heats of formation, electron affinities, and fluorine affinities of the lowest few isomers for the transition metal oxide clusters in Groups 4 and 6. To perform these calculations, we used the Feller-Peterson-Dixon composite approach based on *ab initio* CCSD(T) electronic structure calculations extrapolated to the complete basis set limit. The resulting systematic set of structures and energies will be used to improve the training set for transition metal SEMO parameters. We also compared our calculated results with 50 common DFT functionals, allowing us to rank the functionals on the basis of agreement with our *ab initio* results. This work forms a benchmark for selecting DFT functionals for transition metal studies.

Our project ended in FY 2016 with the successful creation of the SIESTA-QETSsc code. We are now carrying out scientific applications under BES Chemical Sciences, Biosciences, and Geosciences support in order to develop future projects.

## Developing Predictive Models of Wide Bandgap Semiconductor Synthesis and Processing

2014-151-R2

Paul H. Fuoss, Jeffrey A. Eastman, Jeffrey W. Elam, Ross J. Harder, Matthew J. Highland, Martin V. Holt, Stephan O. Hruszkewycz, Angel Yanguas-Gil, and Peter Zapol

### PROJECT DESCRIPTION

Through this project, we seek to understand nanoscale physical and chemical processes during the growth of wide bandgap (WBG) semiconductors such as gallium nitride (GaN) and aluminum nitride (AlN), and their fabrication into devices. We examined WBG synthesis using three different growth techniques: (1) sputtering in a reactive environment of nitrogen, (2) atomic layer deposition (ALD), and (3) metal organic chemical vapor deposition (MOCVD). Using advanced X-ray imaging techniques, we followed the evolution of strain and defect behavior during the growth, processing, and cycling of test devices to isolate critical processes. Complementary multiscale computational models predict strain evolution and defect generation.

### MISSION RELEVANCE

WBG semiconductors such as GaN and AlN have enormous potential for revolutionizing the control and transmission of electrical power, but their development requires a deeper understanding of WBG physics and chemistry. Thus, an understanding of the synthesis and processing of WBG materials at the microscopic level will directly impact the DOE energy mission by enabling higher-performance devices.

### RESULTS AND ACCOMPLISHMENTS

In FY 2014, we developed computational tools to simulate the growth of GaN epitaxial thin films by MOCVD and ALD and performed preliminary X-ray studies measuring and imaging defect generation in WBG semiconductor thin films. Building on these results in FY 2015, we continued to develop these experimental and computational techniques, and used them to develop multi-scale models of the synthesis of WBG semiconductor thin films. We used *in situ* X-ray scattering to study the growth of AlN nucleation layers via reactive magnetron sputtering and followed the evolution of AlN films. We found that the quality and properties of the films depend heavily not only on the growth conditions, but also on the initial growth surface. We focused modeling work on the development

of atomistic simulations to understand the morphology and growth rate of WBG semiconductors for arbitrary surfaces and orientations. Using energetics obtained from classical potentials developed for these materials, we modeled thin film epitaxy and three-dimensional crystal growth for both GaN and silicon carbide (SiC), and successfully reproduced the transition from step flow to island growth mode on c-plane surfaces. Finally, we mapped out the dependence of growth rate on miscut, the orientation of the surface relative to the nominal crystallographic face, for different growth conditions.

In FY 2016, we continued to extend our experimental and computational capabilities. The three-dimensional distribution of doping and structural defects in the active region of high-power WBG devices is critical to their performance and reliability. In particular, properties such as breakdown voltage and specific on-state resistance depend sensitively on the doping profiles. Since filling a GaN trench requires simultaneous growth on five chemically and structurally different surfaces, the growth and incorporation processes are far more complex than on simpler semiconductors such as silicon. We developed experimental techniques to observe trench-filling growth processes for micron-wide trenches. Our experiments applying those techniques to filling of trenches found a continuous evolution of the main growth facets and, hence, the trench profile.

To develop manufacturing processes for advanced devices and to understand and mitigate degradation mechanisms, a non-destructive method to image electric field and temperatures in operating devices would be extremely valuable. Noting that GaN is piezoelectric, we calculated that the electric fields and temperatures should be measurable during pulsed operation by monitoring the strain state of small device regions, and that those measurements could be done non-destructively. Preliminary experiments on test devices have validated the basic concept, but more development work needs to be performed before this approach will be a practical characterization tool.

Extending our modeling research, we performed a first-principles study of the atomistic growth mechanisms on vicinal orientations of m-plane GaN. We demonstrated that by tuning the chemical potential  $\mu_{\text{Ga}}$  and the excess chemical potential  $\Delta\mu$ , the growth velocities between the five types of edges (a, +c, c, +a +c, and a c) can be controlled. We found that variations of step edge morphologies as a function of the chemical potentials of the various growth species are consistent with the experimental observations of growth on vicinal m-plane surfaces. Our computational approach can help analyze

and control the step-flow growth processes of binary wurtzite thin films.

Development of new substrates for growth of GaN devices may have a significant impact on a variety of devices. An emerging candidate for GaInN epitaxial growth is scandium magnesium aluminate (ScAlO<sub>3</sub>[MgO] [SCAM]) Compared with sapphire (Al<sub>2</sub>O<sub>3</sub>), SCAM has substantial advantages, including its hexagonal structure, cleavage habit along the (0001) plane, small lattice mismatch (1.8% lattice-mismatching with GaN and lattice-matching with Ga<sub>0.83</sub>In<sub>0.17</sub>N), similar thermal properties, and stable physical-chemical performance as demonstrated by highly efficient GaInN-based light emitters on optical excitation. Several groups have suggested using SCAM to replace sapphire as a growth substrate for GaN-based LEDs and laser diodes. We studied the structure of SCAM surfaces in the reactive environment of the metal organic vapor phase epitaxy system to provide detailed information to help understand and optimize growth processes for producing high-quality Ga<sub>1-x</sub>In<sub>x</sub>N films grown on SCAM substrates.

## Bridging the Electronic and Atomistic Scales: Force Field Development for Reactive Interfaces from First Principles

2014-161-R2

Subramanian Sankaranarayanan, Maria Chan, Michael J. Davis, Stephen K. Gray, and Benoit Roux

### PROJECT DESCRIPTION

Atomistic interactions at reactive interfaces and in low-dimensional systems (molecules and clusters) underlie much of energy capture, conversion, and storage by materials. The dynamic processes at such interfaces combine the complexity of interfacial reactions, transport phenomena, and microstructural evolution with the intricacies of defect chemistry and solvation dynamics. The interplay among these phenomena at nanoscale-to-mesoscale ranges determines macroscopic device performance (e.g., battery capacity and lifetime), as well as material stability. Advances in fundamental understanding of the atomic-scale dynamical processes at reactive interfaces and in low-dimensional systems are needed for the development of novel functional materials for energy applications. Our objective has been to develop new, first-principles-based, more accurate, and more robust interatomic potentials for accurate

simulations of dynamical processes at reactive interfaces and in low-dimensional systems. The procedure involves several steps, including (a) generation and manipulation of extensive fitting datasets through electronic structure calculations, (b) defining functional forms, (c) formulating novel highly optimized fitting procedures, (d) dual-Hamiltonian optimization to leverage force fields (FFs) with more accurate approaches, and (e) subsequently coding and implementing these algorithms on high-performance computers.

### MISSION RELEVANCE

This project has developed a core of expertise in fundamental aspects of development of new, first-principles-based, more accurate, and more robust interatomic potentials for reactive dynamics and a more accurate description of low-dimensional systems relevant to a broad class of hard- and soft-matter systems. Our effort can become part of DOE's Materials Genome initiative and is therefore relevant to DOE's basic science mission. This work would also interest the Defense Advanced Research Projects Agency and Defense Threat Reduction Agency as well as to industry.

### RESULTS AND ACCOMPLISHMENTS

During FY 2014 and FY 2015, we started developing a FF fitting methodology for new *ab initio*-based FFs for classical simulations of materials and interfaces. We developed several new reactive *ab initio*-based FFs for target systems; these encompass a broad range of materials: (1) metal clusters, (2) oxides, and (3) soft-matter organic systems. We introduced a new hybrid FF to capture dimensionality effects and global minimum structures in metal clusters. In addition, we derived a new variable charge potential that can successfully predict the relative stabilities of technologically important iridium oxide (IrO<sub>2</sub>) bulk phases and surfaces. We also laid the groundwork for a new agnostic approach to FF fitting by developing a new class of flexible potentials that overcome the limitations imposed by the predefined functional forms traditionally used in all classical MD simulations. We also began development of a more robust Drude polarizable model for organic molecules in solvents.

During FY 2016, we established a FF fitting workflow that allows for development of new *ab initio*-based FFs for classical simulations of materials and interfaces (Figure 1). Specifically, we developed a new class of reactive *ab initio* atomistic as well as coarse-grained FFs for a broad range of materials: metal clusters, oxides, nitrides, two-dimensional materials, and soft-matter organic

systems, as well as universal solvents such as water (Figure 2). We introduced a new bond-order-based FF to capture thermal transport properties in two-dimensional materials such as stanene and silicene. We developed the first reactive FF for stanene, which is a promising thermoelectric material. We developed the first modified embedded atom method FF for zirconium nitride, which is an important nuclear fuel diluent. We also developed a genetic algorithm code for improved sampling to aid in the generation of an extensive *ab initio* training set for fitting potentials, specifically for metal clusters such as gold (Au) and platinum, which are important transition metal catalysts. We originally developed a hybrid bond order potential (HyBOP) for Au clusters, and we are currently extending HyBOP to other transition metals and mixed covalent-metallic interfaces, such as cobalt/carbon. In addition, we developed a new variable charge potential model for evaluating oxidation/oxide characteristics of monoclinic tantalum and cubic tungsten, which are widely used in resistive memory devices. We also began to develop a more robust Drude polarizable model for organic molecules in solvents. We pioneered the use of evolutionary optimization to develop new FFs and to reparameterize existing FFs. For soft-matter systems, we applied this optimization method to parameterize and improve upon well-known FFs such as AMOEBA (Atomic Multipole Optimized Energetics for Biomolecular Applications) FFs for target organic molecules such as benzene, ethane, butane, methanol, and ethanol. We compared various local optimization schemes, such as Levenberg-Marquardt (L-M); Simplex; derivative free optimization such as Optimization by Radial Basis Function Interpolation in Trust-Regions (ORBIT) and Practical Optimization Using No Derivatives for sums of Squares (POUNDERS) with Argonne's Mathematics and Computer Science Division; and local search algorithms with global optimization methods, including multi-start L-M and genetic algorithms. We also tested the advantages of using a multi-objective scheme to remove ambiguities caused by the selection of weights in the single objective optimization. Overall, we successfully established a framework for parameterizing and developing new FFs for a broad class of inorganic and organic materials.

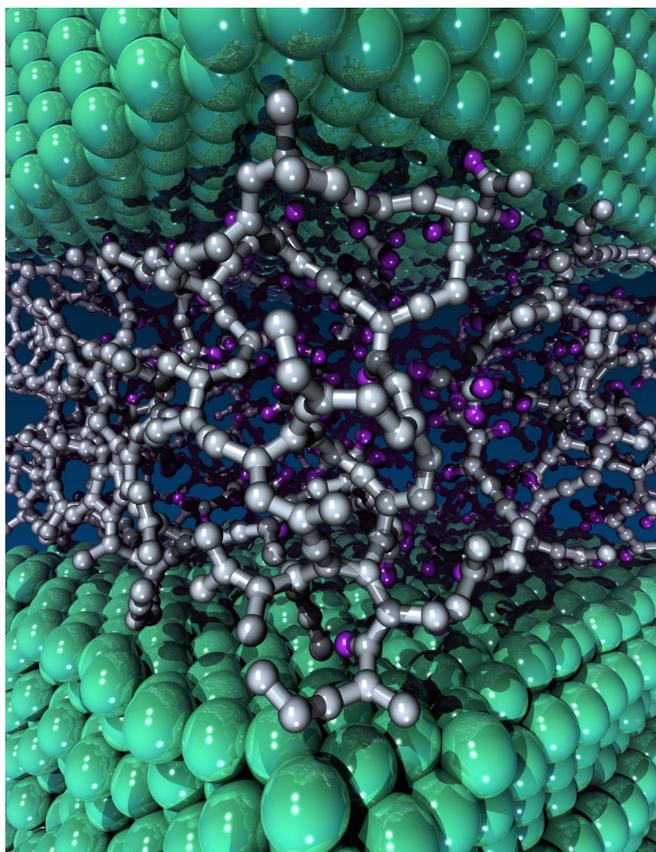


Figure 1. *Ab initio* and reactive molecular dynamics (RMD) simulations enabled design of catalytically active coatings with exceptional anti-wear properties, which drastically reduce friction (by ~25%) at sliding interfaces in automobiles. The reduction in friction occurs because of catalytic transformation of base lubricating oil into anti-wear diamond-like carbon (DLC) films during operation; a snapshot from an RMD simulation is shown here to illustrate this *operando* DLC film formation. This catalytic process, mediated by copper (green), is possible only under the extreme conditions of temperature and pressure afforded by friction at the sliding interface. Carbon and hydrogen atoms are depicted as gray and purple spheres, respectively.

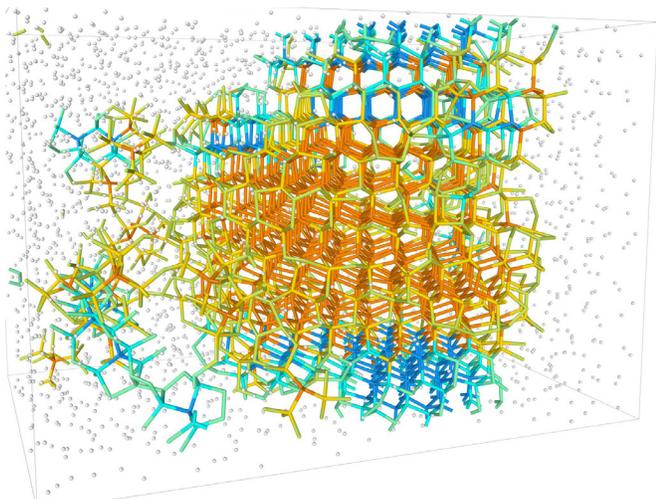


Figure 2. Snapshot from a microseconds-long molecular dynamics simulation showing the homogeneous nucleation of ice in supercooled water. The simulation is performed using a new machine-learned coarse-grained water model developed using a data-driven approach. Blue and orange spheres represent cubic and hexagonal ice, respectively.

## PROPOSED FUTURE WORK

We anticipate the force field development framework developed as part of this LDRD will be an important “science enabler” and see it being a part of upcoming 2017 EFRC (Energy Frontier Research Centers) proposals. Also, a DOE Early Career proposal based on the results and tools developed in this work is currently under review.

## Defect-Localized Spins in Semiconductors for Quantum Optoelectronics

2014-191-R2

David D. Awschalom

### PROJECT DESCRIPTION

The purpose of this project is to create robust electronic spins that can be used as quantum bits (qubits) in gallium nitride (GaN). These spins will be bound to crystalline point defects that are generated in GaN through damage of ion implantation. Therefore, they will be only a few atoms large in scale, making them suitable for use in a number of emerging applications in quantum information processing, quantum communication, and quantum sensing.

Gallium nitride has already proven to be an extremely versatile semiconductor in the microelectronics industry. We would like to leverage the unique capabilities of GaN materials growth and device design to develop a new generation of quantum-enabled electronics. To do this, we must create and discover robust quantum states suitable for integration into GaN-based device structures. Defect-bound spin qubits may be ideal for this purpose, as they have been shown to exhibit exceptionally robust quantum properties in other wide-bandgap systems such as diamond and silicon carbide.

### MISSION RELEVANCE

This project is relevant to DOE’s science mission. Electronic access to the quantum-mechanical phase space of a spin qubit would enable a new class of quantum-coherent optoelectronic devices in which traditional microelectronic interfaces are used to control extended quantum modes throughout a given structure. These fundamental material studies may establish a powerful device paradigm in which the quantum state of a material can be seamlessly interconverted between electronic, magnetic, optical, and vibrational degrees of freedom via the quantized spin of a single point defect. Such capabilities could have profound implications for

energy-efficient electronics, high-speed computing (quantum information processing), secure encrypted communication, and basic sensor technologies.

## RESULTS AND ACCOMPLISHMENTS

During the first two years of this project, we successfully created new spin-controllable quantum materials based on the addition of magnetic ions in semiconductors. Specifically, we characterized the ground state of the new electronic structure and demonstrated coherent spin control of the ground state of chromium ions, a transition metal point defect, in both gallium nitride (GaN) and silicon carbide (SiC). To do so, we constructed a variable-temperature magneto-optical spectroscopy apparatus that resonantly excites the defects and enables optically-detected magnetic resonance measurements.

### Photoluminescence Characterization of Gallium Nitride:Chromium

With a new equipment setup—including both non-resonant (710 nm) and resonant (1040–1070 nm) lasers and a liquid nitrogen-cooled indium gallium arsenide (InGaAs) spectrometer—we began to identify the defect photoluminescence (PL). Non-resonant excitation of the defect revealed a sharp zero phonon line (ZPL) and a weak sideband. A calibrated PL experiment, revealed that >73% of the total light emitted was contained within the Cr<sup>4+</sup> ZPL. Through pulsing the non-resonant laser and collecting the PL as a function of decay time only from the gallium nitride:chromium (GaN:Cr) ZPL using a monochromator, we measured an optical lifetime of  $T_{\text{opt}} = 110.1 \pm 13.1 \mu\text{s}$ .

### Resonant Characterization of the Gallium Nitrogen:Chromium Zero Phonon Line

By scanning the wavelength of the laser and measuring the sideband, we probed the ZPL. At magnetic field  $B=0$  Gauss (G) and temperature  $T=30$  K, we observed two peaks with average line widths of  $\sim 8$  GHz that were about  $\sim 7$  GHz apart. By repeating this measurement as a function of magnetic field, we observed the lower-energy peak splitting and the higher-energy peak staying stationary. This is the expected behavior for an optical transition between an excited-state spin singlet and a ground-state spin triplet.

We characterized the magnetic-field-dependent behavior more precisely at lower temperatures using optical spin polarization. Selective optical excitation of one ground-state spin sublevel with a narrow-line laser pumped the system into another sublevel via resonant excitation followed by spontaneous emission. A polarized ion then remained dark and inaccessible to the laser until

a spin-flip occurred. This phenomenon allowed us to measure the spin-lattice relaxation time  $T_1$  as a function of temperature.

At temperatures below  $\sim 20$  K, the spin-lattice relaxation time  $T_1$  of the Cr ions became much longer than the optical relaxation time  $T_{\text{opt}}$ . This resulted in a substantially reduced PL excitation (PLE) signal at these lower temperatures. A recovery of luminescence, however, should be observed if both spin sublevels are excited simultaneously.

To test this assumption, we performed two-color experiments on the defect ensemble at  $T = 15$  K and  $B = 0$  G (see Figure 1). When the sidebands are resonant with other spin energies, we recover the phonon line. By scanning the magnetic field and fitting to the centers of the recovery peak frequencies, we measure a  $g$ -factor of  $2.14 \pm 0.04$  and a  $D = 7.335 \pm 0.002$  GHz.

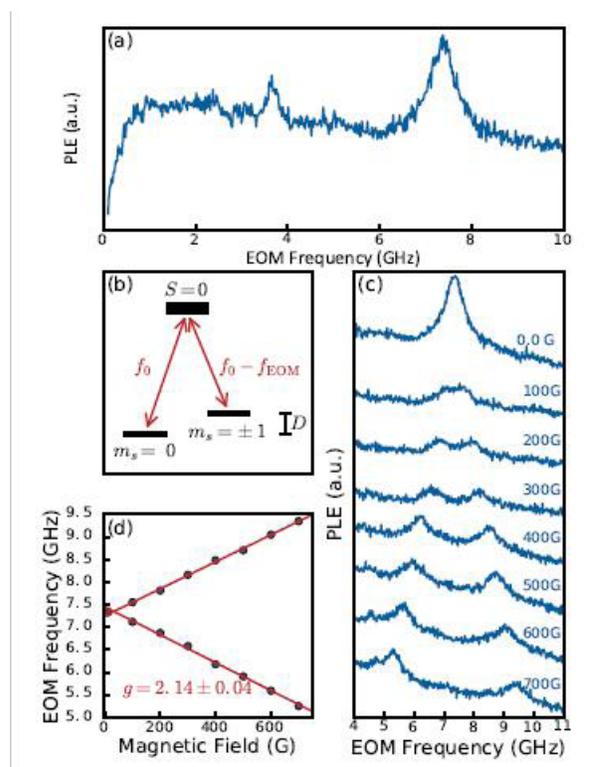


Figure 1. (a) Two-color excitation of GaN:Cr ions at  $T = 15$  K and  $B = 0$  G. GaN:Cr spins are polarized into the  $m_s = \pm 1$  sublevels via resonant optical excitation of the  $m_s = 0$  sublevel. (b) Schematic of the Cr<sup>4+</sup>-level structure and two-color resonant optical excitation. (c) Two-color excitation experiment as a function of magnetic field applied along the crystal  $c$  axis. The recovery feature at  $f_{\text{EOM}} = 7.252 \pm 0.003$  GHz splits in two, as expected for a  $S = 1$  system. (d) Fits to the peaks in panel (c) yield  $g = 2.14 \pm 0.04$ . Error bars are 95% confidence intervals, which are  $\sim 7$  MHz and smaller than the point size. (EOM stands for electro-optic modulation.)

We also performed optically detected magnetic resonance (ODMR) of the optically polarized spin ensemble, and probe the coherent time-dynamics of the spin ensemble (see Figure 2). We excite the sample with a single optical frequency tuned to the center of the

$m_s = 0$  optical transition and apply continuous microwave excitation to the sample while scanning the microwave frequency between 0 and 10 GHz.

The ODMR data for the GaN:Cr spins reveal a clear Zeeman relationship consistent with an  $S = 1$  spin system. Using fits to the data, we extract a  $g$ -factor =  $1.95 \pm 0.17$ .

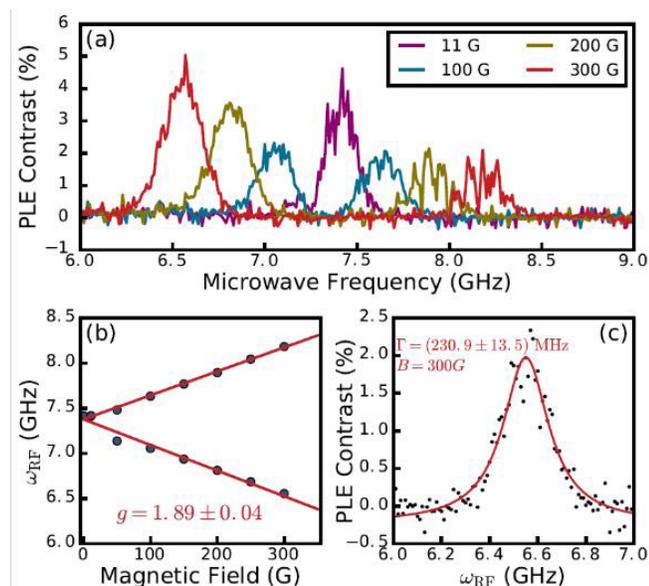


Figure 2. (a) Optically detected magnetic resonance (ODMR) of GaN:Cr spins as a function of magnetic field applied along the crystal  $c$  axis at  $T = 15$  K. Poor microwave transmission in the  $7.2 \pm 7.4$  GHz range leaves a dead-spot artifact in the ODMR signal. (b) Fits to ODMR peaks as a function of magnetic field reveal a clear Zeeman relationship consistent with an  $S = 1$  spin system with  $g = 1.95 \pm 0.17$ . Error bars are 95% confidence intervals, which are  $\sim 4$  MHz and smaller than the point size. (c) Low-power ODMR measurement at  $B = 300$  G to limit power broadening yields a line width of  $230.9 \pm 13.5$  MHz. This value corresponds to an inhomogeneous spin coherence time  $T_2 = 1.37 \pm 0.08$  ns.

## PROPOSED FUTURE WORK

Now that we have a spin system in GaN and we understand the spin and electronic structure better, we will focus on improving the spin properties. To this end, we are working on implanting Cr ions in high purity, semi-insulating 4H-SiC and annealing at high temperatures above  $1500^\circ\text{C}$ . Once we improve coherence times and line widths through material studies, we can further characterize the spin properties through time-resolved measurements.

We also note that optical transitions are protected from the influence of strain and phonons, yet the ground-state spin still couples readily to mechanical degrees of freedom. Once the spin and material properties are improved, we plan to build a setup where we can measure the effect of a known strain on the spin sublevels. Understanding this effect could pave the path to coherent quantum control over a localized spin state using mechanical degrees of freedom.

## Computational Spectroscopy of Heterogeneous Interfaces

2014-192-R2

Giulia Galli

### PROJECT DESCRIPTION

This project aims at the development and application of large-scale quantum simulation methods to model, at the microscopic scale, the physical and chemical processes involved in photoelectrochemical (PEC) energy conversion. The main focus is on processes occurring at the interface between solid photoelectrodes and simple electrolytes (e.g., water with dissolved salts). Although primarily applied to PEC systems, the results of this project are also relevant to other problems of interest in renewable energy applications, including electrical energy storage and solar to thermal energy conversion.

This project encompasses *ab initio* molecular dynamics simulations to obtain atomic trajectories and compute ensemble averages of thermodynamic properties, and the development and use of first-principles methods to obtain vibrational and electronic spectra of heterogeneous interfaces. These methods are applied to oxides and semiconducting electrodes interfaced with simple aqueous solutions, with two main goals: (i) to provide knowledge and computational tools to interpret a large body of ongoing experiments on fuel production from water and (ii) to establish design rules to predict Earth-abundant, nontoxic oxides and semiconductors with interfacial properties optimally suited to oxidize and reduce water.

### MISSION RELEVANCE

The project fits well with the DOE's energy security mission that includes development of renewable energy sources, as supported by DOE's Office of Basic Energy Sciences (BES). Within Argonne, the results of this project have impact on activities on materials for energy ongoing at the Center for Nanoscale Materials, the Advanced Photon Source (APS), and the Materials Design Laboratory. This project is also well aligned with several ongoing activities at the Joint Center for Energy Storage Research, and with several of the Materials Genome Initiative (MGI) activities supported by the National Science foundation (NSF) and the National Institute of Standards and Technology (NIST).

## RESULTS AND ACCOMPLISHMENTS

### Fiscal Year 2014

By combining *ab initio* molecular dynamics simulations and many-body perturbation theory calculations of electronic energy levels, we determined the band edge positions of functionalized silicon (Si) (111) surfaces in the presence of liquid water, with respect to vacuum and to water redox potentials. We considered surface terminations commonly used for Si photoelectrodes in water splitting experiments, encompassing hydrophobic (methyl-(CH<sub>3</sub>-)Si(111), hydrogen-(H-)Si(111) and fluorine-(F-)Si(111)) and hydrophilic (carboxyl-(COOH-)Si(111)) surfaces. A snapshot representative of one of our simulations is presented in Figure 1. We found that when exposed to water, the semiconductor band edges were shifted by approximately 0.5 eV in the case of hydrophobic surfaces, irrespective of the termination. The effect of the liquid on band edge positions of hydrophilic surfaces was much more significant, and determined by a complex combination of structural and electronic effects. These include structural rearrangements of the semiconductor surfaces in the presence of water, changes in the orientation of interfacial water molecules with respect to the bulk liquid, and charge transfer at the interfaces, between the solid and the liquid. Our results showed that the use of many-body perturbation theory is key to obtaining results in agreement with experiments; they also showed that the use of simple computational schemes that neglect the detailed microscopic structure of the solid-liquid interface may lead to substantial errors in predicting the alignment between the solid band edges and water redox potentials.

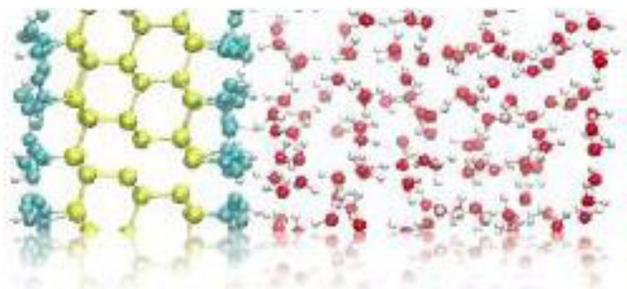


Figure 1. Snapshots representative of *ab initio* simulations of water (right hand side) on functionalized Si surfaces (Left hand side).

### Fiscal Year 2015

We developed a new computational technique to compute surface sensitive sum frequency generation (SFG) spectra that will be applied in the future to study heterogeneous interfaces. In particular, the method is based on density functional theory and the use of maximally localized Wannier functions to compute the response to electric

fields. It includes the effect of electric field gradients at surfaces. In addition, it includes quadrupole contributions to SFG spectra, thus enabling the verification of the dipole approximation, whose validity determines the surface specificity of SFG spectroscopy. We compute the SFG spectra of ice I<sub>h</sub> basal surfaces and identify which spectra components are affected by bulk contributions. Our results are in good agreement with experiments at low temperature.

We studied interfaces between photoabsorbers and catalysts, in particular the ability to extract charges (see Figure 2). The design of optimal interfaces between photoelectrodes and catalysts is a key challenge in building photoelectrochemical cells to split water. Iridium dioxide (IrO<sub>2</sub>) is an efficient catalyst for oxygen evolution, stable in acidic conditions, and hence a good candidate to be interfaced with photoanodes. Using first-principles quantum mechanical calculations, we investigated the structural and electronic properties of tungsten trioxide (WO<sub>3</sub>) surfaces interfaced with an IrO<sub>2</sub> thin film. We built a microscopic model of the interface that exhibits a formation energy lower than the surface energy of the most stable IrO<sub>2</sub> surface, in spite of a large lattice mismatch, and has no impurity states pinning the Fermi level. We found that, upon full coverage of WO<sub>3</sub> by IrO<sub>2</sub>, the two oxides form undesirable Ohmic contacts. However, our calculations predicted that if both oxides are partially exposed to water solvent, the relative position of the absorber conduction band and the catalyst Fermi level favors charge transfer to the catalyst and hence water splitting. We propose that, for oxide photoelectrodes interfaced with IrO<sub>2</sub>, it is advantageous to form rough interfaces with the catalyst, e.g., by depositing nanoparticles, instead of sharp interfaces with thin films.

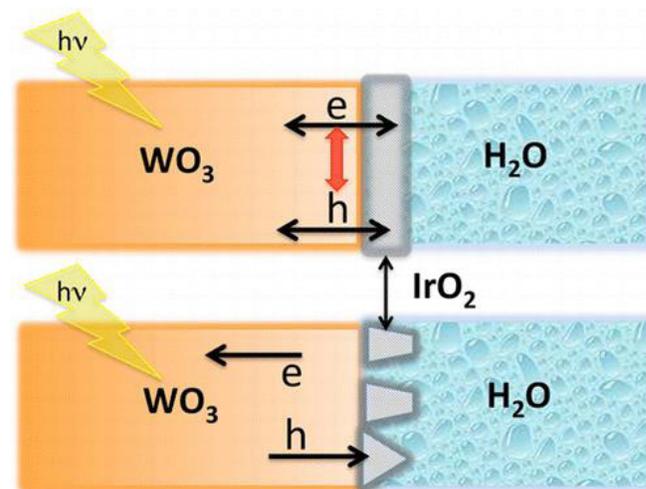


Figure 2. Schematic representation of different catalyst morphology on WO<sub>3</sub> and their influence on charge extraction (see text).

**Fiscal Year 2016:**

We computed [2] photoelectron (PE) spectra of an aqueous solution of sodium chloride (NaCl), and we compared the results with experiments carried out at the Free University in Berlin, Germany. We found excellent agreement with experiments on an absolute energy scale for peak positions as well as for photoemission intensities (see Figure 3). The agreement between theory and experiment is equally good for the energy levels of the isolated ions and for ions in water. The comparison of our many-body perturbation theory (MBPT) ( $G_0W_0$ ) ( $G$  denotes the single particle Green's function and  $W$  the screened Coulomb potential) results and those obtained with range-separated and self-consistent hybrids shows that these functionals yield a semi-quantitative agreement of PE spectra with experiment at a relatively modest computational cost. In addition, they may be the method of choice, especially when analysis of trends and predictions of qualitative features are of interest.  $G_0W_0$  calculations may then serve as a benchmark and refinement of less computationally expensive hybrid calculations.

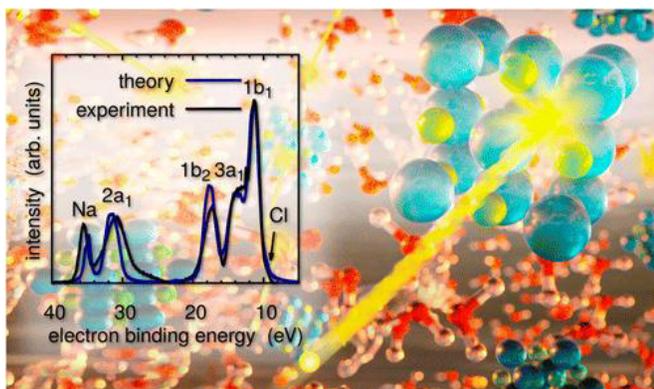


Figure 3. Comparison between computed (blue line) and measured (black line) photoelectron spectra of a 0.9-M NaCl solution in water. The cartoon depicts the physical process occurring during photoelectron excitations of the liquid.

We emphasize that accurate first-principles calculations of the electronic properties of solutions have been out of the reach of researchers for a long time because of the limited accuracy of existing density functional theory (DFT) methods and the lack of adequate codes for MBPT calculations on large samples. Our results open the way to accurate, predictive calculations of the electronic properties of electrolytes that are useful for solving a variety of energy problems.

We contributed a perspective article for *Nature Materials* on “Modeling Heterogeneous Interfaces for Solar Water Splitting.”

**PROPOSED FUTURE WORK**

The main ongoing work concerns the implementation and use of coupled first-principles molecular dynamics and GW, or Green's function, techniques for surface and solution calculations, using the Qbox and WEST codes (<http://www.west-code.org/>). The materials we are focusing on are  $WO_3$  and NiOOH. [NSF-CCI grant (CHE-1305124)].

## Framework for Integrating Multi-Modal Imaging of Materials for Energy Storage

2015-144-R1

Doga Gursoy, Charudatta Phatak, Lynn Trahey, and Xianghui Xiao

**PROJECT DESCRIPTION**

Lithium-ion (Li-ion) batteries have had a remarkable effect on the adoption of portable electronic devices. Improving batteries requires understanding the interaction of many materials at multiple length scales, ranging from micro (structure of various components, transport of ions/charge) to nano (electronic interactions, local charge accumulation). To address this challenge, we are investigating battery materials using a combination of electron microscopy (EM) and X-ray microscopy. Our goal is to integrate the data from each modality by using the computational imaging tools that will be developed within this project. We will develop improved computational methods based on probability theory for faster and reliable analysis, reconstruction, and correlation of multi-dimensional micro- and nanoscale datasets. This approach will allow us to understand the nano- to microscale changes in the material as a function of electrochemical cycling. This research will help create pathways for breakthroughs in the design of battery electrodes.

**MISSION RELEVANCE**

The tools of the project will be used to address fundamental questions in DOE's energy storage research program. The Joint Center for Energy Storage Research (JCESR) battery hub has identified metal anodes as important materials for its energy goals. JCESR is coordinating its efforts with the DOE Energy Frontier Research Centers and other programs in the DOE technology offices and in ARPA-E. The scientific knowledge obtained by combining imaging and spectroscopy, as proposed in this research, will help create pathways for breakthroughs in the design of battery electrodes.

## RESULTS AND ACCOMPLISHMENTS

Two classes of materials have been chosen for study: (1) Li-ion battery cathode materials and (2) multivalent anode plating and stripping. The Li-ion battery positive electrode class LMR-NMC (lithium- and manganese-rich, nickel manganese cobalt oxides) represents a leap forward for cathode materials if the high reaction potentials and high energies can be stabilized during cycling. The microscope and imaging capabilities realized through this effort will be used to watch the nano- to microscale changes of single cathode particles and networks of particles as a function of electrochemical cycling. Information about crystallinity (X-ray diffraction [XRD]), composition (XRD, X-ray fluorescence [XRF]), bonding (X-ray absorption spectroscopy [XAS]), and shape change (X-ray computed tomography [XCT]) will be combined with atomic resolution EM data from the same sample area. Seeing the interplay of the many degradation pathways unfold will help in designing new and improved battery materials. The tools also will be used to study the fundamental passivation and corrosion behaviors of metals for anodes in multivalent battery conceptions.

### Progress in Scientific Goals

- *Collection of Preliminary Datasets from the New Kirkpatrick-Baez (K-B) Mirror System:* Preliminary datasets showing good phase contrast from  $\text{LiCoO}_2$  particles were collected. A coin cell design was finalized to perform *in situ* imaging of battery operation using the coin cell geometry. Advanced Photon Source beam time in FY 2016 was used to study the *in situ* cycling of the Li-ion battery with focus on  $\text{LiCoO}_2$  particles, in combination with full-field tomography and scanning X-ray absorption near-edge structure (XANES) imaging modes. Beam time was dependent upon the installation of the new ultra-high vacuum (UHV) chamber used to protect the mirror system from the ambient environment.
- *Analysis of Chemistry and Phase of Cycled Cathode Particles:* A preliminary investigation was conducted to determine that the cycled cathode particle (Li-NMC) consisted of multiple phases with different crystal structures using electron diffraction. Preliminary mapping of charge density was also performed using off-axis electron holography to obtain holograms from small areas of the sample that can be related to the local charge density variations.

### Progress in Multimodal Instrument Framework Development

- *Commissioning of the New K-B Mirror System:* K-B mirrors from JTEC, a Japan-based company, were installed and tested at the 34-ID-E beamline of the Advanced Photon Source (APS) during the third quarter of FY 2015. The new mirror system is capable of forming a  $\sim 100$ -nm focused X-ray beam. The UHV chamber, designed to protect the new KB mirrors from potential damage by the ambient environment, was installed in August 2016.
- *Partner User Proposal:* A Partner User Proposal entitled “Integrated Multimodal Imaging of Energy Materials Based on Projection Microscope at 34ID-E,” was prepared so that up to 8% of the total beam time (about 1 week per cycle) could be used to implement the instruments and conduct battery materials research. The first experiment with the new K-B mirror-based microscope system was conducted during the first quarter of FY 2016. The new microscope is capable of 100-nm tomography with reasonable temporal resolution (a few minutes). The initial results of integrated imaging with XANES and full-field tomography are promising and provide clues for feasible XANES imaging experiments of a real battery system.

### Progress in Computational Aspects

- *Development of Machine Learning Methods for Tomography:* The application of machine learning methods, such as dictionary learning (DL) and convolutional neural network (CNN), are being tested to integrate the information from X-ray and EM tomography datasets. The CNN method has been implemented to find the rotation center in tomography automatically, which can help automate the entire tomography workflow, as well as to remove ring artifacts in X-ray tomography data. Both the CNN and DL methods were used to correlate X-ray data and EM data and improve the resolution of the X-ray data. These methods offer the advantage of automated analysis once the parameters and the training data are established. We are also working with Argonne’s Mathematics and Computer Science Division (MCS) for simultaneous visualization of the two 3D datasets using Paraview, which is open-source cross-platform data analysis and visualization software.

**PROPOSED FUTURE WORK**

We propose to efficiently combine structural and chemical imaging and data analysis from a cross-phase modulation (XPM)-based X4 microscope with complementary charge distribution and electric field mapping obtained from EM using a robust computational framework. These techniques will be employed to study the plating and stripping of metal anode materials and Li-ion intercalation cathode materials that are of interest to the Argonne battery program and the Joint Center for Energy Storage Research (JCESR) battery hub.

Our initial focus will be on understanding the degradation mechanisms related to phase change that happen with the charging and discharging within LMR-NMC cathode material. We will perform phase imaging using off-axis electron holography to analyze the local charge density distributions in the sample and correlate them with the structural features as well as phases (crystal structure).

Furthermore, we propose to prepare site-specific samples using the Focused Ion Beam for investigation using EM. Multiple through-focus series images of the sample will be acquired with and without *in situ* electrical biasing in a transmission electron microscope (TEM). Initial experiments will be performed on a standard sample to fully characterize the transfer function of the microscope. The phase shift of the electron wave will be obtained and the gradient of the phase shift then gives the local electric field variations. Computing the Laplacian of the phase shift gives the local charge distribution. This information then will be correlated with the structural and chemical data obtained from the X4 microscope.

**Objectives**

- Computational framework development
  - Improve phase retrieval and tomographic reconstruction algorithms suitable for *in situ* battery cell imaging (DG/BG/PD1)
  - Test the algorithms on major supercomputing facilities (National Energy Research Scientific Computing Center [NERSC], Argonne Leadership Computing Facility [ALCF]) (DG/PD1)
- Multimodal instrument framework development
  - *In situ* operando imaging using the battery cell to reveal chem physical dynamics occurring on positive/negative electrodes (XX/DV/LT/PD2)
  - Prepare TEM samples from various stages of *in situ* X-ray imaging experiments for mapping of charge density (CD/PD2)

## Integrated Imaging, Modeling, and Analysis of Ultrafast Energy Transport in Nanomaterials

2015-149-R1

Tom Peterka, Nicola Ferrier, Ross J. Harder, Sven Leyffer, Ian McNulty, Todd Munson, Subramanian Sankaranarayanan, and Haidan Wen

**PROJECT DESCRIPTION**

Integrating ultrafast imaging with molecular dynamics (MD) modeling, data analysis, and visualization can provide crucial insights for energy research. The temporal behavior of externally stimulated materials beyond equilibrium can lead to breakthroughs in controlling, for example, the heat dissipation of next-generation semiconductors, conversion of waste heat into electricity in thermoelectric (TE) materials, and electrochemical processes across liquid-solid interfaces in water purification. These diverse applications all transport energy through phonons (sound waves that carry heat) in a time-evolving crystal lattice. We are researching an integrated approach to predict, image, and analyze phonon dynamics that can be applied to externally stimulated systems. The project consists of three main components: modeling, analysis, and imaging.

**MISSION RELEVANCE**

Lattice vibrations in individual nanoparticles affect phase transitions, bond softening/hardening, ferroelectricity, solid/liquid interfaces, heat dissipation, phononic local structure, phase front propagation, and spectrometry. Understanding such phenomena can enable energy applications such as photocatalysis, photonics, thermoelectrics, semiconductor design, groundwater photo-remediation, and heat transfer in battery interfaces—all critical to DOE's mission to design new materials for energy. The novel integration of model-guided imaging and image-guided modeling allows iterative feedback between the two processes, which ultimately enables improved utilization of valuable resources at the Advanced Photon Source (APS) and Argonne Leadership Computing Facility (ALCF). Modeling information such as the sample temperature and image resolution allows researchers to conduct measurements that are scientifically significant. Likewise, the veracity of simulated results, crucial to the outcome of the experiments, is improved by timely analysis of reconstructed experimental images. In the context of the APS upgrade for transformational sciences, this proposal

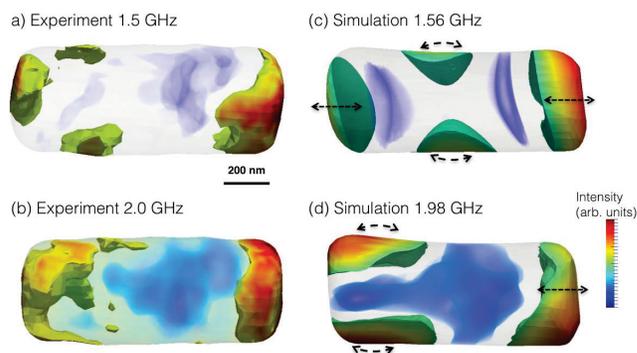
addresses the need for high-speed, high-volume data processing for novel time-resolved imaging, and it aligns with other strategic directions in hard X-ray sciences and advanced computing.

## RESULTS AND ACCOMPLISHMENTS

In the first year of the project, we developed a methodology for executing MD simulations, analyzing the models to compute trajectories from phonons, and using these trajectories to generate strain fields. Such data analysis is the “glue” between forward modeling and reverse image reconstruction. These methods allow us to explain phonon dynamics in chemically reactive systems.

In the second year, we developed workflow models for both forward and reverse problems of comparing simulated and measured results in real and reciprocal space, respectively. Experimental measurement produces a 3D electron density, along with the lattice orientation information from which atomic positions can be derived. Fitting the atomic positions is conceptually straightforward; however, computational challenges arose. The difference in scale between the measurement (voxels in the electron density are roughly  $6 \text{ nm}^3$ ) and the atomic lattice unit cell for our gold sample ( $0.406 \text{ nm}^3$ ) resulted in a large dimension for the lattice ( $\sim 200$  million atoms), along with potential aliasing effects. An isosurface computed from the electron density forms the shell of the material (and reduces aliasing). We initially developed an approach to fit a lattice to the density data, but then discovered a similar effort with publicly available code called nanoSCULPT. This code appeared to be implemented and tested, and has all of the features we were developing. On a version of a sample scaled down 10 times, nanoSCULPT required almost six days of CPU time (on a single 64-bit computer server) to produce an atomic lattice for our sample. After analyzing the code, we were able to reduce that time to a few hours.

Experiments involving several scientifically and industrially relevant systems have been performed both at APS beamlines 34-ID-C and at 7-ID-C. At 7-ID-C, ultrafast imaging of the lattice dynamics of ZnO (zinc oxide) and gold nanocrystals following excitation with a 355-nm-wavelength, 10-ps laser “pump” was performed (see Figure 1). At 34-ID-C, the reduction of ascorbic acid on gold was characterized. To successfully perform the experiment, it is essential to have good spatial overlap of the X-ray beam and laser spot, each of which is  $\sim 5 \mu\text{m} \times 5 \mu\text{m}$ . To this end, a stable laser delivery system to focus the pulsed laser source, while providing an in-line camera view of the sample, was built and deployed.



**Figure 1.** Imaging and simulation of the modal response of a ZnO nanocrystal. Representative high-frequency deformation modes with frequency (a) 1.5 GHz and (b) 2.0 GHz imaged through CDI. Corresponding simulated deformation modes at (c) 1.56 GHz and (d) 1.98 GHz are also shown. Arrows show the nature of the deformation.

The theory-guided data interpretation via either the forward or reverse workflow is an exciting and novel technique that can be extended to a wide scope of projects carried out at both the APS and ALCF because of the rapid convergence of time and length scales accessible by both experiments and simulations. We have successfully developed a framework that allows us to integrate experimental observations with multimillion-atom MD simulations to enhance the fundamental understanding of the behavior of materials under external stimulation. As part of our workflow, the experimental systems investigated via Bragg coherent diffractive imaging (BCDI) at 34-ID-C and at 7-ID-C were simultaneously simulated via atomistic MD and continuum finite element modeling (FEM) to reveal structural and dynamical insight into ultrafast phenomena unresolved by the reconstructions of the BCDI images alone. In particular, we performed (a) FEM calculations on experimentally reconstructed ZnO nanocrystals subjected to laser heating, (b) MD simulations on Au (gold) and Au/Al (gold/aluminum) core-shell nanocrystals, (c) MD-informed FEM simulations to model ascorbic acid decomposition reaction on gold nanocrystals, and (d) reactive MD simulations elucidating the atomistic processes underlying methanol formation from methane on Pt (platinum) nanoparticles.

## PROPOSED FUTURE WORK

We will continue to develop the Fast Phasing Library (FPL) for recovering the phase from BCDI experiments. We will meet with other groups conducting integrated imaging to identify both the potential for joint efforts and needs for modeling + experiment workflows. These potential participants include photocatalysis that uses STEM, TEM, and fluorescence microscopy, brain imaging (MD, neuroscience) to incorporate streaming and processing workflows into their imaging and reconstruction of brain

slice images, self-assembly of ligand-nanoparticles, multimodal imaging to see whether ptychographical reconstruction is appropriate for electron, and ptychography and fluorescence multimodal imaging. We will conduct further pump-probe experiments both at APS and at the Linac Coherent Light Source (LCLS) to image the same types of effects but on samples that have had their surfaces roughened by acid etching.

We will also study the corrosion of Cu (copper) nanoparticles in saline water. We will continue to model other material systems (aqueous corrosion of copper nanoparticles) using ReaxFF, and post-process the MD trajectories to derive structural and dynamical correlation functions (pair correlation functions, structure factors, etc.) to compare/complement the experiments. We will also carry out equilibrium and non-equilibrium multimillion-atom MD simulations to study phonon transport across solid-liquid interfaces, such as in the gold-ascorbic acid system, as well as absorption and damping of phonon modes in piezoelectric crystals such as ZnO.

## Integrated Imaging to Understand and Advance Photocatalysis

2015-154-R1

Jeffrey R. Guest, Zhonghou Cai, Maria Chan, Yuzi Liu, and Ian McNulty

### PROJECT DESCRIPTION

The photocatalytic conversion of carbon dioxide (CO<sub>2</sub>) to liquid fuels has the dual advantages of performing carbon recycling for global climate change mitigation and solar energy capture for renewable energy development. Acquiring the ability to harness sunlight directly to convert CO<sub>2</sub> and water to energy-dense products (formic acid, formaldehyde, and methanol) would allow easy collection, storage, and transport. However, the obstacles in photocatalytic CO<sub>2</sub> reduction are large, because the process involves many proton-coupled electron transfer reactions that pose several fundamental challenges in electrochemistry, photochemistry, and semiconductor physics. A fundamental understanding of active sites in catalytic and photocatalytic materials and their role in charge distribution, charge transport, and efficiency of catalytic reactions trails that of the technological development of materials for energy.

The objective of this project is to simultaneously (1) advance the understanding of elementary processes involved in CO<sub>2</sub> reduction to liquid fuel and spatial

and kinetic control of the active sites, and (2) develop integrated imaging and visualization approaches. We are developing our integrated imaging approach on promising next-generation materials, such as copper(I) oxide (Cu<sub>2</sub>O), that may hold advantages for photocatalytic processes. The major tasks of this project include developing a cross-platform sample holder (for transmission electron microscopy [TEM], scanning fluorescence X-ray microscopy (SFXM), and ultrahigh vacuum [UHV] scanning tunneling microscopy [STM]) for performing multimodal imaging studies on a single system and the corresponding computational modeling.

### MISSION RELEVANCE

This project supports the DOE mission in use-inspired fundamental science and photocatalysis. This problem presents an opportunity and an ideal testbed to develop the experimental, theoretical, and analytic methods for attacking a complex problem that spans orders of magnitude in length and time scales and requires the complementary modalities of various microscopy and spectroscopy platforms (X-ray, electron, scanning probe, optical). The project bridges Argonne's existing expertise in these areas, leveraging it not only to enhance the control and understanding of photocatalytic CO<sub>2</sub> conversion, but also to enable multimodal capabilities for a broader materials design, synthesis, characterization, and modeling program.

### RESULTS AND ACCOMPLISHMENTS

In FY 2015, we successfully synthesized Cu<sub>2</sub>O nanoparticles with well-defined facets in different shapes and with various surface terminations. We characterized these nanoparticle facets with TEM and electron paramagnetic resonance (EPR) experiments and compared these results with first-principle density-functional theory modeling of the various Cu<sub>2</sub>O surface terminations. We also examined catalysis of AgCl nanoparticles in real-time in gas-flow TEM experiments.

In FY 2016, we carried out two joint TEM and SFXM experiments with the cross-platform sample holder to measure the facet-dependent photocatalytic response of the Cu<sub>2</sub>O nanocrystals that we had grown. We used TEM to image specific nanocrystals with a well-defined orientation, then located the *same* nanocrystals by SFXM using the Center for Nanoscale Materials/Advanced Photon Source (CNM/APS) Hard X-ray Nanoprobe at beamline 26-ID (see Figure 1). We spectroscopically mapped the local oxidation state of specific facets using the Cu K-edge while exposing the sample to a CO<sub>2</sub>+ water (H<sub>2</sub>O) gas mixture and optical excitation with a 532-nm

laser and compared that to control spectra under no-gas and dark conditions. The spectra indicate a chemical shift of about 1 eV on the higher index facets (e.g., [110]), whereas no shift was observed on the (100) facets.

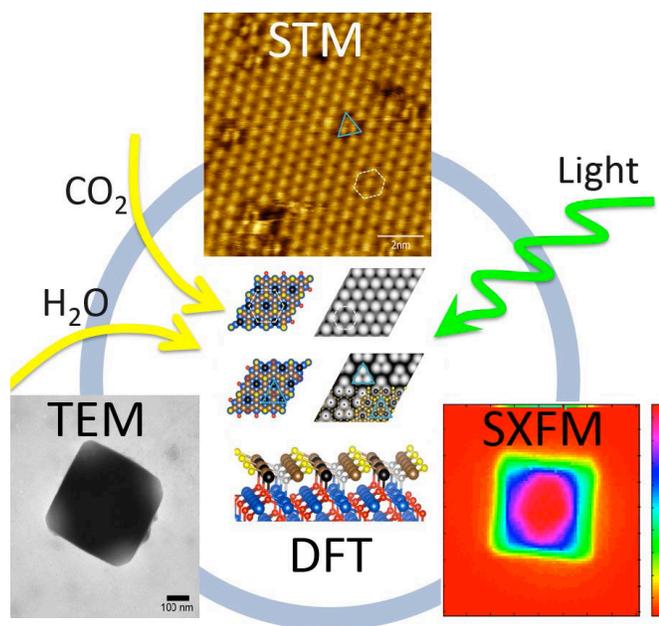


Figure 1. Integrated imaging of a proposed photocatalyst for CO<sub>2</sub> reduction (Cu<sub>2</sub>O) using *in situ* gas flow TEM, *in situ* gas flow SFXM, and ultrahigh-vacuum STM, in conjunction with first-principles density functional theory (DFT) modeling and image simulations. The TEM and SFXM measurements are made on the same particle.

In order to resolve the atomic-scale structure of defects that are critical to photocatalytic functioning, UHV STM studies were performed on macroscopic crystals of Cu<sub>2</sub>O. Our topographic imaging of the Cu<sub>2</sub>O(111) surface revealed defect states on the surface (as shown in the figure). Based on comparison with our calculations, we believe the dark spots correspond to missing Cu atoms, while three-fold symmetric bright spots correspond to missing O atoms. STM studies on crystalline surfaces enable the identification of defect and adsorption sites that are responsible for catalytic activity; allow us to connect with the theoretical calculations at the atomic scale; and provide input to the analysis of STM images of nanoparticles, spectra from SFXM, and TEM images.

In conjunction with experimental work, we performed first-principles calculations to study the ground and excited electronic states of Cu<sub>2</sub>O and modeled the STM signals as well as SFXM spectra for a Cu<sub>2</sub>O(110) surface with various adsorbates. Our simulation showed that CO<sub>2</sub> and carbon monoxide (CO) molecules have distinct appearances under positive bias voltage under STM and cause different absorption peak features under SFXM. Therefore, the

experimental observations can be directly mapped to the underlying surface chemistry.

We also designed and built a new cross-platform sample holder that enables optical excitation of the sample through an optical fiber. This holder will allow us to exploit both TEM and SFXM to explore photocatalysis measurements *in operando* with gas flow at atmospheric pressure on the same sample for future measurements.

### PROPOSED FUTURE WORK

In FY 2017, we plan to extend and connect our studies across the various imaging modalities and under the necessary conditions for photocatalysis. We will continue to explore TEM, electron energy loss spectroscopy (EELS), and SFXM measurements under illumination and under gas load to investigate and quantify photocatalytic activity on various Cu<sub>2</sub>O nanoparticle facets, with an effort to correlate measurements on the same particles. UHV STM measurements will be extended to other surface terminations of Cu<sub>2</sub>O and performed after exposure to CO<sub>2</sub>. Future computational work involves modeling X-ray fluorescence spectra and STM measurements on more Cu<sub>2</sub>O surface types.

## Coherent X-ray Studies of Materials Synthesis and Dynamics

2015-167-R1

G. Brian Stephenson

### PROJECT DESCRIPTION

Advances in accelerator technology now being implemented will produce thousand-fold increases in the brightness of hard X-ray sources, enabling *in situ* coherent X-ray studies of synthesis mechanisms down to the atomic scale with the needed sub-nanosecond time resolutions. In parallel, orders-of-magnitude increases in computing power are enabling *ab initio* simulations, not just of ground-state materials structure and properties but also of the competing chemical reactions and materials kinetics that occur during synthesis. Both coherent X-ray techniques and atomic-scale modeling enable us to see beyond the average behavior of a fluctuating system

This project focuses on understanding materials synthesis and processing mechanisms by developing new techniques to observe and model the atomic-scale mechanisms, such as using more complex space/time correlations that go beyond standard pair correlations.

Synthesis processes and materials studied (e.g., growth of nitrides by chemical vapor deposition) will be chosen to illustrate fundamental materials synthesis issues (e.g., control of surface morphology, formation of defects, creation of metastable phases, and impurity incorporation)

This project will focus on advancing the capabilities of X-ray photon correlation spectroscopy (XPCS), because its space and time resolutions are well suited to studies of synthesis dynamics.

The standard XPCS method determines the time spectrum of fluctuations in the speckle intensity at each location  $q$  in reciprocal space, which gives the dynamics of the pair correlations as a function of  $q$ . However, it should be possible to go well beyond current XPCS analysis. In principle, analysis of intensity correlations between two or more  $q$ 's in the speckle pattern obtained with a coherent beam can reveal spatial correlations of a higher order than pair correlations, which are inaccessible in conventional incoherent X-ray analysis. Furthermore, non-equilibrium processes, such as phase transformations, can have nonsteady behavior that is best characterized by two-time correlation functions. In addition, recent work indicates that correlations between two  $q$ 's and two times will allow separation of diffusive rearrangements and deformations.

Measurement and analysis of these complex space/time correlations during materials synthesis will be explored in this project. Initial experiments will be carried out at the Advanced Photon Source (APS) on a new instrument being commissioned at beamline 12-ID-D.

Multiple length-scale and timescale simulations of atomic-scale dynamics during synthesis will be developed to guide the design and analysis of the experimental studies. These models will allow prediction of the complex space/time atomic-scale correlations that will be observed.

### MISSION RELEVANCE

This project will further the DOE Basic Energy Sciences mission to design, discover, and synthesize new materials through atomic-scale control. It addresses the Grand Challenge that asks, “[h]ow do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?” A critical mission of the national laboratories is to make breakthroughs in discovering the new materials and processes needed to address global challenges in energy, the environment, health, and security. Not only do we need to understand the proper arrangement of atoms in materials and nanostructures that gives the desired functionality, but we need to learn how to synthesize and stabilize these arrangements.

### RESULTS AND ACCOMPLISHMENTS

During FY 2015, we commissioned a new diffractometer capable of performing coherent X-ray measurements, as well as a new system for *in situ* materials growth, at APS beamline 12-ID-D. Initial surface scattering tests were made with the new growth chamber. Simulations of gallium nitride (GaN) growth began using three-dimensional (3D) kinetic Monte Carlo methods to compare growth mechanisms on different crystal orientations and predict coherent X-ray scattering.

In FY 2016, we carried out the first demonstrations of new coherent X-ray methods combining experiment and simulation to characterize atomic-scale mechanisms of materials synthesis. Initial coherent X-ray measurements of surface dynamics during growth were made. Signal levels were very low with the existing X-ray focusing optics. The optics were redesigned to use compound refractive lenses. Although the project ended as planned on April 30, 2016, work continued through follow-on project support. The new optics were installed and provided much higher signals for coherent X-ray measurements.

In parallel with the experiments, kinetic Monte Carlo simulations of GaN growth on various crystal surfaces were carried out, and the behavior of coherent X-ray speckle patterns from these surfaces was investigated. These results, such as the predicted two-time correlation functions during growth shown in Figure 1, are guiding follow-on experiments. Simulation results provide examples of what will be possible with the much higher coherent flux of the future APS Upgrade.

Additional work was carried out to develop a new Bragg Coherent Diffractive Imaging technique for time-resolved imaging studies using coherent X-ray beams. A publication on this method appeared in FY 2016.

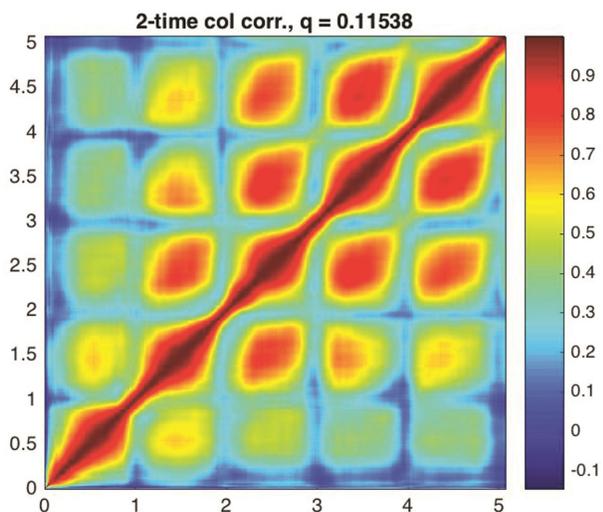


Figure 1. Two-time correlation function calculated from kinetic Monte Carlo simulation of layer-by-layer growth of 5 monolayers of GaN on the (0 1 -1 0) m-plane. The “checkerboard” pattern in the range between monolayers 1 and 5 indicates that atomic-scale islands nucleate in almost the same arrangement for the growth of each layer, beginning with layer 2. These complex correlations, useful in optimizing synthesis processes for materials critical for electrical energy efficiency, will be revealed by coherent X-ray methods.

## The Computational Design of New Functional Materials from Complex Transition Metal Oxides

2015-168-R1

Hyowon Park

### PROJECT DESCRIPTION

The goal of this project is to study theoretically novel electronic and structural phases of complex oxide materials in which the strong correlation of electrons plays an important role. Strongly correlated oxides exhibit novel electronic behaviors intimately coupled to their spin, charge, orbital, and lattice degrees of freedom. For this project, we adopted the state-of-the-art *ab initio* method called density functional theory plus dynamical mean field theory (DFT+DMFT). The main objectives are to (1) calculate various spectroscopic quantities of complex oxides in both bulk and hetero-structured forms, and (2) develop a code for computing inter-atomic forces within DFT+DMFT to investigate the structural properties and energetics of oxides. The output of DFT+DMFT calculations will be directly compared to experimental measurements including photoemission, X-ray scattering, X-ray absorption, and neutron scattering spectra. Ultimately, our project can lead to the computational design of functional oxide materials or devices with a desired functionality.

### MISSION RELEVANCE

This project is relevant to the DOE’s Basic Energy Sciences mission. This project addresses the fundamental understanding of the relationship among charge, spin, orbital, and lattice degrees of freedom. Ultimately, the knowledge of electronic correlations among different degrees of freedom will provide the ability to control and design new functional materials. For example, novel electronic phases and chemical reactions occurring at interfaces or surfaces can be used for new electronic devices or energy materials such as batteries. Our project is also relevant to other federal agencies, including the National Science Foundation (NSF) and the Defense Advanced Research Projects Agency (DARPA).

### RESULTS AND ACCOMPLISHMENTS

During FY 2015, we quantified the electronic correlation in LaNiO<sub>3</sub> films using DFT+DMFT by computing the momentum-resolved spectral function and the mass enhancement in strained thin film and compared them to experimental data from angle-resolved photoemission spectroscopy (ARPES). We also calculated the orbital polarization of strained LaNiO<sub>3</sub>/LaAlO<sub>3</sub> superlattices consisting of four layers of nominally metallic NiO<sub>2</sub> and four layers of insulating AlO<sub>2</sub> separated by LaO layers. We showed that the overall dependence of orbital polarization on strain computed using DFT+DMFT is qualitatively consistent with recent X-ray absorption and resonant reflectometry measurements.

During FY 2016, we computed the momentum and energy-dependent magnetic excitation spectra of CePd<sub>3</sub>, in which strongly correlated Ce *f* electrons are hybridized with rather itinerant Pd *d* electrons. DFT+DMFT was adopted to compute the dynamical magnetic susceptibility that includes both single-particle and two-particle vertex functions, allowing the treatment of both coherent quasi-particle excitations and incoherent scatterings. The resulting magnetic susceptibility shows good agreement with experimental inelastic neutron scattering data (see Figure 1).

Second, we computed the energetics of the spin-state transition occurring in bulk LaCoO<sub>3</sub>. The total energy of different spin states was computed using DFT+DMFT as a function of crystal volume and compared to DFT and DFT+U (where “+U” means the static Hartree-Fock contribution beyond DFT) calculations. We found that as the volume increases, the low-spin state in LaCoO<sub>3</sub> changes to higher spin states, and the first-excited state is the mixture of the high-spin and low-spin states. All DFT-based calculations predict this mixed-spin state; however, only the DFT+DMFT total energy curve is

quantitatively consistent with the experimental excitation gap, whereas both DFT and DFT+U overestimate the tendency toward the higher-spin states.

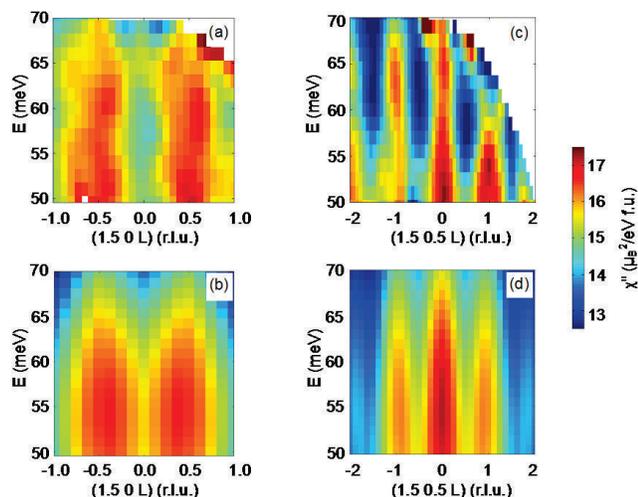


Figure 1. Dynamical magnetic susceptibility of  $\text{CePd}_3$  at 5K ((a) and (c) neutron scattering data) and the DFT+DMFT calculations at 100K ((b) and (d)) represented by an L-w slice at  $K=0.0$  ((a) and (b)) and  $K=0.5$  ((c) and (d)). (r.l.u. are reciprocal lattice units. Also, (H,K,L) means the reciprocal vector in a unit of  $2\pi$ , and  $w$  means the energy.)

Finally, we also implemented the atomic-force calculation code based on the charge-self-consistent DFT+DMFT calculation using the Wannier function as a correlated orbital. We applied the code to the DFT+DMFT calculation of the atomic force for the cubic structure of bulk  $\text{LaNiO}_3$ . The force was computed as a function of the displacement of nickel (Ni) and oxygen (O) atoms, and the integrated force was successfully compared to the total energy as a function of the displacement. This code will be applied to the study of efficient structural relaxation and energy calculation of realistic and complex transition metal oxides.

FY 2016 was the final year of this LDRD project. Based on FY 2016 accomplishments, we will complete the current projects—total energy and atomic force calculations for bulk  $\text{LaCoO}_3$  and  $\text{LaNiO}_3$ —and submit the results to high-profile academic journals. We will also apply the implemented code for computing energies and forces within DFT+DMFT to the study of structural and electronic properties of transition metal oxides in a nanostructured form. The DFT+DMFT force calculation will allow the performance of the efficient structural relaxation of oxide materials in the surface or interface of strained films. For example, the origin of the higher-spin state transition at the surface of  $\text{LaCoO}_3$  film is not yet understood. In addition, the accurate force calculation will lead to the study of phonon softening occurring in many oxide materials at high temperatures, which is closely related to the high-temperature phase transition resulting from

their phonon entropy changes. Our work will be continued under BES FWP 59001, in which Dr. Park will participate as a co-Project Investigator.

## Magnetic Phases in Highly Oxidized, Low-Dimensional Oxides

2015-175-R1

John F. Mitchell, Nathaniel Schreiber, and Hong Zheng

### PROJECT DESCRIPTION

This is a discovery crystal synthesis project that leverages the high oxygen fugacity achievable in a recently installed high-pressure floating zone (FZ) image furnace to stabilize new materials. We will follow a control strategy of using this high  $p\text{O}_2$  to grow stoichiometric phases that are known at ambient pressure either to develop anion vacancies or to decompose upon heating because of a high targeted metal oxidation state. Such materials with high oxidation states are an open area of opportunity because of the difficulty of growing specimens but offer views on the role of O  $2p$  hole states on the electronic structure and the variation of magnetic and orbital ordering. The material system in question,  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ , is one that we have previously characterized using polycrystalline specimens; however, the lack of single crystal specimens has prevented a complete and definitive study of the unique intrinsic magnetic phenomena. In particular, a region of the phase diagram near  $x=0.7$  anomalously shows no magnetic long-range order. We have developed a framework for understanding this result based on short-range orbital order “seeding” a short-range magnetic order that would be nearly invisible to the neutron powder diffraction studies to date.

### MISSION RELEVANCE

This project concerns fundamental science. The work directly supports DOE Basic Energy Sciences (BES) missions in discovery science, particularly in its grand challenges in control of matter at the level of electrons, understanding and harnessing correlated systems, and synthesis of new functional compounds. The beneficiaries will be the wide base of scientists who work on transition metal oxide condensed matter and, in particular, those who have worked on correlated electron manganites (a very large percentage of the community).

## RESULTS AND ACCOMPLISHMENTS

The objective of the present work is to create these heretofore ungrowable crystals and to explore magnetism and phase competition unique to their low-dimensional electronic structure using a combination of X-ray and neutron scattering tools. We successfully prepared several crystals in this phase region, including specimens of sufficient size for neutron experiments that were carried out at Oak Ridge National Laboratory's (ORNL's) Spallation Neutron Source (SNS). We discovered the following as a result of combined X-ray and neutron diffraction experiments:

- An incommensurate charge-ordered state was confirmed in the  $x=0.7$  sample, with ordering temperatures  $\sim 335$  K. This result had been missed in our previous powder diffraction work.
- Neutron scattering showed clear incommensurate magnetic peaks that had never been observed previously. This finding indicates that some form of weak magnetic modulation has developed and answers the long-standing question that we initially posed in this research. The intensity of these peaks is extremely weak, and they were simply not observed in our powder neutron experiments of more than 15 years ago.
- It appears that the charge and spin modulations obey the relationship  $q_{\text{charge}} = 2q_{\text{spin}}$ , which is a well-established relationship in charge- and spin-stripe nickelates. If correct (and additional experiments will be required to verify), then it implies that in this region of doping, the underlying antiferromagnetic structure is of the G-type (all neighboring spins being antiparallel) rather than of the zig-zag CE-type that is expected in manganites with charge order, nor the layered antiferromagnetic A-type or rod-like C-type order found in neighboring phases.

In addition, high-pressure oxygen was used to grow crystals of other high oxidation state phases, such as  $(\text{Pr,Ca,Y})\text{CoO}_3$ . These crystals were studied at Argonne's Advanced Photon Source (APS) to understand whether any structural component was associated with a magnetic transition. The result was that no structural phase transition accompanied it.

## Towards Ionotronics: First-Principles Strategies for Coupling Electronic and Ionic Properties in Complex Oxides

2015-178-R1

James Rondinelli

### PROJECT DESCRIPTION

This project aims to deliver control strategies over defects (e.g., vacant cation or anion sites) in a designed fashion to establish a materials platform for an ionic-based electronic device. Anion-deficient  $\text{ABO}_{3-\delta}$  oxides, so-called brownmillerites, based on the perovskite structure, are the materials platform for investigation; they could be the ideal channel materials for an ionics-based field-effect transistor (FET). Although they have been studied experimentally, the main focus has been on exploring polymorphic crystallography based on redox chemistry rather than on phase stability or electronic properties. The polymorphic flexibility of these materials is the topic of focus in this project.

### MISSION RELEVANCE

This project relates to the scientific discovery and innovation aspects of DOE's science mission. The ability to manipulate the ion concentration in an ultrathin oxide film via electric fields represents an exciting new operational platform for solid-state devices because of the sensitive coupling between stoichiometry and functional properties. The main effort of the project is to develop an understanding of how to manipulate the electronic structure of complex oxides through engineered static and dynamic control of the anion structure. The incorporation of such novel materials into advanced nanoelectronics has implications for the development of superior computing technology and reduced power consumption, while at the same time, forging pathways to new state variables beyond temperature or voltage that would represent a game-changing advance in computing.

### RESULTS AND ACCOMPLISHMENTS

In FY 2015, we focused on understanding the polymorphic stability of  $\text{SrFeO}_{2.5}$  in bulk and under epitaxial strain. The structure consists of alternating layers of  $\text{FeO}_6$  octahedra and  $\text{FeO}_4$  tetrahedra, viz., ordered arrangements of oxygen vacancies. Electronic structure calculations based on density functional theory (DFT) were performed to explain the stability of the equilibrium (strain-free) and thin-film structures to both previously identified and new

descriptors. The simulations indicate that cation size and intralayer separation of the tetrahedral chains provide key contributions to the preferred ground state. Interestingly, the bulk ground-state structure is retained in the ferrates over a range of strain values; however, a change in the orientation of the tetrahedral chains (i.e., a perpendicular orientation of the vacancies relative to the substrate) is stabilized in the compressive region. The structural stability under strain is largely governed by maximizing the intraplane separation of the dipoles generated from rotations of the  $\text{FeO}_4$  tetrahedra. Understanding the change in atomic structure is important because it directs the electronic band gap in these materials. Thus, the atomistic understanding established by the DFT calculations provides key insight that may be used to design the electronic properties of thin-film materials in thin-film  $\text{SrFeO}_{2.5}$  and related compounds.

In FY 2016, we identified a universal strategy for realizing polar materials from centrosymmetric parent compounds through atomic-scale ordering of anion vacancies and cations, and we utilized it to realize a new polar material (see Figure 1). Remarkably, nearly all approaches to date that were aimed at creating noncentrosymmetric crystals relied on electronic-driven mechanisms that lead to cation off-centering (e.g., the second-order Jahn-Teller effect). We demonstrated digital and hierarchical control of anion vacancies. That adds a completely new dimension to material design as vacancies are usually viewed as detrimental to properties, whereas they are essential to our strategy. Static cation order can expand the available chemistries able to support electric polarizations. This approach is completely general and delivers a new tool for materials chemists to sculpt the structure and properties of materials at the level of atoms.

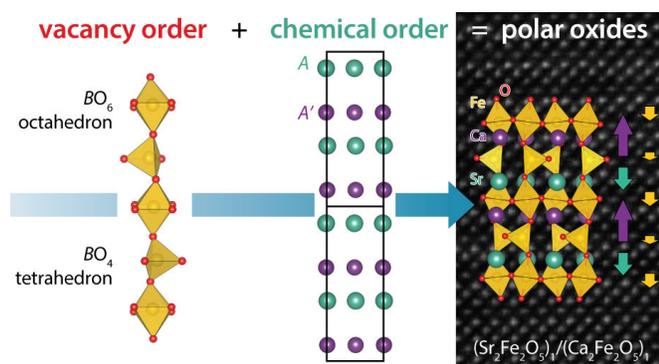


Figure 1. Illustration of the atomic-scale design principles used to realize polar crystals through oxide vacancy (defect) order. The combination of ordered oxygen vacancies with chemical cation order (shown on the left) results in a polar material (right) in the brownmillerite crystal structure predicted from density functional theory calculations, which is overlaid on a high-resolution STEM image of the laboratory-realized material. Arrows indicate the direction of local dipoles that sum to produce a net polarization in the crystal.

Specifically, we derived crystal-chemistry design rules, applicable to a wide array of cation chemistries, using symmetry (group theory) analyses. The design rules were further confirmed using DFT calculations on  $(\text{SrFeO}_{2.5})_n/(\text{CaFeO}_{2.5})_n$  superlattices, which illustrate how the layering of two centrosymmetric compounds leads to an acentric polar crystal. Working with experimental colleagues, we then synthesized the predicted superlattices by molecular beam epitaxy and characterized them with advanced synchrotron X-ray diffraction and aberration-corrected scanning transmission electron microscopy (STEM). The experimental work confirms the feasibility of controlling both anion vacancy and cation ordering at the atomic scale, while more importantly providing a direct measurement of the polar displacements, in excellent agreement with the DFT results.

The implications of this work extend well beyond ferrite superlattices, as the design strategy can be broadly applied to brownmillerite  $\text{ABO}_{2.5}$  compounds and related crystal families that exhibit layered vacancy structures. For example, these compounds are being studied intensely for oxygen reduction and evolution reaction chemistry, and our strategy offers an added control knob by which to tune material performance. Our approach retains the functional properties of the  $\text{ABO}_{2.5}$  constituent layers, thereby further allowing for multifunctional combinations of polar behavior with physical properties found in the chemically diverse brownmillerite crystal class, such as robust magnetic ordering for spintronics, semiconducting band gaps for photovoltaic applications, and ionic conductivity for battery and fuel cell technologies.

## PROPOSED FUTURE WORK

In FY 2017, the focus will be on formulating a quantitative theory of anion-deficient structural (polymorphic) stability based on the previous results, which will be required to reversibly move ions and induce electronic transitions. This objective will be achieved by (1) enumerating symmetries and structure types available to the tiling of two polyhedral units followed by (2) performing *ab initio* DFT calculations on  $\text{SrFeO}_{3.5}$  and  $\text{SrMnO}_{3.5}$ , which are anticipated to result from the tiling of the anion-deficient polyhedral motifs.

# Development of a Cryogenic Correlative Confocal Light Microscope (C3LM) for Integrated Imaging

2015-185-R1

Amanda Petford Long and Chris Jacobsen

## PROJECT DESCRIPTION

This project seeks to develop a cryogenic confocal light microscope (C3LM) for correlative studies of soft and hard materials under vacuum. The microscope will be configured with an in-vacuum microscope objective (that is maintained at room temperature) and an out-of-vacuum confocal microscope head. A cryo-robot will be used for sample exchange. Once developed, the C3LM will be used to study soft and biological materials and will provide much-needed microscopic capabilities for the cryo-analysis of these materials. Using the same cryogenic sample handling system as is used for scanning X-ray ptychography and fluorescence microscopy (XRF) at the Advanced Photon Source at Argonne will allow us to combine visible light fluorescence and emission microscopy with X-ray microscopy studies of the same specimen. Visible light fluorescence provides information about molecules with chemically specific binding affinities, while X-ray ptychography provides structural views down to a resolution of 20 nanometers. XRF offers a means of imaging trace metal concentrations independent of specific chemical binding affinities.

## MISSION RELEVANCE

This C3LM is relevant to DOE's mission in science by enabling studies of soft materials, quantum devices, and biological and environmental science specimens. The microscope will contribute to Argonne's emerging efforts in brain connectomics (an area to be supported by DOE's Offices of Biology and Environmental Research [BER], Basic Energy Sciences [BES], and Advanced Scientific Computing Research [ASCR]) and to a bioimaging program aimed at exploring microbial communities in soil (an area supported by BER). The instrument will also contribute to the APS upgrade project (supported by BES) by permitting exploration of the effects of X-ray irradiation on samples under various cryogenic conditions.

## RESULTS AND ACCOMPLISHMENTS

The project was awarded in September 2015. In that month, we developed a design and evaluated commercial components for possible use. We then acquired the confocal microscope and some components of the-vacuum micropositioning system, along with some associated hardware.

In FY 2016, we obtained additional components such as the robotic specimen handling system, vacuum valves, pumps, and interlock control hardware. The mechanical design of the vacuum chamber has neared completion for final system assembly and commissioning. The confocal microscope is expected to provide a transverse spatial resolution of better than 0.3 micrometers, with sensitive detection of visible light fluorescence from a selected depth plane with a resolution of better than 3 micrometers. It should allow acquisition of a three-dimensional image stack in less than 10 minutes.

## PROPOSED FUTURE WORK

FY 2016 was the final year of this LDRD project. APS support will enable equipment acquisition for completing and commissioning the C3LM. We hope to use it for initial studies in two areas. One will involve looking at synapses in hippocampal neuron cultures; the objective will be to understand the relationship between total zinc as measured by XRF and visible light confocal fluorescence images of zinc bound to molecular labels (there is reason to believe that tight molecular binding of zinc to enzymes such as superoxide dismutase can make zinc invisible to molecular fluorophores; by comparing total zinc measurements with XRF, and visible fluorescence reporters for zinc in C3LM, we can help resolve this question). Another use will involve carrying out basic studies of radiation damage in polymers such as those used in organic photovoltaics. By seeing the degree to which visible fluorescence dyes are deactivated or even removed (via mass loss) from these polymers as a function of radiation dose at cryogenic temperatures, we can better understand the ultimate resolution that we can reach in X-ray imaging studies of these materials and how that relates to the range of exciton transport at the boundaries of immiscible polymers.

# Supported Single-Site Catalysts for Selective Alkane Oxidation

2016-131-N0

Jeffrey C. Bunquin, Xing Chen, Massimiliano Delferro, Magali Ferrandon, Patricia Ignacio-de Leon, Rachel Klet, Cong Liu, Scott Nauert, SonBinh T. Nguyen, Justin Notestein, and Louisa Saveriede

## PROJECT DESCRIPTION

This project aims at producing platforms of single-site, multimetallic alkane-oxidation catalysts with enhanced selectivity for early-stage oxidation products, targeting the upgrading of natural gas. Specifically, we proposed to generate well-defined multimetallic active sites on a range of modified main-group oxides that allow for control and tuning of local catalyst environments. By depositing *molecular* metal cluster species on these supports, we can synthesize precisely organized multimetallic catalyst sites and use them to elucidate the critical factors that influence alkane oxidation reactivity and selectivity, including (1) active-site nuclearity and dimensionality, (2) active-site composition (homonuclear versus heteronuclear active sites), and (3) local electronic structures (spin and charge states). The effects of these active-site descriptors on surface oxygen reactivities will be studied and applied in the development of catalysts with improved reactivity and selectivity toward the key elementary steps involved in catalytic alkane oxidation (e.g., carbon-hydrogen [C–H] bond scission, carbon-oxygen [C–O] bond formation) and competing side reactions (e.g., C–C bond cleavage).

## MISSION RELEVANCE

This project is relevant to DOE's basic science mission and its goal of "understanding fundamental principles behind rational design of catalysts and deliberate control of chemical transformations." This multidisciplinary research project combines sophisticated synthetic chemistry with state-of-the-art chemical engineering strategies/principles for tuning catalyst activity, selectivity, and stability for alkane partial oxidation. From a broader perspective, the selective production of oxygenates from direct alkane C–H oxidation would provide an efficient strategy for the direct conversion of gaseous hydrocarbons into value-added chemicals, thus addressing challenges associated with valorization of natural gas hydrocarbon components.

## RESULTS AND ACCOMPLISHMENTS

Isolated metal ions and/or homonuclear bimetallic clusters were installed on modified silica (SiO<sub>2</sub>) supports via atomic layer deposition (ALD) and solution-phase deposition of molecular precursors to target supported metal ions known for catalytic oxidation activity (e.g., copper [Cu], cobalt [Co], iron [Fe], manganese [Mn]). The effect of promoter ions on catalyst reactivity, selectivity, and stability under hydrocarbon oxidation conditions (e.g., propylene to acrolein and propane to propylene) has also been investigated. Specifically, we have examined the effects of both Lewis acidic promoter ions (titanium [Ti], zirconium [Zr], zinc [Zn], aluminum [Al]) and redox-active promoters (chromium [Cr], Co, cerium [Ce]).

*Propylene Oxidation to Acrolein.* Gas-phase propylene oxidation studies were carried out to evaluate the intrinsic reactivity of M/SiO<sub>2</sub> catalysts (M = Cu, Fe, Co) as well as the effects, if any, of various metal promoters on selective oxidation. Notably, the presence of transition metal (e.g., Ti, Cr) and main group (Al) promoter ions can stabilize Cu/SiO<sub>2</sub> catalysts, which tend to undergo facile deactivation. A comparison of the promoter effect suggested that cationic early and mid-transition metal promoters enhance the catalytic performance in terms of acrolein yield: Ti<sup>4+</sup>, Cr<sup>6+</sup> > Zr<sup>4+</sup> > Co<sup>2+</sup>, Zn<sup>2+</sup>.

*Propane Oxidative Dehydrogenation to Propylene.* We also extended the bimetallic design strategy to the development of selective and stable catalysts for the oxidative dehydrogenation of propane to propylene. As in the propylene-to-acrolein transformation, we investigated the effect of promoter ions on the transition metal active sites that are known to be susceptible to sintering under oxidative conditions. Preliminary results suggested that in the presence of cationic promoters (M), dehydrogenation active transition metals (M') form heterobimetallic sites (M–M') with enhanced activity, selectivity, and sintering-resistance under oxidation conditions can be synthesized.

## PROPOSED FUTURE WORK

We are currently elucidating the mechanistic aspects concerning the use of promoter ions to stabilize catalytic-site ions in alkane partial oxidation. Specifically, spectroscopic characterizations will be carried out to reveal the active metal coordination environments and electronic properties. Density functional theory calculations are also under way to gain insights into the mechanism of stabilization and reactivity enhancement by metal promoter ions.

# Managing Emission and Thermal Absorption

2016-133-NO

Pierre Darancet, Maria Chan, Stephen K. Gray, Alex Martinson, Subramanian Sankaranarayanan, Richard D. Schaller, and Gary Wiederrecht

## PROJECT DESCRIPTION

The objective of this project is to simultaneously (1) advance our understanding of non-equilibrium heat generation and transport in nanoscale materials and (2) develop novel spectroscopic tools and theoretical models able to probe the fundamental interactions among electrons, photons, and phonons underlying thermal management in such systems. As the energy scales of the above interactions lead to a wide variety of phenomena, improving nanoscale thermal science requires a trifecta of capabilities: advanced characterization, materials synthesis, and multiscale modeling. Using such a synergistic approach, we aim to demonstrate how the new degrees of freedom offered by nanomaterials in controlling these interactions can lead to new paradigms in thermal management. Specifically, we will show how radiative heat can be engineered by plasmonic degrees of freedom, how non-equilibrium electron-phonon interactions lead to nonclassical heat transport pathways, and how the thermal conductivity of low-dimensional structures can be advantageously tuned by phonon-phonon interactions.

## MISSION RELEVANCE

This project is relevant to DOE's basic science mission. This effort addresses issues related to all five of the DOE-Basic Energy Sciences (BES) grand challenges, as it involves (1) control of the electron dynamics; (2) design of materials with tailored properties for energy harvesting; (3) properties emerging from the complex correlations between electronic and atomic degrees of freedom; (4) new nanoscale designs of electronic circuits with improved thermal management; and (5) understanding and characterization of non-equilibrium systems.

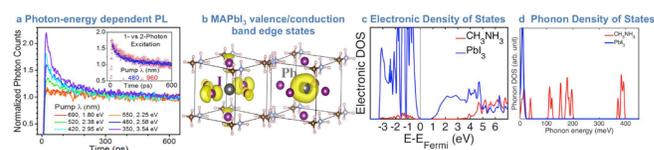
## RESULTS AND ACCOMPLISHMENTS

In FY 2016, we made significant progress on the three research thrusts of this program, specifically, on probing and understanding the role of photon-phonon, electron-phonon, and phonon-phonon interactions in thermal management. Specifically, we (1) predicted a spectrally selective thermal emitter, (2) demonstrated carrier-induced non-equilibrium distribution of phonons in hybrid

perovskites, and (3) found a low-band-gap 2D material with extremely low thermal conductivity. Moreover, we have developed the experimental infrastructure for probing electron-phonon interactions at the picosecond time scale and phonon-phonon interactions in 2D materials.

In photovoltaics, the energy in incident photons is partially lost because of hot carrier thermalization. Elucidating the dynamics of energy transfer between charge carriers and phonons is crucial for the understanding and management of such loss. We have investigated such dynamics in methylammonium lead iodide/chloride, which is a promising new photovoltaic in the class of organic-inorganic hybrid perovskites. We used time-resolved photoluminescence (PL), density functional theory (DFT) calculations, and non-equilibrium *ab initio* molecular dynamics simulations to investigate the time-dependent carrier recombination behavior. We found separation between the organic and inorganic sublattices in both electronic and phonon properties, and hence unusually long phonon equilibration time scales between the two subsystems, which give rise to photon-energy-dependent PL lifetimes.

Figure 1 shows the photon-energy-dependent PL behavior of methylammonium lead iodide (MAPbI<sub>3</sub>), the structure and band-edge state electronic density of MAPbI<sub>3</sub>, and the electronic and phonon densities of states of the components. Higher-energy photons excite the electronic states associated with the methylammonia organic component, which then excite a non-equilibrium population of high-frequency phonons via electron-phonon coupling.



**Figure 1. Unusual carrier thermalization in methylammonium lead iodide, which was studied using ultrafast photoluminescence (PL) and density functional theory.**

We developed a new Tersoff-type interatomic potential for single-layer tin, known as stanene, by training the parameters to reproduce DFT thermal and mechanical properties. Using this potential, we performed large-scale molecular dynamics simulations to study the temperature-dependent thermal conductivity of stanene monolayers. We found that the thermal conductivity is strongly dependent on the temperature, as a consequence of the increasing anharmonic contributions to phonon scattering. We also found that the temperature dependence of the thermal conductivity depends on crystalline orientation—

the thermal conductivity decreasing by 50% along the zigzag direction, and by 24% along the armchair direction when the temperature increases from 100 K to 300 K. Intriguingly, these preliminary results indicate that the thermal conductivity of this 2D material does not follow an expected  $1/T$  behavior.

Experimentally, a femtosecond simulated Raman spectroscopy capability is being developed. This technique, once operational, will enable us to examine electron-phonon couplings and phonon-phonon couplings with phonon-mode specificity, as well as with sufficient time-resolution that the early stages of non-equilibrium (down to  $\sim 50$  fs) can be examined. This measurement technique engenders a fair degree of complexity, but we now have all laser components present (this is a three-pulse method) and have measured stimulated Raman signals. We will specifically focus on the means to probe especially low-frequency phonons that no other research group in the world can currently examine in this manner. Accordingly, we have begun theoretical efforts to model electron-phonon interactions in 2D cadmium selenide (CdSe) nanoplatelets. With their controllable thicknesses and areas, and the tunability of the vibrational modes of their organic ligands, these semiconducting systems constitute an ideal test bed for understanding non-equilibrium phonon dynamics in nanoscale materials.

## PROPOSED FUTURE WORK

### Electron-Phonon Thrust

- We will improve existing thermostats for non-equilibrium ab initio molecular dynamics for simulations toward understanding thermalization effects in photovoltaics.
- We will obtain initial stimulated Raman signals using the nascent laser setup built during FY 2016.
- With this method in hand, we will pursue measurements of electron-phonon and phonon-phonon coupling in 2D semiconductor materials in colloidal suspension.
- We will use the electron-phonon and phonon-phonon scattering rates in CdSe nano-platelets, computed from first principles, to compute the non-equilibrium phonon dynamics in these systems.

### Photon-Phonon Thrust

- We will focus on delivering and testing a stable, high-performance, spectrally selective emitter structure based on the design principles derived in FY 2016. Our calculations indicate that it could improve the spectral efficiency for thermophotovoltaic (TPV) emission to a record-high 76%.

- We will produce and characterize novel alloys for use as thin-film absorbers, and experimentally characterize the emissivity and thermal emission properties of the resulting integrated TPV device.
- We will refine theoretically determined design parameters utilizing the experimentally determined optical constants of novel alloys.
- We will conduct device-level optimization and fabrication of emitter structures integrated with thermal sources.
- We will experimentally characterize the emissivity and thermal emission properties of the resulting thermal emitters.

### Phonon-Phonon Thrust

- We will demonstrate time-of-flight transient absorption detection of heat flow in thin noble metal films where extinction varies with heat, and demonstrate nonlinear absorption changes in phase-change materials, such as films of vanadium dioxide that undergo strong extinction changes as a result of a temperature-driven, metal-insulator phase transition.
- We will apply our optimized interatomic potential to the study of thermal conductivity in more exotic nanostructures, such as ribbons and nanotubes.



# LDRD PRIME – NATIONAL AND GLOBAL SECURITY

# Crime on the Urban Edge: Simulating the Interface between Transnational and Local Crime

2014-194-R2

Pamela Sydelko, Ignacio Martinez-Moyano, and Michael North

## PROJECT DESCRIPTION

The goal of this project was to create a systemic intervention framework whereby soft and hard system methods and computational system modeling are used to study very complex and highly interdependent (termed “wicked”) problems impacting many stakeholders. In this context, the term “intervention” refers to any action taken to improve a system or affect the problem. The overall goal of this research is to develop a mixed-method approach for systemically structuring wicked problems, anticipating system adaptation to intervention strategies, and designing interagency meta-organizations that are explicitly aligned to address wicked problems. This mixed-method approach falls within systems science theory of systemic interventions. The case study, Crime on the Urban Edge (CUE), demonstrates this systemic intervention approach that focuses on the interagency effort to combat converging transnational criminal groups and urban street gangs. The CUE framework engages with multiple local, state, and federal agencies involved in addressing this problem.

## MISSION RELEVANCE

The project is relevant to DOE’s science and energy missions. This systemic intervention framework can be applied to any class of complex problems where there are many interdependencies and multiple stakeholders and where interventions (purposeful actions to create change) can create 2nd- and 3rd-order (and several other) effects. This project is especially relevant to DOE’s research in systems and policy analysis, where energy policy and energy security problems are often complex and wicked, and to DOE’s research on the complex interplays of energy/water/environmental system elements.

## RESULTS AND ACCOMPLISHMENTS

In FY 2014, we conducted research and developed a methodology for this project based upon Soft Systems Science and the more hard-systems approaches such as systems dynamics modeling. We gathered subject matter experts and stakeholders together to conduct

a preliminary problem structuring session around transnational organized crime and gangs. This exercise formed the basis for our work going forward. We also began to explore the use of systems dynamics modeling to address the supply chain portions of the system.

The work during FY 2015 consisted of (1) selecting stakeholders for the study; (2) conducting individual problem structuring sessions with each stakeholder; (3) creating computerized system maps for each stakeholder and then merging them to create a common systems map; (4) writing the code for an anticipatory model called AnticipatoRy Complex Adaptive Network Extrapolation (ARCANE), which is a genetic algorithm system for automatically generating system dynamics models that represent potential system adaptations; and (5) experimenting with visualizing system maps using 3-D printing.

## Participatory Systemic Problem Structuring (Soft Systems)

The FY 2016 intervention required bringing stakeholders together to cooperatively and holistically define and structure the wicked problem. Problem structuring was conducted with nine additional stakeholders, and two group problem-structuring sessions were conducted at which system maps were created. All individual system maps were merged in a computer program and used for the two group problem-structuring sessions until a common system map was agreed upon.

## Systemic Organizational Design

The Viable System Model (VSM) was used to design an interagency meta-organization that was customized to directly address and adapt to the very complex and wicked problem of how to battle against converging transnational criminal groups and urban street gangs trafficking illicit drugs. Five of the twelve stakeholders participated in a VSM session, during which they were guided through the development of an example meta-organization that would be designed specifically to manage the wicked problem they had structured through the problem-structuring process described above.

## Anticipatory System Dynamics Model

Anticipatory modeling seeks to find possible new configurations for complex adaptive systems in advance of actual system adaptations. As part of the project, we developed two different anticipatory modeling approaches. System dynamics is widely used to model complex systems with embedded feedback loops. For the project, we developed a set of system dynamics models

of complex networks, especially anticipatory modeling of supply chains. In addition, we developed an automated method for generating candidate anticipatory models of complex networks using the system dynamics approach. The research question is whether or not genetic algorithms can be used as a method to automatically generate anticipatory models of complex networks.

## Agent-Based Behavioral Modeling of Ebola Spread in Chicago and Other Large Urban Areas

2015-169-R1

Charles Macal

### PROJECT DESCRIPTION

This project was initiated to understand the threat that the Ebola Virus Disease (EVD) outbreak in West Africa poses to U.S. national security and emergency preparedness. After the Ebola threat was addressed, several new diseases emerged with their own sets of questions concerning the threat to the U.S. population. These questions are of such a granular nature that they can only be addressed with large-scale computational models of disease transmission for entire populations. The objective of this project in FY 2016 was to generalize the Ebola-specific agent-based model (ABM) developed in FY 2015 to be applicable to a wide range of other diseases, including pandemic influenza and HIV/AIDS. The resulting model, the Chicago Social Interaction Model (chiSIM), has been successfully scaled to the city (Chicago), county (Cook), and Chicago metropolitan area. The chiSIM is also being tested to model the spread of information about healthcare programs in the community via socially connected agents, and used in testing intervention strategies for disease transmission through projects spawned by this project.

### MISSION RELEVANCE

In October 2014, the Secretary of Energy pledged his support to the President and to the Secretary of Health and Human Services in responding to the Ebola outbreak in West Africa and its consequences, under the President's One Government Initiative. The Secretary asked the national laboratories to develop technical proposals based on each of their unique capabilities. Argonne proposed adapting an existing infectious-disease model, the Chicago MRSA ABM, developed for Community Associated Methicillin-Resistant

*Staphylococcus aureus* (CA-MRSA), a virulent bacterial pathogen, to EVD.

### RESULTS AND ACCOMPLISHMENTS

#### An Ebola-Specific Agent-Based Model (ABM) Was Developed in FY 2015

In FY 2016 our research focused on implementing computer models to run faster and more efficiently and at larger scales. We developed new algorithms for efficiently partitioning and distributing models across distributed computing resources so that different parts of the model could be run in parallel. We also developed models of decision making behavior to model people's dynamic response to disease outbreaks and interventions. Finally, we developed a simplified compartmental model for Ebola that could be run much more quickly than the full agent-based model, but at less fidelity.

Accomplishments in FY 2016 included the following:

- Software and code were developed for ultra-large-scale simulation and analysis, including (1) logging of model events and results at the agent level, (2) statistical analysis of model-generated contact networks and characterization of the networks by their topological properties, and (3) visualization of contact networks.
- Workflows were developed for efficiently manipulating ultra-large-scale data sets and analyzing the topological properties of the networks generated by the dynamic behaviors of agents in the model. Figures 1 and 2 show networks generated by the model. Figure 1 shows the network of infections occurring in a given hour of the simulation. The network links infected individuals with the individuals who infected them. Figure 2 shows a contact network for a subset of individuals in the population during the course of a week. Individuals are represented as nodes. Contacts between individuals are represented as edges.
- A behavioral ontology was completed for EVD and other pandemic diseases. The ontology is the knowledge base for models of people's dynamic response to disease outbreaks and interventions. The dynamic response models will be included in the next implementation of the chiSIM model.
- An Ebola compartmental model was developed. This work is novel in its exhaustive exploration of the disease transmission parameter space using workflows and computational approaches. The compartmental model will be used to identify candidate solutions to explore in the large-scale ABM. Our results also suggest how fragile the healthcare preparedness system may be in responding to a pandemic event.

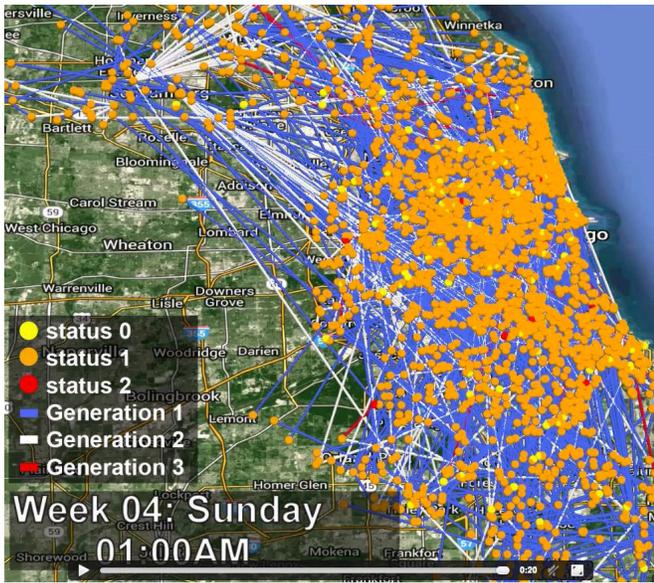


Figure 1. Disease transmission event traces showing the network of infections occurring in a given hour of the simulation. The network links infected individuals with the individuals who infected them.

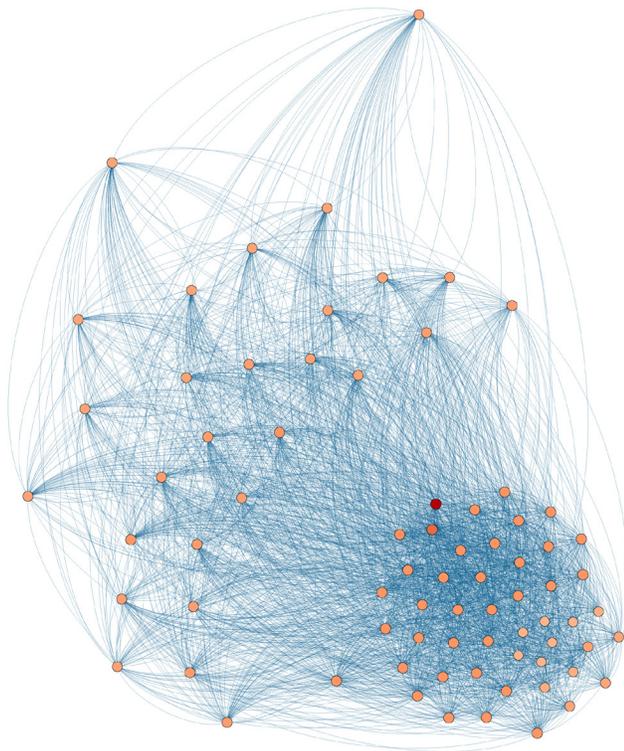


Figure 2. Contact network generated by chiSIM as a result of agent movement between places and activities in Chicago during the course of a week. Individuals are represented as nodes. Contacts between individuals are represented as edges.

## PROPOSED FUTURE WORK

In FY 2017, we propose the following task areas to improve aspects of disease modeling and the computational efficiency of the model:

### Disease Modeling

1. *Extend chiSIM to Model Disease Vectors.* Adding disease vectors (e.g., animals such as mosquitos) to chiSIM will allow much broader application of the model to a range of diseases carried by animal vectors.
2. *Extend chiSIM to Model Pandemic Influenza in Chicago.* Influenza outbreaks recur on an annual basis. There is a need to forecast the severity of influenza each flu season. We propose to apply chiSIM to model influenza within the chiSIM disease-modeling framework.
3. *Develop an Infectious-Disease Modeling Suite.* We propose to develop two additional disease models of less complexity than the ABM to complement chiSIM--a compartmental model (i.e., a differential-equation analytical model that is standard in the field) and a simple ABM with reduced structure in time and space that can be configured and run very quickly to answer urgent policy questions. These two models will be used to calibrate and inform the full ABM on promising areas of the parameter space that contain optimal intervention policies. The three models together will form a suite of models that span the key dimensions of the modeling space: (1) complexity/veridicality, (2) ease of use, and (3) timeliness in responding to urgent policy questions.
4. *Implement Behavioral Models for Infectious Diseases.* In FY 2016, we completed development of the behavior ontology that describes all human behaviors that have been observed in response to a pandemic or infectious-disease outbreak. We propose to encode the ontology into the chiSIM model and to develop code that can drive dynamic behaviors of agents in response to endogenous events occurring in the model.

### Computational Efficiency Development

1. *Update Synthetic Populations for Chicago Agents.* Synthetic populations are the basis for creating the population of agents in the ABM. The existing population data will be updated to the most recent data sets available, which are for 2010.
2. *Multi-Scale Modeling.* We propose to complete our process modeling capabilities (e.g., flows of patients and resources through hospitals) so they can be seamlessly integrated into area-wide population-based activity models.

# Integration of Multiple Infrastructure Dependencies and Interdependencies into Infrastructure Hazard Analysis

2015-177-R1

Megan Clifford and Charles Macal

## PROJECT DESCRIPTION

Models of infrastructure dependencies have typically used a sequential approach in which the outputs of one infrastructure model are inputs to another. This linear process limits the evaluation of interdependencies among multiple infrastructure systems and does not accurately reflect how infrastructure systems actually interact. To create more realistic models, we are using novel approaches to dynamically integrate infrastructure system models. We are also developing new models for infrastructure interdependency analysis where such models do not currently exist. The integrated modeling framework will be used to simulate interdependent infrastructure system behaviors and will be the basis for a virtual user facility (VUF) for infrastructure interdependency analysis. We are demonstrating the use of such models to indicate critical components of interconnected infrastructure systems, to simulate the process of cascading failures caused by infrastructure interdependencies, and to identify new ways to make infrastructure systems more resilient.

## MISSION RELEVANCE

Infrastructure dependencies and interdependencies create complexities that lead to emergent systemic risks. A disruption to a small number of nodes or transmission links in an infrastructure network can result in significant economic and physical damage on a local scale and can be propagated to regional scales in other infrastructure far removed from the point of the initial disruption. The methods developed as part of this project are relevant to national security and preparedness efforts at the Federal, state, and local levels. Federal departments include DOE and the U.S. Department of Homeland Security (DHS). DOE's 2015 Quadrennial Energy Review calls for an analytical framework and tools to assess the resilience and security of energy infrastructure. DHS's National Protection and Programs Directorate leads the national effort to protect and enhance the resilience of the nation's physical and cyber infrastructure.

## RESULTS AND ACCOMPLISHMENTS

Technical results in FY 2015 included 1) writing an automation algorithm to integrate the geospatial distribution of the infrastructure asset(s), the geospatial distribution of the hazard(s), and the failure criteria of each asset, 2) integrating EPfast and NGfast models using Data Centric Modeling/Simulation (DCMS), and 3) inputting the automated failure analysis into the integrated models. Our team also reformulated the model optimization solver, enabling numerical stability and faster solution time.

We also implemented optimization problems for EPfast and NGfast. Finally, we applied the developed methods to a hypothetical 64-bus electric grid set on the coast of Louisiana.

The technical work for this LDRD project focused on three areas in FY 2016:

1. Enhancing and developing new infrastructure models with capabilities to capture dependencies and interdependencies and to simulate cascading effects,
2. Building new modeling tools for scalable interdependent infrastructure models, and
3. Developing workflow tools that manage the distributed parallel computation of large-scale, dynamically interacting infrastructure models.

Our focus is on electric power, natural gas, telecommunications, water and wastewater, and transportation lifeline infrastructure. In FY 2016, research proceeded on modeling the interdependencies among these infrastructures. Accomplishments in FY 2016 in each area are noted below.

### Developing Interdependent Infrastructure Models

*Mathematical Model Formulation and Solution.* This task is to review the state of the art in infrastructure modeling from the perspectives of model formulation and solution. By comparing current modeling capabilities with key stakeholders' requirements for answers to infrastructure-related questions, we are able to identify research needs for new model formulations and solution algorithms.

- Implemented an electric power (EPfast) model and began implementation of a natural gas (NGfast) model in C++ code for High Performance Computing.
- Designed a prototype telecommunications model and began implementation in C++, to be completed in early FY 2017.
- Developed a concept paper on alternative approaches to modeling transportation systems and interdependencies.

- Reviewed the state of the art of models for water and wastewater systems. This activity is continuing into FY 2017.
- Formulated a novel “critical element detection” model for the EPfast system and coded it in the Julia language.
- Developed a set of model requirements in the form of unanswered stakeholder questions. Many stakeholder questions concerning infrastructure interdependencies cannot be answered by existing infrastructure models.
- Developed the Interdependent Infrastructure Modeling Matrix (IM2) to match the capabilities of and the requirements for new model formulations. The IM2 is a systematic framework for comparing models by their time-step resolution across all lifeline infrastructure. Alternative model formulations exist for each infrastructure; for example, AC, DC, and transient-effects models for the electric power sector. Alternative models can also be formulated on the basis of the alternative objectives included within the models, such as minimize cost, maximize reliability, minimize outage time, and maximize service to critical customers. New model formulations are also required to determine the optimal sequencing of infrastructure assets to restore normal functioning after a disruption.
- Systematically cataloged interdependencies for lifeline infrastructure at the component level. These infrastructure interdependencies will be the basis for incorporating infrastructure interdependencies into the infrastructure models in FY 2017.

*Stakeholder Decision and Behavior Modeling*

- Developed a taxonomy for the decision behaviors of infrastructure stakeholders.

*Data Accessibility and Analysis*

- Began an infrastructure data dictionary for infrastructure data items by data source and to link data items to model parameters for the various model formulations. In FY 2016, we identified relevant databases. We assessed data availability, accessibility, and restrictions with respect to use of the infrastructure data in the models. We determined that data issues are both technical and institutional in nature, and we developed solution paths for each.

**Building New Modeling Tools**

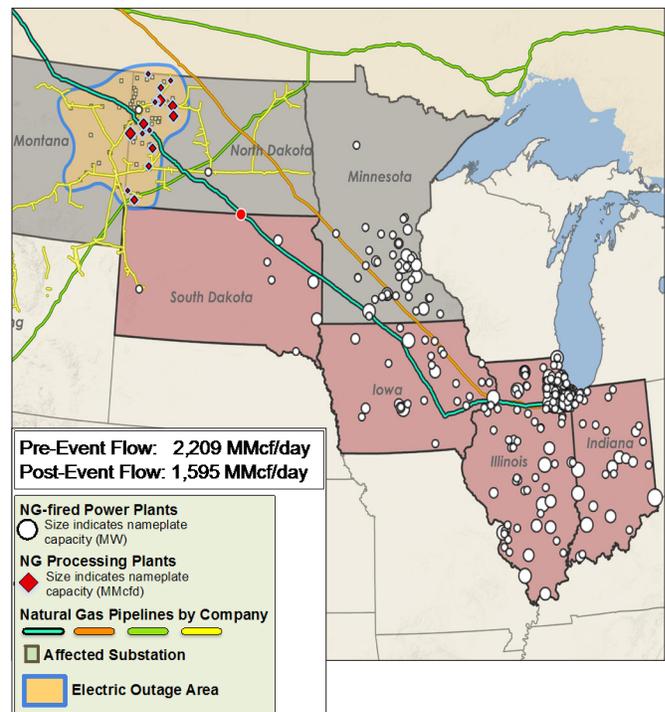
*Efficient Algorithms for Model Development and Scalability.* Scaling large-scale network models from local to regional to national contexts presents significant research challenges. New tools are required to efficiently specify complex models; new solution methods for solving hundreds of millions of equations are needed.

- Initiated work on PLASMO (Platform for Simulation and Modeling Optimization) for the efficient specification of interdependent infrastructure models.

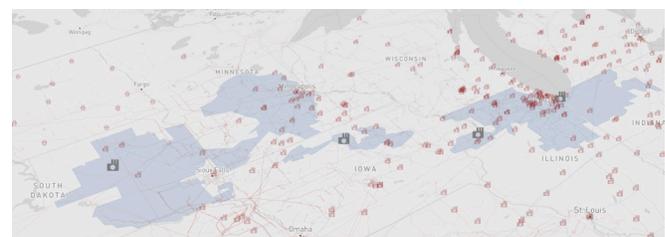
*Visualization of Infrastructure Interdependencies*

Summarizing and conveying complex interdependency information in an intuitive, interactive, and insightful way are critical to ensuring that model results can be interpreted efficiently and effectively by decision-makers.

- Explored alternative approaches to visualizing the results of infrastructure interdependency models (see Figures 1 and 2).
- Developed a visualization tool for visualizing dynamic infrastructure networks.



**Figure 1.** Case study in which a disaster triggers disruptions of electric power production along the U.S. northern border and impacts natural gas production, which reduces gas flow and causes power outages throughout several Midwestern states. (MMcf/d = one million cubic feet per day.)



**Figure 2.** Experimental visualization of model results showing propagation of a local disruption to regional effects on electric power and natural gas systems and service areas. The blue areas represent Local Natural Gas Distribution Companies’ service areas. The gray symbol represents a powered off natural gas power plant. The red symbols represent a powered on natural gas power plant. (Natural gas delivery is impacted given powered off power plants.)

## Developing Workflow Tools

*Workflows for Ensemble Modeling on High-Performance Computing (HPC) Platforms.* Using HPC resources, we developed workflows using Parallel Works, which is based on Swift/T, for running ensembles of simulation models.

- Established workflows for “N-1” analysis, in which individual infrastructure components are removed from the network, simulations are run for each case, and components are ranked according to their criticality and impact on resilience.

## PROPOSED FUTURE WORK

We will continue work in the following areas in FY 2017:

### Developing Interdependent Infrastructure Models

#### *Mathematical Model Formulation and Solution*

- Complete implementation of NG model (NGfast) and incorporate it into the workflow tool.
- Incorporate more sophisticated infrastructure models into the workflow tool.
- Develop dynamic coupling of EPfast and NGfast models in C++ and implement linkage into workflow.
- Explore alternative interdependent infrastructure model formulations and coupling strategies using the IM2.
- Complete implementation of telecommunications model prototype in C++. Determine linkages between telecommunications and other critical infrastructure.
- Explore the cyber connection in the telecommunications model.
- Design water and wastewater infrastructure models with interdependency linkages.

#### *Stakeholder Decision and Behaviors*

- Use the model capabilities documented in IM2, combined with the identified stakeholder requirements, to specify models that could fill the gap in answering infrastructure interdependency questions that cannot currently be answered.

#### *Data Accessibility and Analysis*

- Continue to assemble an infrastructure data dictionary for data items by data source, and link data items to model parameters across model formulations.

## Building New Modeling Tools

### *Efficient Algorithms for Model Development and Scalability*

- Continue development of PLASMO to make it a more robust platform.
- Implement new physics-based infrastructure models in PLASMO.
- Explore the use of PLASMO vs. DMNetwork for large-scale solution of infrastructure models, and develop strategy for determining when these tools are most appropriate to use.

### *Visualization*

- Continue to explore novel technical approaches to visualizing the results of interdependent infrastructure models.

### Developing Workflows for Dependency and Interdependency Modeling

#### *Workflows for Ensemble Modeling on HPC Platforms*

- Develop a prototype VUF for interdependent infrastructure modeling and analysis.
- Develop workflows and model linkages for using the models and databases as they are incorporated into the VUF.

## New <sup>6</sup>Li-Rich Semiconductors for Neutron Detection

2016-123-N0

Mercouri G. Kanatzidis and Duck Young Chung

### PROJECT DESCRIPTION

This project focuses on the design, synthesis, and characterization of lithium (Li)-containing semiconductors to realize an efficient, solid-state neutron detector based on <sup>6</sup>Li. In the first year, we primarily targeted three families of compounds for synthesis and for evaluation of their physical properties relevant to efficient neutron detection: lithium pnictide binaries and ternaries and lithium chalcogenide materials. Scintillator based devices can have good thermal neutron detection efficiency; however, their ability to achieve adequate neutron/gamma discrimination is limited. Additionally, because of the required photomultiplier tube, the ruggedness can be poor and the required operating voltage is large. These two factors significantly impede the field deployment of these devices for certain applications. In contrast,

semiconductor based devices can have a low operating voltage, small device footprint and excellent stability.

## MISSION RELEVANCE

Solid-state neutron detectors that are highly efficient, small, lightweight, portable, and low-cost are of high importance in U.S. national security efforts to detect and prevent the proliferation of illicit nuclear materials. This project is therefore relevant to DOE's nuclear security mission. The materials for these devices are subject to stringent requirements, as they must efficiently absorb thermal neutrons and transport the generated charge for detection. To date, only one compound has been investigated in this regard: lithium indium selenide ( $\text{LiInSe}_2$ ), which contains the scarce element indium and requires a challenging experimental procedure because of the high reactivity of lithium. Therefore, there exists the opportunity to vastly expand the portfolio of Li-containing semiconductors and realize efficient, low-cost detectors through materials exploration and design. Lithium-based semiconductors are underexplored in the literature, and those with our target properties (i.e., moderate band gaps and good charge transport) may also be promising for gamma-ray detection and optoelectronics. Furthermore, the synthesis of lithium-containing compounds is nontrivial—especially with regard to crucible selection—and requires the development of novel growth techniques. Thus, the results of this project are expected to be of broad interest, with long-lasting impact on detector applications and other fields.

## RESULTS AND ACCOMPLISHMENTS

In a semiconductor neutron detector, bulk materials composed partially of one or more neutron reactive elements can yield devices by affixing conductive contacts on opposite sides. The device has a voltage applied across the bulk material and neutrons can be absorbed directly within the body of the detector, whereupon the resulting charged particle reaction products are released directly within the detector itself.

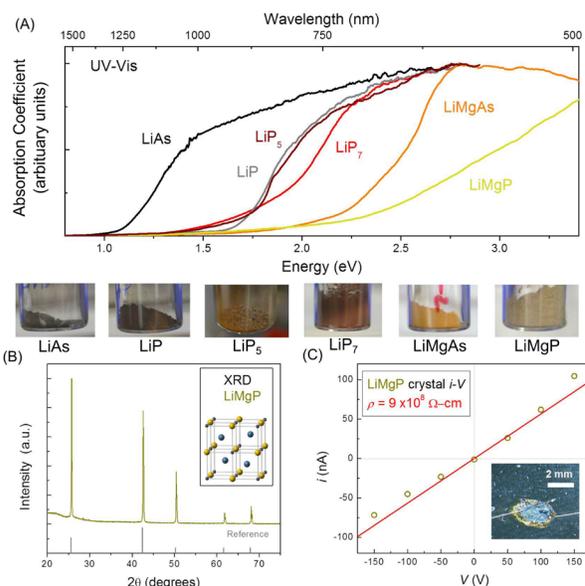
A good neutron absorbing semiconductor material can generate over  $10^6$  holes and electrons per neutron absorbed. This can be detected directly without further amplification. But standard device semiconductors do not contain a high enough density of neutron-absorbing nuclei to give reasonable neutron detection efficiency.

The key feature of lithium in the materials in this project as possible neutron detectors is that the lithium has a large neutron capture cross section [940 barns (b)] for thermal neutrons [energy of 0.0259 electron volts (eV)]. The interaction of a neutron with a  ${}^6\text{Li}$  atom is given by

${}^6\text{Li} + n \rightarrow {}^3\text{H} (2.73 \text{ MeV}) + \alpha (2.05 \text{ MeV})$ . The high energy reaction products emitted from the reaction lead to greater ease of detection.

For efficient operation, the semiconductor should have the following features: (a) sufficiently large band gap (at least 1.6 eV) to minimize dark current (see below) but provide a high conductivity change at room temperature (b) suitable charge carrier transport parameters (mobility-lifetime product,  $\mu\tau$ ) of holes or electrons of higher than  $10^{-5} \text{ cm}^2/\text{V}$ , and (c) availability of high-density crystal samples of adequate dimensions for high absorption. Conventional device semiconductors (based on doped Si, Ge) do not contain a high enough density of neutron-absorbing nuclei to give reasonable neutron detection efficiency. The promising materials should be high quality single crystals without mid-gap electronic states and defects that may act as carrier traps.

Within the given materials criteria above, we identified and synthesized lithium phosphides and lithium arsenide,  $\text{LiP}_7$ ,  $\text{LiP}_5$ , and  $\text{LiP}$  and  $\text{LiAs}$ , as candidate binary pnictide compounds using alumina or niobium crucibles. These materials exhibit a wide range of band gaps spanning the visible region (Figure 1A) and melt at relatively low temperatures ( $<700^\circ\text{C}$ ). A desirable band gap ( $\sim 1.8 \text{ eV}$ ) combined with stability in air makes  $\text{LiP}_5$  a standout candidate, and it will be targeted for growth of large single crystals.



**Figure 1. (A)** Ultraviolet-visible (UV-Vis) spectra of the synthesized compounds. The material's band gap is estimated by the extrapolated onset of the absorption slope on the energy axis.; **(B)** X-ray diffraction pattern of  $\text{LiMgP}$  we prepared showing phase purity compared with the calculated diffraction pattern; and **(C)** 2-point current-voltage characteristics of a  $\text{LiMgP}$  crystal (inset:  $\text{LiMgP}$  sample with carbon contacts).

In addition, the ternary pnictide compounds LiMgPn (Pn = P, As, and antimony [Sb]) were successfully synthesized (Figure 1B). The P and As analogues were found to have appropriate band gaps (Figure 1A), but the band gap of LiMgSb was too narrow ( $< 0.7$  eV). Small crystals of LiMgP were obtained during synthesis, and resistivity measurements confirm the insulating nature of the material (Figure 1C), which is promising for future study. For efficient operation at room temperature, the detector materials must have a wide enough band gap ( $>1.6$  eV) to avoid dark current and consequent high noise. Our experiments showed that LiMgP and LiMgAs react with typical crucible materials at the temperatures required for crystal growth; therefore, we will utilize boron nitride or vitreous carbon crucibles for growing large single crystals.

To overcome the air sensitivity common to many of the pnictide compounds, we also targeted lithium chalcogenide ternaries. The compounds  $\text{Li}_2\text{SnS}_3$  and  $\text{Li}_2\text{SnSe}_3$  are being synthesized using various crucible materials (e.g., alumina, niobium, and graphite).

### PROPOSED FUTURE WORK

We will continue to explore Li-containing metal chalcogenides and phosphides to search for the best-performing candidates for neutron detection. This work also involves developing experimental processes for synthesis, purification, and crystal growth of the materials. Characterization of all materials will follow and will be fed back to the experimental process to further improve the quality of the materials, which will enable us to down-select the best-performing candidate materials through the synthesis and growth process for large-scale and high-purity single crystals.

## A Novel Interferometric Terahertz Phase Imager (THz-PI) for National Security Applications

2016-136-NO

Shaolin Liao and Thomas Elmer

### PROJECT DESCRIPTION

We are developing a novel interferometric terahertz phase imager (THz-PI) to support the strategic mission of national and homeland security. Terahertz waves, long considered a frequency gap (300 GHz to 30 THz), can penetrate a variety of materials and thus play an important role in national and homeland security applications, such as airport security screening, explosives identification, and mail package scanning. The THz-PI can obtain a terahertz-phase image using only one interferometry intensity measurement. It is a simple, low-cost, in-phase/quadrature (I/Q)-mixerless THz-PI based on the Michelson-type optical interferometry technique. It is novel in that it employs a terahertz modulator as a reference beam to interfere with the reflected sample signal. Both amplitude and phase can be obtained through exploring relations among different frequency bands of the measured interferometry intensity signal. These frequency bands include the band centered at DC (zero center frequency base band, FB-0), that centered at first reference frequency harmonics (FB-1), that centered at second reference frequency harmonics (FB-2), and so forth.

### MISSION RELEVANCE

This project supports DOE's national security mission. The THz-PI is important in many national and homeland security areas such as airport screening, explosive spectroscopy, and mail/parcel scanning. Interested parties include government agencies such as the Transportation Security Administration (TSA), DOE's National Nuclear Security Administration (NNSA), the U.S. Department of Homeland Security (DHS), and the U.S. Department of Defense (DOD).

### RESULTS AND ACCOMPLISHMENTS

In our first year, we achieved the following: (1) We developed terahertz-phase extraction Matlab code based on the Levenberg-Marquardt (LM) nonlinear fitting algorithm. Figure 1 shows the phase extraction result from a simulated interferometry intensity signal with a signal-to-noise ratio (SNR) of 10. (2) We assembled a single-

pixel THz-PI model with a sub-terahertz multiplier source (40 to 120 GHz) and a broadband pyroelectric terahertz detector (Figure 2). (3) We measured the dielectric constants of materials. Figure 2 shows the experimental result of a 1-mm-thick z-cut quartz slab and its fitting with the theoretical calculation, giving a dielectric constant of  $\epsilon = 2.107$ .

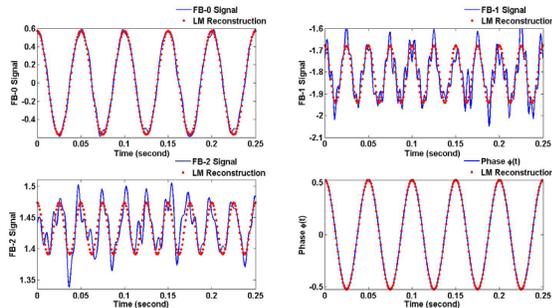


Figure 1. Matlab simulation with LM fitting algorithm for a simulated interferometry signal with SNR = 10. Different frequency bands signals and terahertz phases (blue lines) and their corresponding LM fitting results (red dots) are shown. Top left: frequency band centered at DC (FB-0). Top right: frequency band centered at first reference frequency harmonic (FB-1). Bottom left: frequency band centered at second reference frequency harmonic (FB-2). Bottom right: terahertz phase.

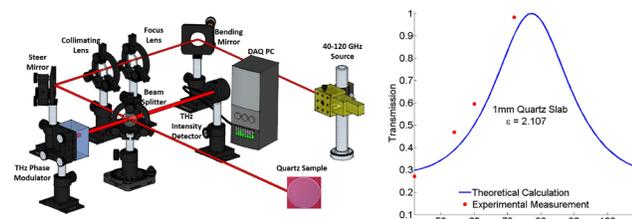


Figure 2. Left: experimental setup of a 40- to 120-GHz model for phase measurement of the object under imaging; the incidence beam is split into the sample object beam and the reference beam, the reference beam is modulated by a terahertz modulator, and the sample object beam is reflected from the sample; both beams combine and the intensity is measured by a terahertz intensity detector. Right: experimental measurement of a 1-mm-thick, z-cut quartz slab and its fitting with the theoretical calculation, giving a fitting dielectric constant of  $\epsilon = 2.107$ .

## PROPOSED FUTURE WORK

We will carry out the following tasks in FY 2017: (1) extend the THz-PI model device to a higher frequency range from 0.22 to 0.325 THz; (2) extend the single-pixel THz-PI to a two-dimensional THz-PI; (3) conduct laboratory tests of more materials; and (4) try different types of THz detector as well as THz interferometry architectures to optimize the THz-PI.

# Understanding the Resiliency of Interdependent Infrastructures Using Multiscale Agent-Based Simulation

2016-156-NO

Charles Macal and Diane Graziano

## PROJECT DESCRIPTION

Infrastructure dependencies and interdependencies create complexities that lead to emergent systemic risks. A disruption to a small number of nodes or transmission links in an infrastructure network can result in significant economic and physical damage on a local scale, which can be propagated to regional scales in other infrastructure assets far removed from the point of the initial disruption. At the physical level, an infrastructure can be viewed as a network in which commodities flow according to the laws of physics. For example, electric power flows through the power grid as defined by Kirchoff's Laws for current and voltage; natural gas flows through pipelines, constrained by pressure, volume, and mass relationships. Interdependent infrastructure assets can be thought of as networks linked together at specific points of dependencies and sharing common components. Lifeline infrastructure is increasingly interdependent, leading to the potential for widespread, cascading failures when particular components in any individual infrastructure network are affected.

The agent-based modeling (ABM) approach is novel in that it allows the decision-making behaviors of producers, consumers, and operators to be explicitly incorporated into the physical processes of the infrastructure. Although some work on infrastructure modeling has been performed, to the best of the authors' knowledge, no fine-grained dynamic, agent-based models or ABMs of the infrastructure of the type proposed here have been previously developed.

Yet infrastructure assets do not operate, maintain, expand, or fix themselves. Managing the growing interdependencies among infrastructure assets requires not only a grasp of the physics involved, but also an understanding of the decision-making behaviors of owners, operators, producers, consumers, transporters, and distributors, etc. Achieving this understanding is challenging because the markets are complex, nonlinear, self-organizing, emergent, and sometimes chaotic. Traditional tools, such as linear programs, are ill-suited to representing these dynamics. We propose

to take a complex adaptive system (CAS) approach, based on agent-based modeling, that can represent both the physics and the decision-making agents of interdependent-infrastructure assets. In our modeling approach, the physical infrastructure assets are each represented as a layer of networked physical components connected to an industry-specific decision-making layer. The decision-making layer contains the decision-making agents for operating and using the infrastructure (see Figure 1 for an example within the electric power and natural gas infrastructure assets). As currently envisioned, the ABM will focus on these five key infrastructure sectors and their interdependencies: electric power, natural gas, petroleum, transportation, and water.

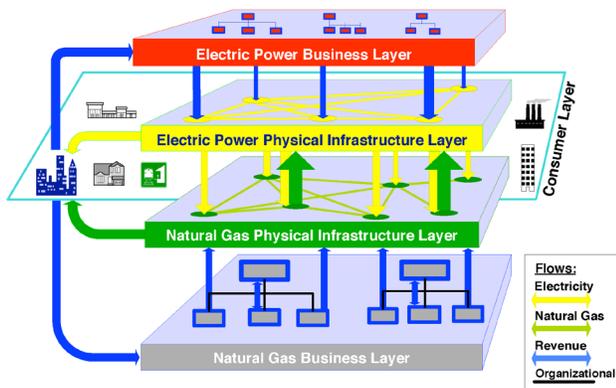


Figure 1. Model of Interdependent Decision-Making and Physical Infrastructure.

## MISSION RELEVANCE

The project is relevant to DOE’s mission in energy. Energy infrastructure resiliency has recently emerged as a high-priority issue for the U.S. Government. In 2015, DOE issued a Quadrennial Energy Review (QER) focused on the infrastructure for energy transmission, storage, and distribution, with the goal to “identify the threats, risks, and opportunities for U.S. energy and climate security, enabling the Federal Government to translate policy goals into a set of analytically based, clearly articulated, sequenced and integrated actions, and proposed investments.”

A key recommendation articulated in the QER is to: “develop comprehensive data, metrics, and an analytical framework for energy infrastructure resiliency, reliability, safety, and asset security. DOE, in collaboration with the U.S. Department of Homeland Security (DHS) and interested infrastructure stakeholders, should develop common analytical frameworks, tools, metrics, and data to assess the resiliency, reliability, safety, and security of energy infrastructures.”

This project directly addresses the energy infrastructure security issues raised in the DOE reports by developing a multiscale ABM for understanding and improving the resiliency of interdependent energy and lifeline infrastructures. Resilience for a socio-technical system is defined here as: “the ability to adapt to changing conditions and prepare for, withstand, and rapidly recover from disruption.” The methods developed as part of this project are relevant to national security and preparedness efforts at the federal, state, and local levels. Federal departments include DOE and DHS. The *2015 Quadrennial Energy Review* called for an analytical framework and tools to assess the resilience and security of energy infrastructures. The DHS National Protection and Programs Directorate leads the national effort to protect and enhance the resilience of the nation’s physical and cyber infrastructure.

## RESULTS AND ACCOMPLISHMENTS

In FY 2016, the technical work for this project focused on developing new infrastructure models with the capabilities to include decision-making behaviors by infrastructure operators and stakeholders. The lifeline infrastructure sectors we are focusing on are electric power, natural gas, telecommunications, water and wastewater, and transportation. In FY 2016, research proceeded on modeling the interdependencies among these infrastructure systems.

Accomplishments in FY 2016 in each area are noted below. In addition, Argonne led a Technical Exchange (TechX) meeting for the purpose of establishing the state-of-the-art in interdependent infrastructure modeling.

### Developing Interdependent Infrastructure Models

#### *Mathematical Model Formulation and Solution*

- Developed a set of model requirements in the form of unanswered stakeholder questions. Many stakeholder questions concerning infrastructure interdependencies cannot be answered by existing infrastructure models. These questions are the basis for developing new model formulations with the capabilities to answer these questions.
- Systematically cataloged interdependencies for lifeline infrastructure assets at the component level based on the unique expertise of Argonne subject matter experts. These infrastructure interdependencies will be the basis for incorporating infrastructure interdependencies into the infrastructure models in FY 2017.

*Stakeholder Decision and Behavior Modeling*

Developed a taxonomy for the decision behaviors of infrastructure stakeholders. Little research exists on the kinds of decisions that infrastructure stakeholders make during normal operations in response to a disruption and to restore systems to normal operations.

*Data Accessibility and Analysis*

Began an infrastructure data dictionary for infrastructure data items by data source and to link data items to model parameters for the various model formulations. The data task is driven by the need for infrastructure data by the models. In FY 2016, we identified relevant databases. We assessed data availability, accessibility, and restrictions with respect to use of the infrastructure data in the models. We determined that data issues are both technical and institutional in nature, and developed solution paths for each. We identified the need to acquire or develop synthetic data sets that we can use to exercise our precursor infrastructure models.

**Technical Leadership***Technical Exchange (TechX)*

Organized and hosted a Technical Exchange for the purpose of surveying available models and capabilities for dependency and interdependency modeling. More than 25 representatives from 10 research organizations participated in the one-day exchange. Five needs for advancing infrastructure dependency and interdependency modeling were identified:

1. Better define end-user requirements.
2. Identify data needs for modeling.
3. Explore development of integrated modeling approaches and architectures.
4. Deliver usable models to users that produce relevant information in the time frame it is needed.
5. Foster collaboration among the R&D community.

## Fabrication and Testing of a Borosilicate Microchannel Plate Thermal Neutron Detector with Optimized Geometry

2016-173-N0

Robert Wagner, Patrick De Lurgio, Jeffrey W. Elam, Anil Mane, Howard Nicholson, Michael Pellin, Jingbo Wang, and Lei Xia

**PROJECT DESCRIPTION**

Our project addresses the detection of nuclear materials via the neutrons produced by fissile materials such as uranium and plutonium. For many years,  $^3\text{He}$ -based detectors have been the standard for detection of thermal neutrons. However, the supply of  $^3\text{He}$  has been depleted and the cost has risen significantly.

A less expensive alternative to  $^3\text{He}$  is  $^{10}\text{B}$ , which also absorbs thermal neutrons efficiently. To allow the daughter products ( $^4\text{He}$  and  $^7\text{Li}$ ) of  $^{10}\text{B}$ -neutron interactions to escape to the sensing medium,  $^{10}\text{B}$  is typically incorporated as a gaseous boron compound or as a thin layer on the surface of the detector; both of these have low  $^{10}\text{B}$  density and, therefore, a low probability for neutron interaction. We seek to develop an improved  $^{10}\text{B}$ -based neutron detector by incorporating  $^{10}\text{B}$  into microchannel plates (MCPs), which—even for a 100- to 300-micron thickness—have a high probability of absorbing neutrons and allowing the daughter nuclei to escape into the MCP pores, hit the pore walls, and produce electrons that are gain-multiplied to produce a signal. With pores on the order of 10 microns in diameter and pore walls  $\sim 1$  micron thick, the MCP has a very high open-area ratio (fraction of entire volume occupied by empty pores). The  $^{10}\text{B}$  in the MCP wall structure allows most thermal neutrons to be absorbed, but presents minimal material for gamma-ray interactions, which constitute a background. The fine pore structure also allows the neutron interaction location to be determined with millimeter or better precision. In our project, we have pursued two paths for the development of  $^{10}\text{B}$ -enriched MCPs: 1) fabricate MCPs using borosilicate glass containing  $\sim 20\%$  fraction of  $^{10}\text{B}$ -enriched boron oxide and 2) incorporate  $^{10}\text{B}$  into a 3-dimensional (3D)-printed MCP substrate.

We are using Pu-Be neutron and  $^{60}\text{Co}$  gamma-ray sources available at Argonne to demonstrate neutron detection and measure the sensitivity to gamma rays. A  $^3\text{He}$  gas tube detector is used as a comparison standard.

## MISSION RELEVANCE

Thermal neutron detection is relevant to DOE's mission in national security, with applications such as detecting clandestine fissile nuclear materials, and for research applications such as studying material structure using neutron scattering. For security applications, a portable detector with an overall efficiency of at least 75% is required. This efficiency would match the typical efficiency of  $^3\text{He}$ -based detectors. The thin profile and light weight of the glass MCP detector package make this a potentially field-deployable solution for neutron detection. The potential cost for mass production of  $^{10}\text{B}$ -loaded MCPs could be much less than the cost of  $^3\text{He}$  usage.

## RESULTS AND ACCOMPLISHMENTS

During the first year of the project, we established a neutron and gamma-ray testing setup, demonstrated neutron detection with an existing borosilicate MCP photodetector, fabricated thicker MCPs (5-mm- and 10-mm-thick plates), and began testing the ability to 3D-print capillary structures. The test setup uses an existing Pu-Be neutron source, a  $^{60}\text{Co}$  gamma-ray source, a  $^3\text{He}$  gas tube for calibration (see Figure 1), and a multichannel analyzer to produce the energy spectra of the detected signals. The High Energy Physics Division's MCP photodetector group has been producing small-format (6-cm  $\times$  6-cm active area) photodetectors with pairs of 1.2-mm-thick MCPs for gain multiplication. The standard  $\text{B}_2\text{O}_3$  fraction of about 13% in the glass and the use of naturally abundant boron gives a  $^{10}\text{B}$  fraction of 1% or less in the detector. Nevertheless, we were able to demonstrate an enhancement above the background when the detector was exposed to the neutron source (see Figure 2). Because the gain produced in the MCPs depends on the depth at which the neutron is captured, a well-defined neutron peak is not produced in the MCP photodetector. To obtain higher efficiency and possibly produce a neutron peak, we functionalized thicker glass capillary arrays into MCPs. These will be studied in a vacuum test chamber that allows easier operation of MCPs than incorporating them into a hermetically sealed detector package.

We are now turning our attention to developing methods of 3D-printing MCPs for use in the thermal neutron detector.

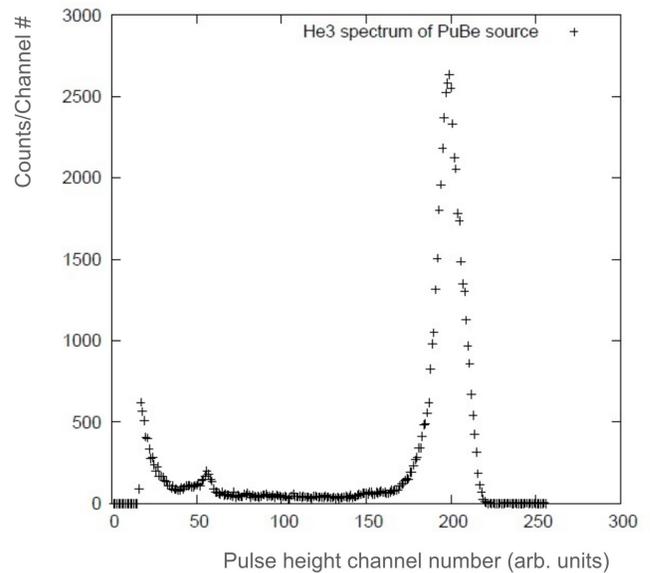


Figure 1. Pulse height spectrum produced by neutron source in  $^3\text{He}$  standard tube.

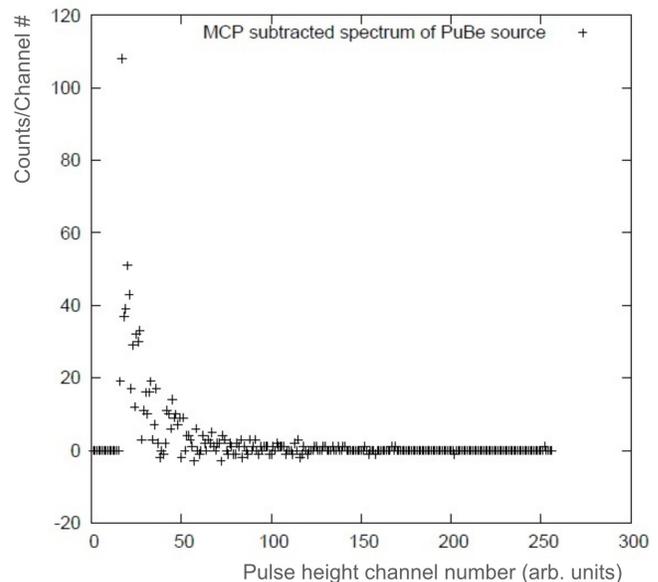


Figure 2. Background subtracted spectrum observed with MCP photodetector exposed to neutron source.

## PROPOSED FUTURE WORK

We will concentrate our future work on studying the 3D-printing option, which has been the subject of a recent invention disclosure.



# LDRD PRIME – NEXT GENERATION COMPUTING

## Developing an Integrated Sensor Network for Science

2014-160-R2

Peter Beckman, Nicola Ferrier, Yuki Hamada, Katarzyna Keahey, and Rajesh Sankaran

### PROJECT DESCRIPTION

The availability of small, inexpensive, networked sensors is dramatically changing many data-driven science domains. At Argonne, modeling urban environments, terrestrial ecosystems, and soil biology are just a few research areas that are using sensors. However, several computer science challenges must be overcome: (1) the design of a secure and extensible sensor computing platform capable of *in situ* data processing; (2) the design of an architecture that supports data movement, caching, and verification between the sensor and the computing platform; and (3) a system design that can support local autonomous actuation and control.

### MISSION RELEVANCE

Advanced sensors, computational science simulation and modeling, and climate science are all key parts of DOE's mission, especially as that mission pertains to Advanced Scientific Computing Research (ASCR), Climate and Environmental Sciences Division (CESD), and Energy Efficiency and Renewable Energy (EERE). Effectively leveraging these to provide near-real-time data for predictive simulations will enable DOE to better understand energy usage, infrastructure threats, and our environment. Furthermore, DOE has started a "Smart City" initiative, and Argonne is well positioned to deploy our sensors as part of that initiative in urban environments.

### RESULTS AND ACCOMPLISHMENTS

In 2014, we completed the first iteration of Waggle. The system is comprised of two components: the Waggle Field node and Waggle Cloud infrastructure. The Waggle Field node affords a modular, scalable, fault-tolerant, secure, and extensible platform for hosting sensors and actuators in the field; supports *in situ* computation; and works in concert with the Waggle Cloud infrastructure. The Waggle Cloud infrastructure was designed to be scaled to several hundreds of thousands of Waggle nodes. This capability would support real-time scientific simulation and analysis based on data sensed by Waggle nodes, extend methods for inter-node communication and data exchange, and serve raw and processed data to end users and applications running on other high-performance computing resources. Test nodes were deployed indoors and tested outdoors for precision, accuracy, and robustness.

In 2015, we created and deployed a completely integrated sensor node. These nodes were tested in real urban environments at the University of Chicago campus and are currently sending data (see <http://www.wa8.gl>). Our team also assembled a desktop Waggle unit that can be used in the lab for testing, and we have deployed Waggle at the Indian Boundary Prairie near Chicago to study a natural ecosystem.

In 2016, we worked on extending the computer vision and audio processing capabilities of the Waggle Field Node, calibrating the sensor data, and improving resilience and data archiving capabilities. The Waggle Field Node uses a standalone single-board computer (Odroid XU4) to collect images from two cameras and a microphone. This "edge computer," or ability to process data *in situ*, directly in the sensor node, is unique to Waggle. Over the summer, we explored two approaches for computer vision: OpenCV and Caffe. OpenCV is a computer vision library from Intel. With it, simple tasks such as face recognition are possible. We designed a Waggle plug-in module that could recognize faces to demonstrate this capability. Caffe is a deep-learning framework from UC Berkeley that uses machine learning and supports image classification. With it, we explored classification of images that included water on city streets. These capabilities, which are still expanding, allow Waggle to process data at the edge of the computing platform.

The team also worked with Argonne's Environmental Science Division to design calibration procedures for sensors. We expect that Waggle nodes will be test-deployed at the Atmospheric Radiation Measurement (ARM) Southern Great Plains facility. As we continue to improve calibration, we will be able to understand how deploying many inexpensive Waggle nodes can supplement the traditional environmental sensing strategy of deploying relatively few, large, but expensive nodes.

The team also designed and built new resilience mechanisms for the WagMan controller that is part of the core Waggle design. The WagMan controller can detect when a single-board computer (such as the Odroid XU4) fails and can automatically reboot the node. It can also detect whether or not the node has corrupted the flash storage that is used for Linux and then force the node to boot using a different, backup flash memory device that can be used to repair software. Finally, the WagMan can also monitor the power utilization and thermal dissipation of the single-board computers in the Waggle nodes, and take evasive action to keep the node within its operational thermal envelope (Figure 1).

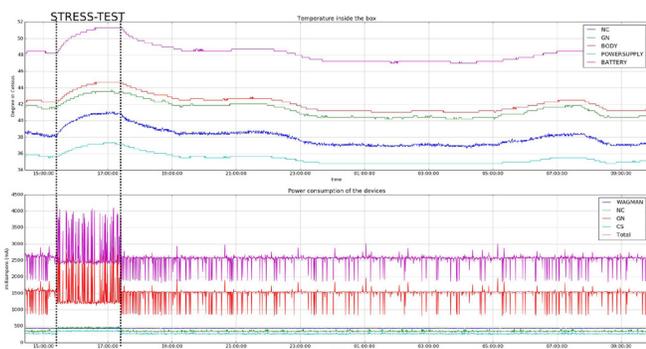


Figure 1. A stress test procedure developed to understand the operating range for nodes and how central processing unit activity can heat Waggle nodes.

## Improving and Validating Models of the Urban-Climature Connection with Dense Sensor Networks

2014-167-R2

Robert Jacob, Charlie Catlett, Beth Drewniak, Rao Kotamarthi, and Rajesh Sankaran

### PROJECT DESCRIPTION

Urban areas change their own climate most famously by creating an urban heat island and by altering the flow of air over, around, and through the city. They also emit pollutants that have strong negative local effects. To better understand how climate change will affect cities, it will be necessary to better understand and model the interactions of each city with its surrounding regional climate. Models of urban areas suffer from a common problem: lack of validation data from within the city. Most climatological and meteorological sensor networks are located outside urban areas to better sample larger regions. They also have not taken advantage of new low-cost compute and sensor devices that the commercial cell phone industry has created. This project will design and deploy a dense sensor network that can measure urban weather and climate in detail and provide validation data for simulations of urban weather and climate.

Our major task is to identify and develop a low-cost, low-power, inexpensive sensor node for measuring basic meteorological quantities. The node will also need software and hardware for managing power and communicating data. We will identify locations for deploying about a dozen nodes to test the hardware and software and assess the quality of the data. We will also augment Argonne’s existing weather station to provide measurements for comparison. Assuming

the initial deployment is successful, we will expand the network to cover more of the City of Chicago (Figure 1). We will combine these data with modeling of the urban atmosphere to help determine both where the models need to improve and where more measurements are needed.

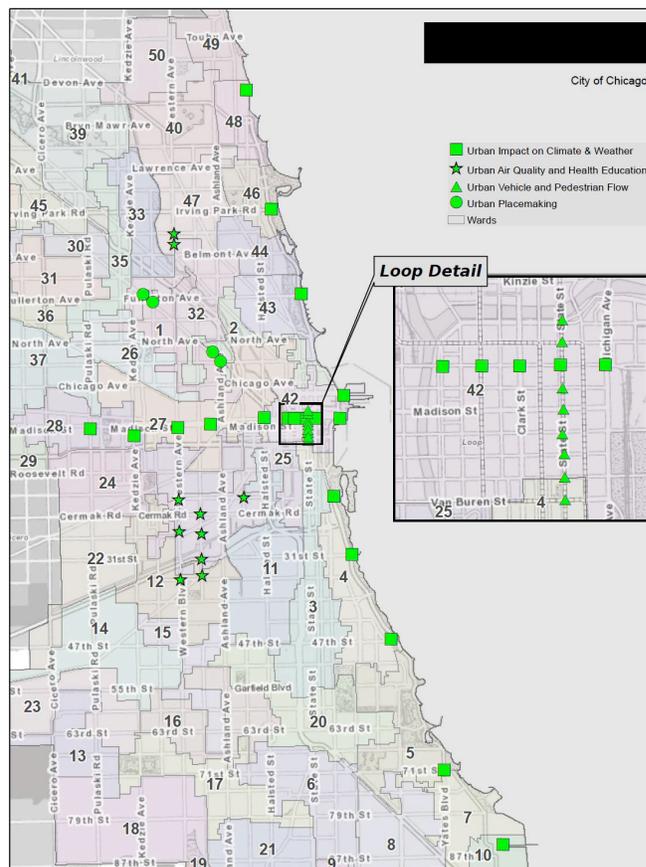


Figure 1. Locations for nodes in the Chicago urban weather network. “Urban Placemaking” indicates areas where underutilized public space will receive pedestrian-friendly development.

### MISSION RELEVANCE

This project is primarily relevant to DOE’s science and environmental quality missions. Our sensor network will have the capability to dramatically improve our understanding of the poorly measured urban boundary layer. Thus, this research is relevant to multiple programs in the Climate and Environmental Science Division of the Office of Biological and Environmental Research. The project is also relevant to DOE’s energy mission. Cities are primary consumers of energy, and data on their environment will be crucial to operating them more efficiently, which is of interest to DOE’s Office of Energy Efficiency and Renewable Energy and one reason that urban science was chosen by a team of senior lab managers as a “Big Idea” to present to DOE management

in the summer of 2016. The National Science Foundation (NSF) and National Aeronautics and Space Administration also have interest in studying cities.

## RESULTS AND ACCOMPLISHMENTS

Early in this project's history, we joined efforts with the LDRD project entitled "Developing an Integrated Sensor Network for Science" (2014-160-R2) and decided to participate in development of that project's Waggle sensing platform instead of using commercial off-the-shelf weather stations. In our project's first year, we developed a printed circuit board with multiple meteorological sensors for temperature, pressure, and humidity. This component was combined with Waggle to produce a networked weather station. We designed a rooftop-mountable model and have deployed two such *Weather Pots* at Argonne and DePaul University (DePaul) in Chicago, using Ethernet to power the node and collect the data.

Toward the end of the first year and during the first quarter of the second year, we began to explore the capabilities of existing urban modeling systems for Chicago and how data from our network might improve them. We worked with the urban version of the Weather Research and Forecast (WRF) system, used WRF's nesting ability to assemble a fine-resolution (up to 1-km) configuration over the Chicago area, and performed test runs with various settings of the urban canopy scheme. In the second year, we also refined the design of our low-cost meteorological sensor board on the basis of the summer, fall, and winter field tests (begun in summer 2014) conducted at Argonne and DePaul.

In the final year of the project, we continued to refine the design of the meteorological sensor board "MetSense." We improved the resilience, reduced the thermal mass around the sensors, and further isolated the sensors from the on-board central processing unit. We identified further improvements after capturing long-term infrared camera images that showed temperature profiles of the various sections of the board. We also added the ability to integrate new sensors. This board will be used in rooftop, field, and street-level deployments, the last of these through the NSF-funded Array of Things initiative. We also made a detailed map showing how an urban weather network might be deployed in the City of Chicago (see Figure 1). Several factors were taken into account, including local climate zones, susceptibility to urban flooding, relations to major features such as Lake Michigan, average building height, and demographics. Finally, we developed calibration procedures for the MetSense sensors.

This was the final year of the project. Portions of this work will continue under the NSF-funded Array of Things project and under the DOE Advanced Scientific Computing Research-funded Exascale Computing Project called Multiscale Coupled Urban Systems.

## Advanced Pipeline for High-Throughput Digitization of Large-Scale Collections

2014-174-R2

Mark Hereld and Nicola Ferrier

### PROJECT DESCRIPTION

Large-scale collections of objects, which can comprise millions to hundreds of millions of specimens, provide data for studies of taxonomy, biodiversity, invasive species, biological conservation, land management, pollination, and biotic responses to climate change. These collections represent a significant societal investment in research and applied environmental science. However, they also present extraordinary challenges to researchers, archivists, and curators. Working with the Field Museum of Natural History, we are developing a means of rapidly digitizing such large collections. In the digital realm, they will be impervious to time, available for richly informative and powerful query-based exploration and analysis methods, accessible to a much wider community of researchers, and deployed in a wide range of outreach activities. In aid of this goal, we are developing a multi-camera head designed for single-shot digital capture of casually aligned pinned insects. In support of this experimental platform, we are developing methods for label capture for input to optical character recognition (OCR) and three-dimensional (3D) model capture in the face of uncertain orientation, position, and occlusion.

### MISSION RELEVANCE

This project supports DOE missions in environmental science, basic sciences, and computer science. Rapid 3D scene and object capture supports advanced manufacturing by reducing assessment time and expense in manufacturing processes, and complements additive manufacturing processes in the rapid manufacturing process cycle. The tool supports environmental science by helping researchers understand the workings and effects of the biosphere through the unique lens of entire collections. It supports basic science by developing computational means for analyzing complex 3D scenes and objects; it also contributes to computer science, and broadly applicable image analysis leveraged by many

disciplines within DOE's Office of Advanced Scientific Computing Research. In addition, the National Science Foundation (NSF) supports basic research in computer vision and image processing, 3D digitization of biological collections, automation engineering, and robotics that this work addresses.

## RESULTS AND ACCOMPLISHMENTS

In previous years, we characterized the collection of pinned insects at the Field Museum of Natural History to determine design parameters (size, speed, resolution, geometry) of the multi-camera head; determined text quality requirements for off-the-shelf OCR devices to set fidelity goals for label capture; designed the modular multi-camera head; and developed camera-based capture and analysis methods for drawer and unit modules of the collection.

In FY 2016, we built a controlled light test chamber to facilitate rapid and reproducible data capture to feed our algorithm development. We built and tested the first of four camera modules. In order to organize the development and testing of 3D capture software components, we designed a software pipeline describing the stages of analysis required to convert raw image data from the multi-camera head into a quantitatively reliable 3D model of the object. Guided by this breakdown of the necessary steps in the analysis pipeline, we tested several feature-matching methods and characterized their performance for the case of widely separated light field cameras.

Figure 1 illustrates some of this progress. Panel (a), illustrates the camera positioning using a visualization tool developed to study the organization and positioning of 12 cameras for the best coverage of the specimen volume. Angle and separation parameters of the four-module design (modules delineated by groupings of camera color) are set with the interactive sliders in the upper left corner. The graphics in the lower left and lower right corners provide quantitative information about completeness and uniformity of coverage around the specimen. Panel (b) shows the first camera module installed in the controlled light test chamber. The artificial pinned specimen with three labels can be seen right of center in the image. Panel (c) shows the view from one of the three cameras in the module after features have been identified and classified as salient (red). Combining the detected features in the three separate camera views allows us to construct a 3D model of the object as shown in panel (d).

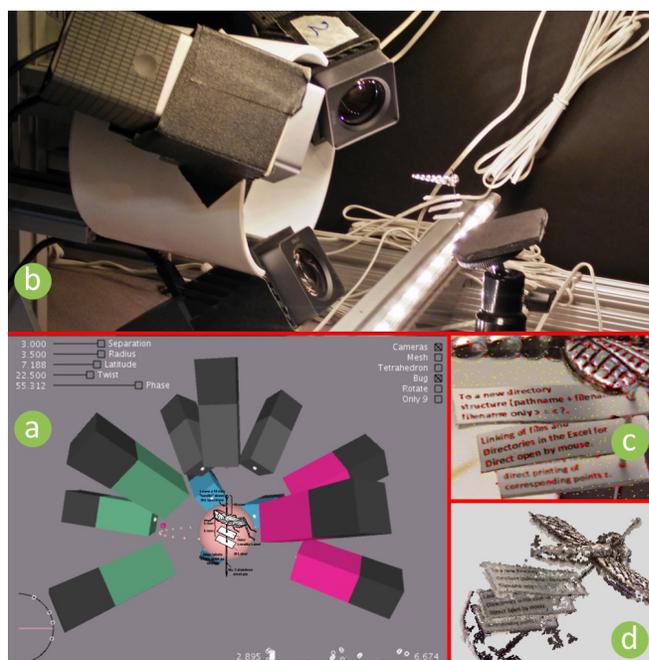


Figure 1. Clockwise from lower left: (a) tool developed to determine camera placement; (b) testing of the first three-camera unit; (c) features detected in one camera view; and (d) multi-view data combined to generate a 3D model of label stack and insect.

## PARIS: Data Knowledge-Based Extreme-Scale Resilience

2014-181-R2

Franck Cappello

### PROJECT DESCRIPTION

As the number of components and the projected use of aggressive power-saving technologies increase, future extreme-scale computational systems will be less reliable than existing systems because of faults from internal or external causes. The high-performance computing community has recognized this “exascale resilience challenge” and is exploring solutions to create numerical science applications that provide correct results. The PARIS project explores the fundamental properties of numerical science applications to improve the resilience of extreme-scale executions and to provide efficient solutions to system failures and silent data corruptions (SDCs).

Objects and phenomena studied using time-dependent numerical simulations and data analytics have important characteristics reflected in the data dynamics and data semantics that could be leveraged to discover new resilience techniques. We seek to leverage the

data dynamics and data semantics to devise new SDC detection, data compression, and self-healing techniques.

### MISSION RELEVANCE

Extracting knowledge from large-scale numerical simulations and data analytics is key to the DOE missions in science and innovation. SDCs and execution failures are severe threats to producing timely and accurate DOE mission-critical results. PARIS provides lossless and lossy compressors to accelerate checkpoint and restart and SDC detectors and correctors to reduce the risk of corrupted results. PARIS provides data compressors and SDC detector mechanisms that are applicable to applications at Argonne, DOE, and other agencies, such as cosmology (HACC), climate (ACME), reactor (Nek5000) and shock (FLASH) simulation codes.

### RESULTS AND ACCOMPLISHMENTS

During the first year, we formulated SDC detection as a time-series prediction problem. We designed and developed a detector that, at each time-step, dynamically predicts the possible range for each next-step data value of the application, based on recent time-series data. The detector considers a value an outlier if it falls outside this range. We also explored the use of data semantics, such as variable correlation, to improve detection and reduce memory consumption and detection complexity. We also proposed a novel compression approach, leveraging the data analytic, that improved by up to 15% the compression ratio while reducing compression time by 50%, compared to state of the art lossless compressors.

During the second year, we designed new lossy compression algorithms guaranteeing error bounds fixed by users. These algorithms outperform significantly all other compressors in compression ratio and time to decompress. We tested these algorithms on 20 benchmarks from FLASH, NEK5000 and ACME and observed compression ratios between 3 and 5 for very hard to compress data sets and 100 for highly compressible data sets. We have started studying how restarting numerical simulations from lossy compressed checkpoints affect the end results of the simulations. We are investigating the diffusion cases using SZ for lossy compression. We have designed and implemented a large variety of SDC detectors based on data analytics. We have combined these detectors with partial replication for regions of the data set difficult to handle by prediction methods.

In FY 2016, we continued research and development on both the SZ lossy compressor and SDC detection. We continue to work on improving the SZ compression

factor for hard-to-compress datasets and on developing tools to characterize the error produced by the compiler. The new version of the compressor is the best-in-class lossy compressor strictly respecting user-set error bounds for scientific datasets. We collaborated on a framework for online machine-learning-based corruption detection with the Barcelona Supercomputing Center. We comprehensively investigated the prediction ability of many machine-learning algorithms in our study, and enabled the detector to automatically select the best-fit algorithms at runtime to adapt to the data dynamics. The framework exhibits low (less than 1%) memory overhead. Experiments based on real-world scientific applications and benchmarks show that our framework can attain a detection sensitivity (i.e., recall) of up to 99%, while the false-positive rate is limited to 0.1% in most cases. In addition, we publicly released the SZ compressor.

### PROPOSED FUTURE WORK

We were part of four successful Exascale Computing Project (ECP) proposals to DOE. The four ECPs will start after the end of this project. The first project, which involves lossy compression, will entail the further development of the SZ compressor. The second project, focusing on fault tolerance, will involve refactoring the two leading multi-level checkpoint environments into a unified framework. The other two ECPs will research the use of SZ in a data reduction and analytics framework and in cosmology applications.

We will continue our research both through these DOE ECPs and through collaboration with the University of Illinois at Urbana-Champaign. The research will explore ways of improving the compression of hard-to-compress datasets and bringing the compression software to production-level quality. We will also explore the mathematical link between lossy compression error and numerical simulation error.

## Dynamic Data Mirroring for Data-Intensive Science

2014-182-R2

Ian T. Foster and Steven Tuecke

### PROJECT DESCRIPTION

This project seeks to address challenges in managing and accessing large amounts of scientific data on heterogeneous storage systems over the data lifecycle by providing a dynamic high-performance data mirroring solution. During the course of a given project, there is

a diverse set of requirements for the type of storage needed for the data, with characteristics such as performance, cost, and access capabilities of the storage system that determine suitable use. This variability results in the potential for multiple copies of the data and different views into the same data. Managing such data on these systems is onerous for researchers in terms of keeping it readily available for processing or access. Our work tests and evaluates options for dynamic data management and mirroring, fueled by user-driven policies and characteristics of the storage system.

### MISSION RELEVANCE

These new methods will provide important support for major data-intensive science projects that are of interest to DOE. In each case, projects at Argonne will provide local drivers as we explore general-purpose solutions. We are deeply familiar with needs at Argonne’s Advanced Photon Source (APS). Meeting these requirements is important if the APS is to realize the promise of next-generation detectors, and solutions that meet those requirements will also be useful at a range of DOE Office of Science (SC) Basic Energy Sciences (BES) facilities, including the Spallation Neutron Source (SNS), Advanced Light Source (ALS), and Supernova Legacy Survey (SNLS). Similarly, cosmology work in high energy physics, mathematics, and computer science speaks to meeting the requirements in cosmology—and more broadly—in advanced simulation. Finally, next-generation radar analysis work in environmental science seeks to provide a new class of national facility that integrates new instrumentation with advanced data analysis and simulation. In each case, the “dropbox for science” capability that we will provide with our project has been identified as an important building block. A program aimed at innovating in this area now, while those programs are still ramping up, will allow them to proceed far more rapidly in future years.

This work will also contribute to the understanding of requirements and architectures for next-generation research campus storage solutions at institutions such as Argonne and other national laboratories. If we are successful in the work proposed here, DOE will gain important knowledge about how to create a big data storage and analysis infrastructure that is able to meet the varying needs of scientists and their collaborators across a multi-program laboratory—a system that will provide those scientists with a competitive advantage. For example, at Argonne, the existence of this solution will enhance the value of facilities such as the APS, the Argonne Leadership Computing Facility (ALCF), the Laboratory Computing Resource Center (LCRC), and the Center for Nanoscale Materials (CNM).

### RESULTS AND ACCOMPLISHMENTS

We established, in partnership with the ALCF, the Petrel storage service. This work involved deploying Globus transfer and sharing capabilities on Petrel and then developing provisioning scripts so that when a principal investigator requests a project store with some specific amount of space, we can easily create a general parallel file system (GPFS) volume with the appropriate size, create the shared endpoints, set up the required access control lists, and so forth. We deployed this capability as a model of the service and enlisted earlier users of APS and other communities. We worked with scientific users to identify use cases that motivate the needs for different forms of mirroring.

Working with the ALCF, we have continued to build on the Petrel storage service: see Figure 1. The 1.7-petabyte (PB) storage system was built using repurposed disks and controllers from ALCF’s Intrepid machine. In the previous year, we worked with the ALCF to set up Petrel and establish a user-driven and project-based allocation mechanism. This system was made available to several projects for trial use, and in the last year, large quantities of data have been moved into and out of Petrel. A website (<http://petrel.alcf.anl.gov>) with resources for Petrel users was also created.

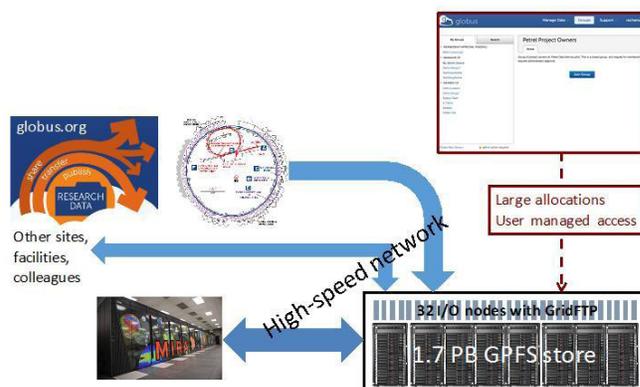


Figure 1. The Petrel data server was developed as part of this project, and its connection with other Argonne research infrastructure was described.

Exemplar users include APS beamlines, which have used Petrel as a resource for dissemination of data associated with published papers, allowing users to reproduce results. Physicists from the University of Chicago have used Petrel to store results from computation runs that are then referenced from Jupyter notebooks that are published and made available to other researchers. Others have used Petrel to backup and share data with external users, in some cases with restricted access. Petrel has also been used to store data associated with the new Materials Data Facility.

The ALCF, APS Information Technology (IT), and Globus team conducted extensive performance tuning to ensure that APS and Petrel transfers use the capacity effectively. Based on the success of using a data-sharing infrastructure, select APS beamlines have also deployed Globus sharing on their acquisition infrastructure to move data directly from that infrastructure to Petrel and to share with their users. A command-line tool to automate data movement was developed and made available, and APS scientists developed tools to apply APS identity and policies on shared data using Globus application program interfaces (APIs).

APS scientists are able to use Petrel as a hub for transfers from the APS to the ALCF and group-specific analysis computers (e.g., Neutron and X-Ray Scattering Research [NXRS] of Argonne’s Materials Science Division [MSD] or Orthros [APS]). Data on Petrel is cataloged using the Globus Catalog for search and integration with application-specific tools (e.g., NeXPY). Petrel was also used as a data transfer hub by Argonne/MSD scientists using the Cornell CHESS synchrotron. Data management techniques developed under DEBD were deployed at CHESS, while backups were moved to Petrel for safety and future use upon their return to Argonne.

New hardware was purchased to replace the existing Petrel stack. The new machines provide two 40-gigabyte (GB) connections, and initial studies show much better performance with the new hardware. We were able to demonstrate 60 gigabits per second (Gbps) transfer performance between Petrel and a remote system at the University of Chicago.

### PROPOSED FUTURE WORK

This project is now completed. Petrel has been adopted by the ALCF as an important part of its infrastructure and is being used on a growing number of projects.

## Implementing a New Extreme-Scale Parallel Programming Model with a Full Sample Application

2015-139-R1

Barry F. Smith and Junchao Zhang

### PROJECT DESCRIPTION

The Message Passing Interface (MPI) programming model is reaching the end of its viability for development of extreme-scale simulations and data analysis. The

addition of threading or task-based parallelism to MPI has extended its viability for a few years—while increasing the complexity of resulting codes—but it does not remove its fundamental limitations. The time is ripe for developing a new, simple, general-purpose model for extreme-scale parallelism that can replace the MPI+shared-X model. Taking the lead in the design and (open source) implementation of the next “standard” high performance computing (HPC) programming model will bring benefits to both DOE and the scientific community as a whole.

The push for ever-increasing levels of concurrency and the increasing complexity of simulation codes require a new parallel programming model that both simplifies the development of extreme-scale codes and makes them more efficient and scalable on newly emerging architectures as well as on graphics processing units (GPUs), many-core systems, and conventional computing systems. For the past twenty years, careful attention to data locality has been crucial to obtaining high performance. The message-passing programming model succeeded in dominating the market because it provided a good approach for ensuring data locality. With exascale systems, data locality will remain crucial, but now resiliency, machine jitter issues, and more adaptive, heterogeneous simulations require a more flexible dynamic placement of data that simply is not achievable with the message-passing model. To expect the programmer to manage the extremely complicated data placement and movement needed in this environment is unrealistic. It can be handled only by having a runtime system that determines both the size and placement of tasks and ensures that the data is where it needs to be when it is needed. But for a runtime to do this, it must be in control of the complex and generally unstructured data, and the user must be able to indicate to the runtime the relationships between the data items so that the runtime can manipulate, partition, and distribute it for efficient tasks.

At the same time, one must keep in mind that HPC software is currently written in C, C++, and Fortran, with occasional high-level code written in Python and with computational kernels possibly written in CUDA and OpenMP. Expecting the entire HPC community to switch to a new (yet-to-be-developed) programming language for HPC is unrealistic and unnecessary. In fact, one of the most important reasons for the success of MPI as the HPC programming model is that it did not require any language changes.

**MISSION RELEVANCE**

DOE has stated that exascale computing is crucial to its role in supporting science. The customers and beneficiaries of this work would include virtually everyone involved in HPC. Specifically, those developing scientific software libraries (e.g., those funded by DOE Advanced Scientific Computing Research (ASCR) applied mathematics) will benefit in the short and long term by having a stable, portable development model for their libraries. Scientific simulation application developers, such as those funded by Basic Energy Sciences (BES) and Biological and Environmental Research (BER), will similarly benefit, as the scientists who use the simulation applications will have the applications available much sooner than otherwise possible. The exascale machine developers (e.g., IBM, Cray) will benefit almost immediately by having a specific common model for which to develop their hardware and software, while still having a great deal of freedom in what specific hardware (e.g., GPUs, many-core, etc.) they can use to accomplish their goals. Since hardware and system software take several years to develop, it is crucial that the model be available sooner rather than later. Finally, those developing exascale operating system (OS) software (e.g., those funded by DOE ASCR computer science) will be able to focus their efforts on providing quality implementations of the model and infrastructure to support the model.

**RESULTS AND ACCOMPLISHMENTS**

In the first year of this project, we designed and implemented the Indexed Programming Model (IPM) as a proposed replacement for the MPI programming model. The IPM is based on having the user define the data dependencies and the IPM runtime manage all the needed communications, as opposed to the MPI model in which the user must explicitly manage all the data movement. The IPM runtime consists of roughly 10,000 lines of C and C++ code.

We completed development of the sample adaptive mesh refinement application for the convection diffusion equation and made direct comparisons, using identical algorithms, with the widely used libMesh and Deal.II MPI-based libraries. Our IPM implementation is more than five times faster, with a much smaller and simpler code base. Even with its much faster runtime, the IPM has slightly higher parallel scalability than the implementations in libMesh and Deal.II. The source code for the IPM-based adaptive mesh refinement application is only several thousand lines of C source code, whereas the libMesh and Deal.II implementations involve hundreds of thousands of lines of C++ source. The convection diffusion

equation we used for the comparison is a model equation for computational fluid dynamics (CFD) that is commonly used as a surrogate for complete CFD simulations.

## Determining Mechanical Properties of Material Systems Using Parameter-Free Metadynamics

2015-172-R1

Carolyn Phillips and Juan J. de Pablo

**PROJECT DESCRIPTION**

In this project, we are developing software and algorithms to perform a new free-energy calculation technique, a parameter-free metadynamics method. This method has the potential to calculate the properties of materials systems with higher accuracy and computational efficiency than was possible with the prior computational methods. Using this method, we are measuring mechanical properties that traditionally have been difficult to extract from either experiment or computation. We will extract values for these properties by implementing the parameter-free metadynamics method in conjunction with a novel constrained molecular dynamics simulation test rig that is designed to isolate each mechanical property. Our first task is to measure the elastic moduli of a liquid crystal and compare the result to the limited set of experimental values. Our second task is to measure the shear coefficient of silicon using an atomistic model. If successful, this project will demonstrate how certain highly sought-after properties can be computed, create a general library to enable the rapid and accurate calculation of the mechanical properties for a diverse set of other material systems, and facilitate the use of large-scale computation in designing new materials. This project will also enable the use of a new fast-converging metadynamics technique for performing other types of free-energy calculations in silico. Jonathan Whitmer of the University of Notre Dame has collaborated on this project.

**MISSION RELEVANCE**

The methods being developed in this project are designed to guarantee the exhaustive sampling of phase space for free-energy calculations. These methods have applications in a wide range of research areas from mechanical calculations, phase transitions, and structural transitions to calculating pathways in systems with complex free-energy landscapes. They can also be applied to a wide range of materials from metallic glasses

to biomolecules. The computational rational design, both of these types of materials and of new energy transfer and storage materials, is an important part of the mission of the DOE Office of Science (SC), Basic Energy Sciences (BES) programs in materials and chemistry.

## RESULTS AND ACCOMPLISHMENTS

In FY 2015, we selected and validated the coarse-grained atomistic model for the 4-n-pentyl-4'-cyanobiphenyl (5CB) liquid crystal in a chosen molecular dynamics simulation engine by demonstrating the correct temperature dependence of the order-disorder transition and density. We began development and testing of the software modules needed to generate a constrained molecular dynamics test rig. During development, we identified limitations as to when certain constraints would work, and we developed protocols to correctly prepare a test rig so that meaningful data would be generated. We also performed initial simulation sweeps of a small system using a classic metadynamics technique parallelized at the node level via a highly parallelized molecular dynamics engine and at a multi-node level by using multiple walkers.

In FY 2016, we finished the development of the software modules needed to perform elastic coefficients calculations. We began to validate the calculations. We identified that the liquid crystal system appears to have long-lived fluctuations and possibly coupled elastic modes. The long-lived fluctuations mean that the liquid crystal model we are using relaxes very slowly. Therefore, substantial simulation time will be required to calculate the elastic coefficients. The evidence of the coupled elastic modes suggests that the atomistic 5CB system may express deformation in more complex ways than the simpler liquid crystalline systems.

## Event-Based Monte Carlo Transport Methods for Next Generation Node Architectures

2016-135-NO

Paul K. Romano and Andrew R. Siegel

### PROJECT DESCRIPTION

Monte Carlo (MC) particle transport methods are unique in their ability to accurately simulate complex phenomena without resorting to approximations. This makes them ideally suited for the simulation of nuclear reactors, which relies heavily on modeling neutron and photon transport.

However, their use in many applications is often severely limited by long integration times, even on leadership-class computing facilities, and thus MC simulations are often confined to one-off hero calculations. While future petascale and exascale supercomputers may offer a tantalizing amount of raw computing power, the task-based parallel algorithm that is implemented in most MC codes is ill-suited for architectures that obtain much of their floating point performance via wide single-instruction multiple-data (SIMD) units, such as NVIDIA graphical processing units (GPUs) and the Intel Xeon Phi co-processor. The goal of this project is to explore techniques for better exploiting vectorization within MC particle transport simulations.

In most MC codes, parallelism is achieved by assigning entire particle histories to different threads. One proposed modification of this algorithm that may better lend itself to vectorization is to use an event-based algorithm wherein the particle history is broken down into a series of “events.” Although the interaction physics is the same, the order in which individual events (e.g., tracking through free space, scattering, secondary particle production) are processed and assigned to threads is completely different. The algorithm involves having many particles “in flight” simultaneously and grouping similar events together to be processed, which takes advantage of the vector units. This approach necessitates making drastic changes in the main loop structure and having significantly different data structures.

Some preliminary work in the community has demonstrated implementations of event-based algorithms in idealized, one-off research codes. Our approach is rather to study the algorithm using a combination of performance models and data measured from a production-level code in order to assess the merits and drawbacks of such an approach in general. A better theoretical understanding of the event-based algorithm will then help guide an implementation within a production code such as OpenMC.

### MISSION RELEVANCE

MC particle transport methods are used in a broad range of scientific and engineering domains that are important to DOE, including nuclear engineering, radiation shielding, radiation detection, medical dosimetry, radiation damage at the molecular level, high-energy physics, and weapons certification. In many of these domains, researchers are struggling with the question of how to best utilize next-generation node architectures. A deep understanding of performance characteristics and general algorithmic challenges on SIMD architectures will therefore be of great benefit.

The results of this research may be particularly relevant to the DOE Exascale Computing Project (ECP). One of the ECP application development projects is preparing two production-level MC particle transport codes for application readiness at exascale. If the event-based algorithm shows promise for improving use of data-level parallelism as a result of our research, these high-performance computing-oriented codes may wish to adopt it.

## RESULTS AND ACCOMPLISHMENTS

In the first year of the project, we developed a performance model with simplified assumptions about application behavior and used it to analyze limits on the efficiency of the event-based algorithm. Data collected from a simulation of a light water reactor (LWR) benchmark model using the OpenMC code allowed us to quantify the upper-bound efficiency as a function of model parameters. Figure 1 shows the overall efficiency of the event-based algorithm as applied to this model as a function of the ratio of the particle bank size (the number of particles that are simulated by a single parallel task) to the hardware vector size. We see that under the simplified assumptions of the performance model, the bank size generally needs to be at least 20 times greater than vector size in order to achieve vector efficiency greater than 90%. This finding implies that for the NVIDIA Tesla GPU, an implementation of the event-based algorithm will require thousands of particles to be tracked simultaneously in order to attain acceptable efficiency. For the Intel Xeon Phi co-processor, the requirements on the particle bank size are a bit more modest.

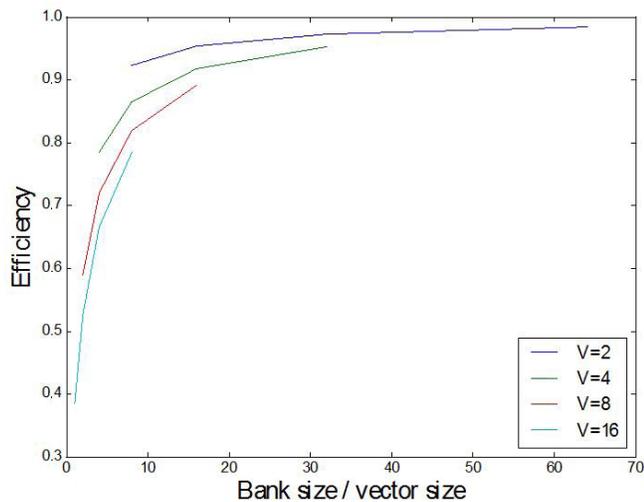


Figure 1. Overall efficiency of the event-based algorithm applied to an LWR model as a function of the bank-to-vector size ratio.

Alongside the work on the event-based algorithm, we also began investigating how to vectorize cross-section lookups that rely on the windowed multipole method, typically one of the most time-consuming operations in the particle transport algorithm. The multipole method allows cross sections to be evaluated at any temperature without using a table look up and can significantly reduce the memory requirements for large-scale simulations. Thus, any improvements in performance of the multipole method could translate directly to improvements in overall application performance for such simulations. The multipole method relies heavily on evaluation of the Faddeeva function; we have been able to demonstrate significant performance gains in evaluating the Faddeeva function over a wide domain on the Intel Xeon Phi by approximating the integral form of the Faddeeva function via a Gauss-Hermite quadrature.

## PROPOSED FUTURE WORK

In the second year, we will extend and improve the performance model to overcome some of the simplified assumptions inherent in our earlier analysis. Namely, we will explicitly account for differences in event execution times and make a first attempt at quantifying the impact of data movement in the algorithm on overall execution time. In addition, we will compare model predictions when events are broken down into finer-grained tasks as may be necessary for a practical implementation. If the performance model demonstrates that the event-based algorithm holds promise for realistic simulations, we then plan to validate the performance model with either a mini-app that implements the event-based algorithm or an implementation in the OpenMC code, if feasible.

In addition to the higher-level work focused on event-based algorithms, we plan to continue investigating vectorization of cross-section lookups. One approach that may hold significant promise is to aggregate cross-section lookups for each nuclide in a material. Not only would this approach expose opportunities for use of the SIMD units, it would also potentially reduce memory traffic by improving the temporal locality of successive cross-section lookups.

# Re-form: Leveraging FPGA Reconfigurability and Floating-Point Capabilities for Next Generation Computing Systems

2016-148-NO

Kazutomo Yoshii, Franck Cappello, Hal Finkel, and Fangfang Xia

## PROJECT DESCRIPTION

The performance progress of microprocessors has been driven by Moore's law, which has doubled the number of transistors every 18 to 24 months. This trend is expected to continue until the mid-2020s when the complementary metal-oxide-semiconductor (CMOS) features will reach 5 to 7 nanometers. After that, performance progress for CMOS-based integrated circuit devices will no longer come from higher levels of integration. To overcome this scaling issue, researchers are intensively investigating new technologies (e.g., carbon nanotubes). However, there is no guarantee that these new technologies will be ready for deployment in the foreseeable post-Moore era.

The basic idea of this project is to leverage field-programmable gate array (FPGA) reconfigurability and floating-point capabilities in order to improve performance and energy efficiency by customizing hardware for each application workload. However, the adoption of FPGAs in scientific computing faces two technical challenges: (1) the lack of high-level parallel programming abstraction, and (2) the weakness in performance optimizations for scientific computing workloads. In this project, we propose to solve these technical challenges and provide a proof of concept.

## MISSION RELEVANCE

This project is relevant to DOE's mission in science and energy. Since the emergence of digital computers, exponential performance growth, driven primarily by Moore's law, has been accelerating scientific discoveries and engineering breakthroughs. The end of progress according to Moore's law, which is expected to arrive in the mid-2020s, is a big concern for DOE. If this project is successful, DOE will have a potential solution for improving the performance and/or energy efficiency of high-performance computing (HPC) systems, without requiring new, uncertain technologies.

## RESULTS AND ACCOMPLISHMENTS

First, we created our FPGA development environment, which includes cutting-edge FPGA platforms, such as Altera Arria10, and the latest generation of software, such as Altera Quartus and Xilinx Vivado. Then we evaluated the performance, productivity, and other aspects of existing vendor tools. Our focus was on high-level synthesis (HLS) tools that translate C, C++, or OpenCL into hardware description language and generate an FPGA bitstream. We confirmed that the latest generation of HLS tools significantly mitigates the complexity involved in programming FPGAs by using traditional hardware description languages, particularly for floating-point-intensive codes.

In FY 2016, we accomplished important milestones on programmability and performance optimization.

Regarding programmability, we initiated an investigation on the translation path from OpenMP 4 to intermediate representation using open-source, low-level virtual machine (LLVM) technology. With Xilinx, we identified which parts of the existing OpenMP 4 implementation, which targets graphics processing units (GPUs) and multicore central processing units (CPUs), can be reused for targeting FPGAs, and we investigated how to interface with vendors' high-level synthesis tools—SPIR-V vs. generating OpenCL code vs. OpenCL (infrastructure only) + custom kernels. We also established scientific collaborations with major players in the area of FPGA programming models, namely, Micron, Intel/Altera, and the Barcelona Supercomputing Center.

As for performance optimization, we focused on the data path in an OpenCL FPGA platform because data movement between off-chip memory and compute logic is often multiple orders of magnitude more expensive in energy consumption than floating-point computation. Another important reason is that optimizing the FPGA data path is generally more complicated than for CPUs/GPUs because of its reconfigurability. Only a few benchmarks are written in OpenCL and target FPGAs, and none of them target the data path in a fine-grained manner. Therefore, we developed our own OpenCL-based microbenchmark code called *iabench*. The predefined kernels included in *iabench* currently cover random access patterns and binary search patterns, combined with simple computations. Random memory access patterns are of great interest because they limit the thread-level scalability of OpenMC, one of the DOE applications we target. *iabench* allowed us to find optimal parameters for random memory access patterns on an Altera Arria10-based FPGA board. We found that the FPGA offers nearly four times higher energy efficiency

than the Intel Xeon 8-core CPU. Although the memory bandwidth of the CPU is 60% higher than that of the FPGA, the FPGA board offers comparable performance to that of the CPU. In addition to the FPGA data path study, we also conducted experiments on the reduced floating-point format on Intel CPUs that support the half-precision floating-point format. Our experiment results showed that the reduced floating-point format offers linear improvement in energy efficiency, which will help us to design custom data path modules for FPGAs in FY 2017.

In FY 2016, we organized an international invitation-only meeting to improve our understanding of the state-of-the-art and scientific/technical challenges associated with the adoption of FPGA in HPC and data analytics.

### PROPOSED FUTURE WORK

In FY 2017, we will port the computation kernel of our selection of DOE applications into OpenCL FPGA platforms, compare performance and performance/watt with up-to-date CPU or GPU implementations, and investigate optimization techniques that improve performance and performance/watt by leveraging the unique characteristics of FPGAs such as customizable internal memory. We will also find an optimal path to compile OpenMP 4 applications, leveraging existing open-source tools and working with vendors and academics.

## Data-Driven Multiscale Coupled Urban Systems Modeling

2016-157-NO

Charlie Catlett, Peter Beckman, Leah Guzowski, and Ralph Muehleisen

### PROJECT DESCRIPTION

Through this project, we seek to extend building-grid interaction codes to model smart buildings and smart grids where buildings can react and change their operation based on the grid's needs (demand response, frequency regulation, etc.). We will also expand the agent models to include agents for building, transportation, and grid operators who will alter the operation of the systems based on changing conditions. Finally, we will extend the Waggle platform to enable the use of image processing to capture surface water flow and accumulation.

### MISSION RELEVANCE

This project is relevant to DOE's emerging initiatives toward understanding metropolitan areas as complex multiscale systems, including the Metropolitan Energy Sciences Big Idea initiative and the DOE Transportation-As-A-Service Initiative, both driven by the Office of Energy Efficiency and Renewable Energy (EERE) (Building Technologies Office [BTO] and Vehicle Technologies Office [VTO], respectively) and the Exascale Computing Program (ECP), driven by the DOE Office of Science (SC). The primary customer for the results from this work is the research community supported by the U.S. Government, particularly by DOE, whose research portfolio is beginning to expand to investigate global urbanization and its impact on the planet's climate and energy supplies as well as the practical urban design, planning, and operations challenges faced by U.S. cities. Similarly, city, state, and federal governments in the United States and abroad require tools and methodologies to transform their growing, diverse data sources into bodies of understanding for both the operation of their cities and to plan for their growth and renovation.

### RESULTS AND ACCOMPLISHMENTS

The original plan was to build on a previous LDRD-funded project, "LakeSim," that used proprietary software. We determined that new, open source software would be a more extensible approach. To this end we selected UrbanSIM, an open source modeling framework developed by the University of California-Berkeley. This move gives us more flexibility in extending the urban simulation software, and it better aligns our work with that at Lawrence Berkeley National Laboratory (LBNL) for future joint efforts to pursue expected Urban Sciences FY 2017 sponsorship opportunities. We are beginning the integration of Argonne's building energy model (called ISOModel) and Argonne's traffic model (called Polaris) with UrbanSIM.

We made progress integrating ISOModel with UrbanSIM, investigating the use of an existing UrbanSIM model to show capabilities, and exploring the integration of Polaris with UrbanSIM. At mid-year, we led a proposal to the ECP to build a coupled urban modeling framework beginning with four models: building energy (EnergyPlus), transportation (Polaris), social and/or economic modeling (ChiSIM), and urban canyon air and heat flow (Nek5000). We were approved for FY 2017 to begin to quantify and characterize the flow of data between these four models. If successful in FY 2017, and provided that there is no major change in the ECP budget, our sponsorship will ramp up in FYs 2018 and 2019.

In the first half of the year, the Waggle sensor integration project team investigated camera technologies, made modifications to the node housing to accommodate cameras (adding lenses and mounting fixtures), and extended the software to enable the use of OpenCV software for image processing. In the second half of the year, we collaborated with the Array of Things (AoT) project—a separate project at the University of Chicago to acquire and modify 500 Waggle nodes for urban installation—to develop guidelines for camera positioning to optimize the view of traffic intersections. We also established initial partnerships with computer vision groups at the University of Wisconsin, the National Applied Research Laboratories (an Argonne partner in Taiwan), and Carnegie Mellon University to explore the use of their image processing software for flood and surface water detection, traffic movement, and other dynamic variables of interest.

#### **PROPOSED FUTURE WORK**

We will continue to work with the ECP program and colleagues at Oak Ridge National Laboratory (ORNL), LBNL, National Renewable Energy Laboratory (NREL), and Pacific Northwest National Laboratory (PNNL) on the coupled modeling framework, focusing in particular on the interactions between the urban canyon large eddy simulation and the EnergyPlus building modeling code (with LBNL), and in particular on the data exchange volume, format, and rate. With the Waggle platform, we continue to learn from external projects deploying test systems, including the University of Chicago AoT project, and projects with Northwestern University, the City of Portland, the City of Seattle (and University of Washington), and the University of Texas—Dallas (with the City of Chattanooga).



# LDRD PRIME – NUCLEAR SCIENCE AND TECHNOLOGY

# Development of a Computational Fluid Dynamics Multiphase Boiling Capability to Predict the Critical Heat Flux in Nuclear Reactor Fuel Assemblies

2014-177-R2

Adrian Tentner, Elia Merzari, Aleksandr Obabko, Dillon Shaver, Ananias Tomboulides, and Prasad Vegendla

## PROJECT DESCRIPTION

The project has developed and expanded Argonne's Extended Boiling Framework (EBF) two-phase flow modeling methodology and implemented it in NEK5000, a high-performance, highly scalable, open-source computational fluid dynamics (CFD) code developed at Argonne. The goal of the project is to develop a new version of the NEK5000 code, named NEK-2P, to simulate the two-phase flow and heat transfer phenomena that occur in a light water reactor (LWR) fuel bundle under various operating conditions, with special emphasis on the prediction of critical heat flux (CHF). Boiling flows are subject to a phenomenon known as "boiling crisis," where, for high cladding surface heat fluxes (exceeding the CHF), the heat transfer between the cladding and coolant deteriorates, leading to sharply higher cladding surface temperatures. Such temperatures lead to a deterioration of cladding structural integrity and ultimately to fuel pin failure and radionuclide release. Avoiding CHF conditions is essential for the safe functioning of LWRs. The proposed computational tool will provide accurate modeling for the study of two-phase flow phenomena in LWRs, which will help reduce uncertainty in the prediction of performance and safety characteristics.

## MISSION RELEVANCE

Multi-phase flow and boiling are of fundamental importance in the design of nuclear reactors used for energy generation, the vast majority of which are cooled by water. The assessment of the fuel assembly behavior under two-phase flow conditions is of particular importance, since many design and safety criteria depend on it. The two-phase CFD code developed by this project will help reduce the number of experiments required to develop new nuclear power reactor designs, thus streamlining design and facilitating prototyping of reactor components. This project therefore supports DOE's mission in energy security. This activity is also particularly synergistic with Argonne's expertise and interest in

high-performance computing, since multi-phase flow simulations are typically very expensive computationally and scalability is of the essence.

## RESULTS AND ACCOMPLISHMENTS

During the first year of the project FY 2014 a homogeneous two-phase flow solver was implemented in NEK5000 and the implementation of the Advanced Boiling Framework was initiated. During FY 2015 a two-phase drift-flux solver was developed, replacing the homogeneous two-phase flow solver and the Advanced Boiling Framework was completed and coupled with the drift-flux solver. During FY 2016, a new two-phase two-fluid solver was implemented in NEK-2P. This replaced the previous solver in NEK5000, which could only track one fluid velocity field. The new NEK-2P Eulerian two-phase two-fluid solver calculates time evolution of the mass, velocity, and energy of the liquid and vapor phases at all mesh locations in the computational domain by solving the mass, momentum, and energy conservation equations for each phase. The momentum equations for the two phases are currently coupled through the pressure, which is assumed to be the same for the two phases. The mass, momentum, and energy phase conservation equations are also coupled through the corresponding interphase transfer terms, which are obtained using the EBF models. The interphase forces considered in the model are drag, turbulent dispersion, virtual mass, lift, and wall lubrication forces. In addition, interphase momentum transfer is associated with mass transfer between the liquid and vapor phases. The treatment of the interphase forces covers the spectrum of flow topologies expected in a boiling water reactor (BWR) fuel assembly. The drag force model, for example, covers bubbles in the sub-cooled or saturated bubbly-flow topology, a mixture of Taylor bubbles and smaller bubbles in the slug-flow transition topology, and droplets in the droplet or mist topology.

The validation effort continued in FY 2016 with NEK-2P analyses of a CHF experiment and a subcooled boiling experiment using the two-phase two-fluid model. The CHF experiment analyzed is one of the CHF experiments conducted earlier by Becker in a 7.0-m-long vertical pipe with diameter 0.01 m and a uniformly heated wall. The pressure was approximately 7 MPa and the inlet sub-cooling was approximately 10.3 K.

The calculated void fraction distribution is shown in Figure 1, where the characteristic sub-channel flow regimes in a pipe with heated walls are simulated. The annular-mist flow regime with annular liquid films on the pipe walls and the mist flow regime are clearly observed

in the void fraction distribution obtained from the numerical simulation. The calculated wall temperature as a function of the distance from the pipe inlet is shown in Figure 2, where the wall temperature calculated with the NEK-2P 2P-2F solver is compared with the corresponding measured temperature and with the wall temperature that was calculated with the STAR-CD code using the EBF. The location of the calculated sharp rise in the wall temperature agrees fairly well with the location of the measured wall temperature rise. The calculated sharp rise in the wall temperature coincides with the disappearance of the calculated liquid film on the pipe wall (Figure 1). Both the magnitude and slope of the calculated wall temperature in the post-dryout region are similar to the corresponding measured temperature magnitude and slope. Separately from the Becker CHF experiment validation, we validated the 2F-2P model in NEK-2P by analyzing one of the Bartolomei sub-cooled boiling experiments that was previously analyzed with the NEK-2P drift flux model and with the STAR-CD two-fluid model. The calculated void fractions are in good agreement with the corresponding measured values and indeed provide a better prediction than the STAR-CD results (not shown). The simulation of two additional CHF experiments performed by Becker was also completed successfully in FY 2016. The results will be included in a paper that is being prepared for the International Conference on Nuclear Power Plants (ICONE) 2017.

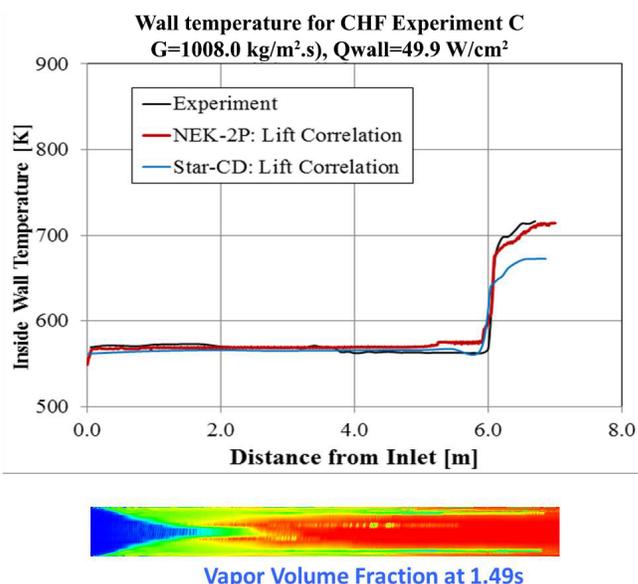


Figure 2. Comparison of measured and calculated wall temperatures for the CHF experiment, analyzed with the NEK-2P code.

We also performed initial simulations of the BWR full-assembly boiling test (BFBT). We plan to simulate the BFBT experiments using the NEK-2P code as part of the NEK-2P validation effort. The initial phase of this effort, performed in FY 2016, includes the simulation of a selected adiabatic single-phase BFBT test using the NEK5000 code. We developed a model of the BFBT fuel assembly and compared single-phase flow results with corresponding results obtained with the commercial CFD code STAR-CCM+ and measured pressure-drop data (not shown). The mesh and BFBT simulation experience accumulated during this exercise will be used in future simulations of heated two-phase flow BFBT experiments using the NEK-2P code.

This project was completed in FY 2016. Future development and validation of the NEK-2P two-phase flow CFD code will be pursued in the framework of the DOE Nuclear Energy Advanced Modeling and Simulation program.

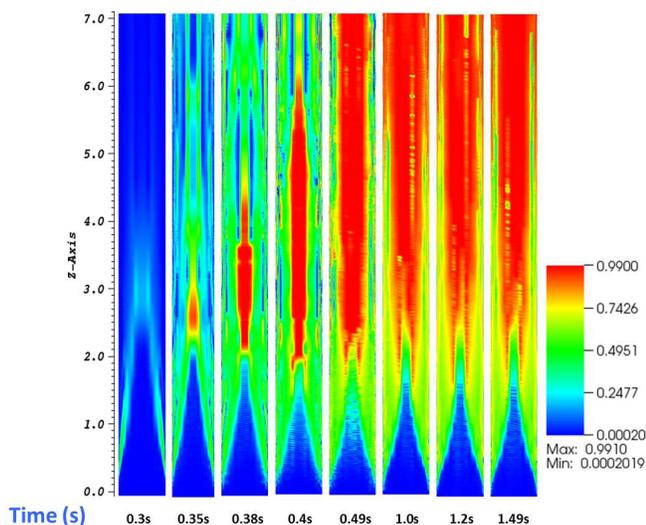


Figure 1. Evolution of vapor volume fraction distribution in a CHF experiment, calculated with the NEK-2P two-phase two-fluid solver and the EBF models. Vapor volume fraction corresponds to colors defined in the legend at the right.

# Economic and Technical Aspects of Nuclear Energy Competitiveness in the Current U.S. Deregulated Electricity Markets

2015-129-R1

Francesco Ganda, Audun Botterud, Fernando de Sisternes, Roberto Ponciroli, Richard Vilim, and Zhi Zhou

## PROJECT DESCRIPTION

The objective of this project is to investigate a wide range of technology, policy, and market issues to identify those options that have the greatest potential to restore the economic competitiveness of nuclear power plants (NPPs) in the United States over the mid- to long-term. Nuclear power in general and existing nuclear reactors in particular are pivotal to achieving the electricity-based carbon emissions reduction goals for 2030 established by the U.S. Environmental Protection Agency in its recently released Clean Power Plan. Yet the economic viability of nuclear energy is increasingly challenged in our nation's restructured electricity markets, as evidenced by some recent nuclear plant closures and discussion about further closings for economic reasons (e.g., "Response to the Illinois General Assembly Concerning House Resolution 1146, Potential Nuclear Power Plant Closings in Illinois," January 5, 2015, Prepared by the Illinois Commerce Commission, Illinois Power Agency, Illinois Environmental Protection Agency, Illinois Department of Commerce and Economic Opportunity, and "Exelon Notifies Grid Operator of Plans to Close Quad Cities," Exelon Newsroom, July 7, 2016). While there are also nuclear construction projects currently ongoing in the United States (e.g., four combined AP1000 units [pressurized water reactor NPPs by Westinghouse Electric Co.] at Vogtle in Georgia and VC Summer in South Carolina), these are all in areas with traditional vertically integrated utility regulation.

Two factors that have a significant impact on the competitiveness of nuclear energy are the abundance of inexpensive natural gas and the increased number of incentive programs that promote deployment of renewable energy capacity, with virtually zero marginal operating cost, well beyond what conventional market forces would dictate. These factors tend to reduce electricity market prices, impeding the cost recovery of the capital investment in NPPs. Understanding how existing and future NPPs can adapt to this situation, from both an economic and a technical perspective, is the focus of this work.

## MISSION RELEVANCE

Understanding how existing and future nuclear technologies can adapt to evolving market conditions is essential to ensuring the economic viability of this zero-carbon-emissions technology, and is therefore relevant to the DOE's energy security and environmental quality missions.

## RESULTS AND ACCOMPLISHMENTS

In the first year of this project, we completed a literature review and established a framework for the model development, including the methodology for estimating resource variability and reserve requirements in systems with increasing shares of wind and solar resources. We also started to explore the extent to which existing NPPs have been affected by low natural gas prices and low-price events caused by excess supply of renewable generation, as well as the economic, regulatory, and technical implications of operating nuclear reactors in flexible mode. We identified the most important technical issues associated with flexible operations and load following, and started developing a framework for an accurate model of flexible operations, with constraints imposed by a detailed representation of the phenomena occurring in the reactor when it is operated in flexible mode.

That model was developed and implemented in the second year of the project: In particular, to investigate the impact of nuclear plant operational flexibility on profitability (i.e., on its revenue as well as on the cost of operating the power system), we extended an existing unit commitment model for power system operations by adding detailed parameters of a nuclear plant and constraints that allow the nuclear plant to provide load-following and ancillary services.

In a case study using actual data from a representative public utility system, we have performed simulations using historical operational data projected to a future state with more wind and solar generation for a one-year period, under different assumptions about nuclear plant flexibility and other conditions. We have found that:

1. With operational flexibility, a nuclear plant may shift part of its capacity from energy to ancillary service provision, thereby increasing its total profit from the electricity market.
2. Nuclear flexibility also contributes to lowering the total cost of operating the system, because it increases overall system flexibility, leading to more efficient scheduling and dispatch of the system.

3. Nuclear flexibility accommodates more renewable energy, as it leads to large reductions in the curtailment of wind and solar generation (e.g., in periods of surplus generation).
4. A production tax credit for wind power reduces the profits for nuclear energy, but the impacts are modest in the test system. Nuclear flexibility has value regardless of whether or not the production tax credit is in place.
5. With additional operational flexibility from nuclear plants, market prices for energy, regulation up/down, and spinning up/down are slightly lower on average.

The results outlined above were based on a representation of nuclear plant flexibility that introduces a fixed constraint for how long a nuclear plant must stay on stable output after a ramp-down in order to stay within safe operating limits. We also developed a more advanced model that reflects the reactions and controls within the nuclear reactor. For instance, xenon neutron poisoning has an important impact on a nuclear plant's operational flexibility. In particular, in the last part of the fuel cycle, when the reactivity margin is reduced, the xenon reactivity contribution becomes a primary limiting factor on the operational flexibility of the reactor, because after a drop in power it might be necessary to wait for several hours before the xenon concentration decays below the required limit for a ramp-up. In the preliminary simulations discussed above, this effect was modeled by imposing a fixed time at stable power after a ramp-down. Such an approach constitutes a simplification and an idealization, given that the impact of xenon neutron poisoning after a drop in power is largely influenced by the amplitude of the power drop and by the available reactivity margin. In order to take this aspect into account, a dedicated criterion was designed. Every day, the corresponding reactivity margin is evaluated, and the nuclear unit operational flexibility is derived accordingly.

The designed flexible operating criterion for the nuclear plant was implemented in the power system code, and the commitment of the nuclear plant along with other power plants in the utility system was evaluated. The results assessed the possibility of improving the revenue for nuclear units (by operating them safely in flexible mode) by simultaneously minimizing the energy costs to consumers.

In a separate but related analysis, we have also investigated the effect of various techno-economic factors on the contribution of nuclear power to electricity production in economic equilibrium in the long run. To this end, we used a capacity expansion model with unit commitment constraints to determine the minimum cost

generation portfolio, while accounting for the technical operational constraints of the different generation technologies in the presence of a carbon emissions limit. The analyses aimed at determining the impact of gas prices, flexible nuclear operation, nuclear capital costs, the discount rate, and emissions caps on the average electricity price and the share of nuclear power. Conducting a long-run analysis in a case study with data representative of the state of Texas, we have found that:

1. Nuclear flexibility allows increasing the investment in nuclear power and the energy contribution of nuclear power. Therefore, under the assumptions used in the case study, the contribution of nuclear power increases when it is allowed to operate in flexible mode.
2. With inflexible nuclear power, there is a penetration ceiling caused by the minimum demand level in the system, as nuclear plants are not allowed to operate below their rated output and provide operating reserves when demand decreases.
3. Reducing the capital cost of nuclear power makes it more competitive; however, when it operates in inflexible mode, the penetration cannot be increased without violating the constraint that sets nuclear power at its rated output.
4. Natural gas prices have a large impact on the deployment of nuclear power, as they determine the competitiveness of combined cycle gas turbines and combustion turbines, which are very attractive investment options under today's low natural gas prices.

## Nuclear Materials under Extreme Conditions

2015-136-R1

Mark Williamson, Chris Benmore, and Rick Weber

### PROJECT DESCRIPTION

The goal of this project, which builds upon capabilities in high-energy X-ray characterization, ultra-high-temperature containerless melting techniques, and nuclear materials, is to develop a dedicated station for the experimental evaluation of nuclear materials under extreme conditions. The dedicated experimental station will allow us to investigate the properties of nuclear materials under well-controlled conditions and determine fundamental data (e.g., structure and bonding) important to nuclear energy systems.

## MISSION RELEVANCE

Shortly after the events that occurred at the Fukushima Daiichi nuclear power station in 2011, the United States Congress directed the DOE Office of Nuclear Energy (NE) to initiate a program in so-called accident-tolerant fuels. Specifically, DOE-NE was directed to "... give priority to developing enhanced fuels and cladding for light water reactors to improve safety in the event of accidents in the reactor or spent fuel pools." The DOE-NE program, composed of research teams from national laboratories, industry, and universities, is pursuing fuel improvements in areas such as enhanced fission product retention, a slower hydrogen generation rate at high temperatures, improved cladding properties, and improved fuel properties. In the area of improved fuel properties, the program emphasizes the need for a more detailed understanding of fuel melting behavior and the interaction of the fuel with cladding and other reactor materials at elevated temperatures. Although substantial progress has been made in identifying potential pathways to enhance nuclear fuel safety and performance, there remains a profound lack of fundamental information on the properties of nuclear materials and associated structural components under extreme conditions such as very high temperatures and in oxidizing or reducing environments.

## RESULTS AND ACCOMPLISHMENTS

A state-of-the-art instrument for containerless, X-ray interrogation of hot crystalline solid and liquid materials at very high temperatures was developed and used in deducing the behavior of solutions of uranium and zirconium dioxide ( $\text{UO}_2$  and  $\text{ZrO}_2$ ) under extreme conditions in FY 2016. The containerless environment allows the investigation of high-purity solids and liquids at temperatures up to approximately 3,600 K. In addition to avoiding container reactions, aerodynamic levitation enables the supercooling of liquids through avoidance of extrinsic nucleation. The containerless environment of the aerodynamic levitation system allows for equilibration of the samples with mixtures of gases to enable the study of materials under the oxidizing environments that may be encountered in severe reactor accident scenarios, or in reducing environments experienced by nuclear fuels contained in metallic cladding. The functionality of the system was demonstrated through a series of experiments conducted in FY 2015 that resulted in X-ray measurements of hot crystalline and molten uranium dioxide, zirconium dioxide, and a solid solution of uranium dioxide and zirconium dioxide.

In FY 2016, the levitation system was significantly improved with the installation of a sample spinning system. X-ray diffraction data collected for hot crystalline

materials during the first year sometimes exhibited severe pattern graininess rather than a ring pattern typical of a powder sample. Rotation of the sample at a rate of 10 RPM averaged out the contributions from different diffracting crystal planes to provide a powder pattern even from coarse-grained samples.

A set of  $(\text{U,Zr})\text{O}_2$  samples, along with  $\text{UO}_2$  and  $\text{ZrO}_2$ , was prepared for a series of experiments designed to interrogate the high-temperature structure of several  $(\text{U,Zr})\text{O}_2$  compositions important to severe reactor accidents. The as-prepared compositions were  $(\text{U}_{0.5}\text{Zr}_{0.5})\text{O}_2$ ,  $(\text{U}_{0.3}\text{Zr}_{0.7})\text{O}_2$ , and  $(\text{U}_{0.15}\text{Zr}_{0.85})\text{O}_2$ . Significant amounts of X-ray data were collected at the Advanced Photon Source for  $\text{ZrO}_2$ , as a function of temperature, to demonstrate the performance of the enhanced levitation system as well as to provide insight into structural changes occurring within the sample. Data were also collected for the crystalline and liquid compositions—namely,  $(\text{U}_{0.3}\text{Zr}_{0.7})\text{O}_2$  and  $(\text{U}_{0.15}\text{Zr}_{0.85})\text{O}_2$ —relevant to severe accident scenarios. Interestingly, the liquid with the as-prepared composition  $(\text{U}_{0.15}\text{Zr}_{0.85})\text{O}_2$  could be supercooled to several hundred degrees below the freezing point.

Successful development of the containerless, ultra-high-temperature, high-energy X-ray experimental station provides a unique tool to elucidate the behavior of nuclear materials under conditions relevant to nuclear energy systems.

## Understanding Embrittlement in Cast Austenitic Stainless Steels and Stainless Steel Welds

2015-145-R1

Yiren Chen, Jonathan D. Almer, Meimei Li, and Ken Natesan

### PROJECT DESCRIPTION

Cast austenitic stainless steels (CASS) and stainless steel (SS) welds are structural materials used as components at the primary pressure boundaries and core internals of light water reactors (LWRs). Consisting of a dual-phase microstructure of delta ferrite and austenite, CASS alloys and SS welds are vulnerable to thermal aging embrittlement and neutron irradiation damage. The service performance of CASS alloys and SS welds are of concern after long-term service exposure to reactor core environments. While the effects of thermal aging and neutron irradiation have been studied separately, it is difficult to predict whether these two degradation

mechanisms will interact with each other, leading to unexpected failures of reactor core components. In this project, we investigated the embrittlement mechanisms of CASS alloys and SS welds subjected to both neutron irradiation and thermal aging. Using advanced microstructural characterization techniques and X-ray *in situ* mechanical testing, we studied (1) the combined effect of thermal aging and neutron irradiation on the microstructural evolution, and (2) the deformation behavior of the dual-phase microstructure responsible for the embrittlement. The outcome of this study can help answer fundamental questions regarding the degradation of LWR core components and can provide a scientific basis for assessing and managing the embrittlement of CASS alloys and SS welds under the combination of neutron irradiation and thermal aging.

### MISSION RELEVANCE

Nuclear power generates about 20 percent of the United States' electricity without contributing to carbon emissions. This critical role of nuclear energy must be maintained for long-term operations to meet the carbon emissions reduction goals for 2030 established by the U.S. Environmental Protection Agency in its recently released Clean Power Plan. The objective of the current project is well aligned with the DOE's Light Water Reactor Sustainability (LWRS) program, which focuses on developing technical solutions to ensure safe and economic operation of existing nuclear power plants. The current project will also benefit the U.S. Nuclear Regulatory Commission (NRC), whose mission is to ensure nuclear safety of current LWRs and other nuclear systems. As the life extension of current LWRs is under consideration, a better understanding of the combined effect of thermal aging and neutron irradiation on the deformation behavior of duplex microstructures will be crucial for assessing the integrity and service lifetime of reactor components. The result of this study can help develop an effective aging management strategy, leading to significant economic benefits and adequate safety margins.

### RESULTS AND ACCOMPLISHMENTS

The research effort during FY 2015 was focused on the microstructural characterizations of thermally aged and irradiated CASS specimens. Using transmission electron microscopy (TEM) and atom probe tomography (APT), we showed that both thermal aging and low-dose neutron irradiation produced G-phase precipitates (a nickel-rich intermetallic silicide) in the ferrite at reactor operating temperatures. The neutron irradiation enabled and facilitated the precipitation that would otherwise

occur too slowly under normal thermal aging conditions. This result confirmed the interplay between neutron irradiation and thermal aging in CASS components, and clarified a general misconception that the two degradation mechanisms are independent and can be managed separately.

During FY 2016, the research effort continued on the microstructural characterizations for the specimens irradiated to higher doses. Working with colleagues at the University of Florida, we demonstrated that irradiation can induce a separation of  $\alpha$  (Fe-rich) and  $\alpha'$  (Cr-rich) domains in the ferrite at reactor operating temperatures, and can further increase the extent of segregation between Fe and Cr resulting from previous thermal aging. The enhanced  $\alpha/\alpha'$  phase separation in the irradiated specimens appeared to be correlated with G-phase precipitation. With the increase of the irradiation dose, the G-phase precipitates and  $\alpha/\alpha'$  phase separation continued to evolve in the ferrite, and irradiation-induced dislocation loops become more evident in the austenite.

To assess the impact of the deteriorated microstructures on the mechanical performance of CASS alloys, we conducted tensile tests on aged specimens at room and elevated temperatures. While both yield stress and ultimate tensile strength were increased, uniform elongations were reduced considerably after thermal aging. To further distinguish the different mechanical responses of the austenite and ferrite, we performed nano-indentation tests on the aged and irradiated samples. As shown in Figure 1, thermal aging and low-dose irradiation did not affect the austenite but increased the hardness of ferrite considerably. This observation is consistent with our microstructural results, confirming the critical role of ferrite in the embrittlement of CASS and SS welds. At high doses, the irradiation hardening became evident in the austenite. The different dose-dependent responses of the austenite and ferrite will affect the extent of embrittlement.

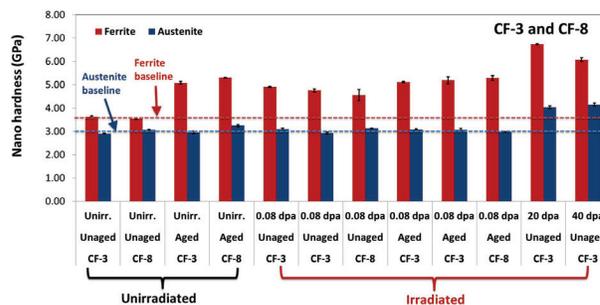


Figure 1. Nano-indentation measurements showing the effects of thermal aging and neutron irradiation in both austenite and ferrite.

Figure 1. Nano-indentation measurements showing the effects of thermal aging and neutron irradiation in both austenite and ferrite.

To understand the embrittlement mechanism, we also investigated the relationship between the deteriorated microstructures and plastic deformation of CASS alloys. Wide-angle X-ray scattering (WAXS) measurements were performed with *in situ* mechanical tests on the unaged and aged specimens at room temperature. The tests were performed with a nominal strain rate of  $1 \times 10^{-4}$ , and the WAXS data were taken with high-energy monochromatic beams. We scanned the entire gauge length of the sample while rotating the specimen about its loading axis. Figure 2 shows the evolution of lattice strains of the slip planes in the austenite and ferrite during deformation. The lattice strain of the aged ferrite was significantly higher than that of the unaged ferrite, indicating a much higher level of stress in the deteriorated ferrite phase. The differences in lattice strains between the austenite and ferrite increased with engineering strain, and were much larger in the aged than in the unaged specimens. An elevated incompatible strain can exaggerate the stress level at the interface of austenite and ferrite, leading to the embrittlement of phase boundaries. This embrittlement mechanism operates at room temperature and originates from the deteriorated ferrite phase in the dual-phase microstructure.

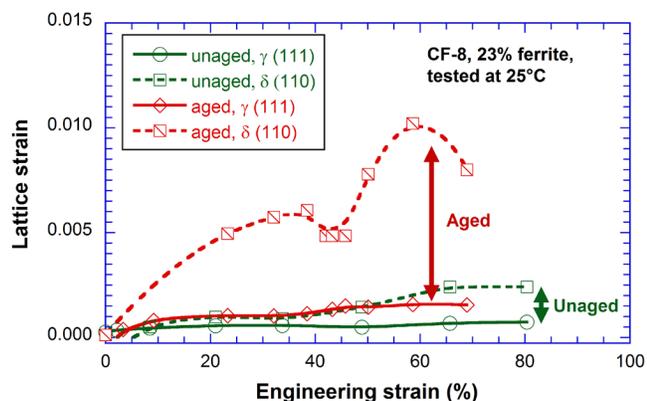


Figure 2. *In situ* WAXS measurements showing a significantly higher incompatible strain between ferrite ( $\delta$ ) and austenite ( $\gamma$ ) in the aged versus the unaged CF-8 alloy.

### PROPOSED FUTURE WORK

This LDRD project was completed in FY 2016. To further develop a strategy to mitigate the degradation of CASS components, additional work is needed to investigate (1) the deformation behavior of irradiated specimens with deteriorated austenite, and (2) the embrittlement mechanism operating at elevated temperatures. To support continuing this work, we will respond to the DOE Consolidated Innovative Nuclear Research (CINR) proposal call to address the degradations of reactor components in supporting the LWRS program. We will also propose to the NRC to expand our research scope in CASS alloys and SS welds.

## Development of Analysis Methods for Non-Destructive Evaluation of Concrete Degradation in Light Water Reactors

2016-140-NO

Alexander Heifetz, Igor S. Aronson, Sasan Bakhtiari, Mitchell Farmer, and Valerii M. Vinokour

### PROJECT DESCRIPTION

Alkali silica reaction (ASR) is a common chemo-mechanical damage mechanism that degrades concrete in old nuclear plants. ASR is a slow chemical reaction between highly alkaline cement and aggregates rich in non-crystalline silica, which are frequently present in many concrete mixes. ASR turns aggregates into a highly hydrophilic gel, which expands upon absorption of moisture from the ambient environment, and causes cracking of reinforced concrete. Significant structural damage due to ASR typically takes several decades to develop.

Currently, there is no standard method for non-destructive evaluation (NDE) of ASR in concrete. Existing methods for ASR detection in concrete structures are based on microscopy and chemical analysis of cored samples. Because chemical processes are precursors to crack formation, we explore methods for assessment of electrophysical and electrochemical properties of concrete for early-stage *in situ* NDE of ASR. Since chemical processes are facilitated via transfer of ionic species through the pore solution, we believe that the pore solution network contains signatures of early-stage ASR. The NDE techniques under investigation consist of microwave dielectric spectroscopy (MDS) and electrochemical impedance spectroscopy (EIS) of concrete. The MDS and EIS techniques are, in principle, sensitive to changes in chemical properties of the pore solution network caused by ASR, and provide electrophysical material property information in the gigahertz and in the sub-hertz-to-kilohertz electromagnetic frequency ranges, respectively.

The initial phase of this project consists of establishing the phenomenological experimental basis of MDS and EIS sensitivity to ASR in concrete. This has been investigated in a year-long measurement campaign aimed at finding correlations between electrical and mechanical properties of small concrete prism specimens at different stages of ASR progression. Because the ultimate objective is developing *in situ* NDE methods, techniques for

one-sided measurements of material properties have been investigated. Next phase of this project consists of investigating correlations between electrical and mechanical properties of large reinforced concrete blocks affected by ASR. In addition, physics-based models for quantitative interpretation of MDS and EIS measurements of ASR in concrete will be developed. In parallel, a complementary year-long study of chemical pore solution analysis in ASR-affected concrete has been initiated, along with preliminary investigations of 3-D imaging of ASR-related crack patterns in concrete using X-ray computed tomography.

### MISSION RELEVANCE

This proposal addresses the DOE's energy security mission with respect to nuclear-energy sustainability. The outcome of this project will be a set of sensing tools and techniques for performing and interpreting *in situ* NDE measurements, and forecasting the condition of concrete materials and structures for light water reactor (LWR) sustainability. The technology also has numerous applications for assessing the condition of concrete in critical civil structures.

### RESULTS AND ACCOMPLISHMENTS

MDS and EIS measurements performed in the initial study have shown a strong correlation between ASR progression and material electrical response. The studies were conducted on a set of reactive concrete prism specimens suffering from premature ASR damage and non-reactive age-matched controls. All concrete specimens were stored in a humidity chamber under the conditions known to favor rapid development of ASR. At specified time intervals, one reactive and one non-reactive specimen were removed from the chamber. Using standard mechanical tests (i.e., measurements of length and mass expansion), ASR damage increasing with dwell time of a specimen in the humidity chamber was confirmed in reactive specimens. Mechanical measurements on age-matched control specimens have shown no sign of ASR damage. Figure 1 displays the time dependence of mean length expansion (averaged across specimens). The value of the y-axis is percent length change, which is calculated relative to the specimen length at day one.

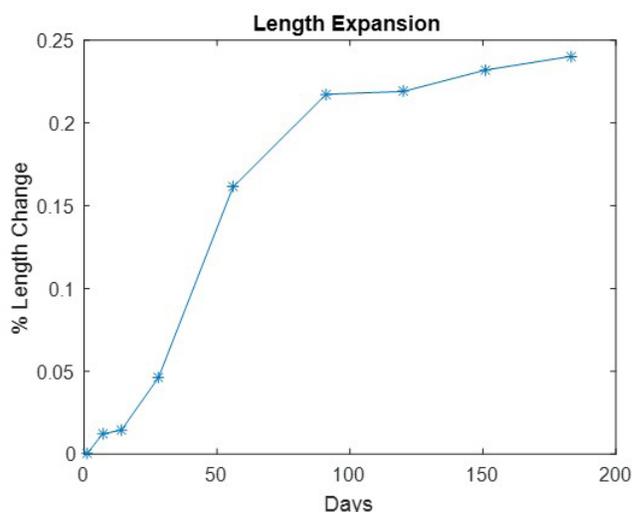


Figure 1. Mean values of length expansion of concrete specimens as a function of time due to progression of ASR.

Subsequently, electrical properties of concrete specimens were measured using MDS and EIS techniques. MDS measurements have been performed in transmission and reflection geometry (one-sided and two-sided measurements). EIS measurements have been performed in four-point probe geometry (one-sided measurements). The results of impedance spectroscopy measurements are shown in Figure 2 in the form of Nyquist diagram, where the values of  $Z_i$  and  $Z_R$  (in units of  $\Omega$ ) for the same frequency  $\omega$  are plotted on the complex plane. The four color-coded curves are impedance measurements of concrete specimens at different maturity levels of ASR progression.

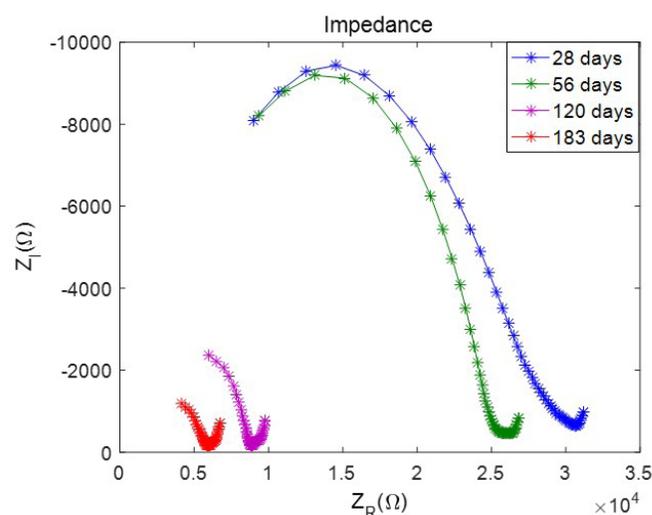


Figure 2. Nyquist plot of complex-valued impedance measured on concrete specimens at different maturity levels of ASR progression.

Results of microwave transmission measurements are displayed in the log-linear plot in Figure 3 as position-averaged values of  $S_{21}$  (in units of dB) as a function of frequency. The four color-coded  $S_{21}$  curves are measurements of microwave transmission through concrete specimens at different maturity levels of ASR progression.

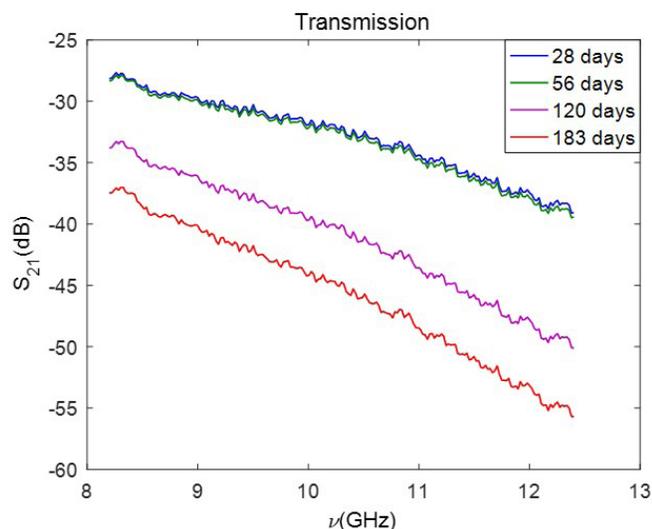


Figure 3. Transmission of X-band microwaves measured as  $S_{21}$  parameter for concrete specimens at different maturity of ASR progression.

### PROPOSED FUTURE WORK

MDS and EIS measurements will be performed on large reinforced concrete blocks suffering from ASR damage. Large blocks provide a more representative environment for testing of NDE methods as compared to small prism specimen. Blocks will be stored in a humidity chamber, and ASR progression will be monitored with standard mechanical testing measurements (i.e., length expansion). In addition, several core specimens will be extracted from the large blocks throughout the study for detailed NDE analysis.

Efforts are currently under way to develop more quantitative analytical and computational models of the observations. The models will provide a better understanding of the penetration depth and interaction region of electromagnetic waves with concrete.

We will conduct companion experiments to understand ASR-driven changes in concrete morphology and pore solution. A study has been initiated to extract and analyze the pore solution from concrete prism specimens at different stages of ASR damage. The solutions will be analyzed for calcium, sodium, potassium, and silicon using inductively coupled plasma spectroscopy. Results will be correlated with observations from NDE measurements.

Preliminary work has been initiated on high-resolution 3D imaging of ASR-induced cracks in concrete using X-ray computed tomography.

## Production of Medical Isotopes Using the Argonne Electron LINAC

2016-158-NO

M. Alex Brown, Jerry A. Nolen, Jr., David A. Rotsch, and George F. Vandegrift III

### PROJECT DESCRIPTION

Radionuclide therapy is an alternative approach to current cancer treatments such as chemotherapy and surgery. The destructive ionizing nature of radioactive isotopes can be systematically delivered to a targeted cancer to destroy malignant cells without compromising the surrounding healthy tissue. Among the thousands of known radioactive isotopes, only a select few are suitable for radionuclide therapy, and these are further categorized on the basis of their radiological properties (i.e., alpha, beta, or Auger radiation). Many of these radioisotopes can only be produced using exotic methods or with highly enriched uranium reactors. Clinical trials with desirable radioisotopes have been hampered by supply and/or purity limitations of the current production methods.

The DOE/NSF Nuclear Science Advisory Committee has designated scandium-47 ( $^{47}\text{Sc}$ ) a “high-priority” medical radioisotope. It is considered a “theranostic” radioisotope, i.e., one with a combination of therapeutic and diagnostic characteristics: Its half-life and beta emission are suitable for treating small metastatic tumors, and it emits appreciable diagnostic photons. Actinium-225 ( $^{225}\text{Ac}$ ) has garnered the attention of the nuclear medicine community as being one of the most promising alpha-emitters. In contrast to beta-emitters, alpha-emitters have a shorter penetration range in the tens of microns and are more useful for leukemias and small micrometastatic deposits of cancer cells. Current production routes toward  $^{225}\text{Ac}$  are hindered by  $^{227}\text{Ac}$  impurities.

Argonne’s Low Energy Accelerator Facility (LEAF) has a recently upgraded 50-mega-electron volt/25-kilowatt (50-MeV/25-kW) electron linear accelerator (LINAC) capable of producing, via photonuclear reactions, radioisotopes that other facilities cannot reliably produce. Using this accelerator, which is unique among the DOE labs, we have directed our efforts to facilitating photonuclear production of in-demand medical radioisotopes. Work has focused on the development

of technologies for the production and purification of  $^{47}\text{Sc}$  and  $^{225}\text{Ac}$  from a theoretical and experimental frame of reference. Using available Monte Carlo-based codes, we are able to predict potential radioisotope yields and optimize their production. We are using the Particle and Heavy Ion Transport (PHITS) code because it is well-benchmarked, well-documented, and user-friendly, and has a database to support photonuclear reaction simulations.

### MISSION RELEVANCE

This project aligns with DOE's mission to advance peaceful nuclear energy technologies. Furthermore, the DOE Office of Science's National Isotope Development Center within the Office of Nuclear Physics coordinates DOE facilities' and universities' efforts in the production, sale, and distribution of stable and radioactive isotopes (medical and other). Our efforts serve as a catalyst for creating a radioisotope production facility that makes use of Argonne's unique LINAC resource and expertise in nuclear engineering, radiochemistry, chemical engineering, and physics.

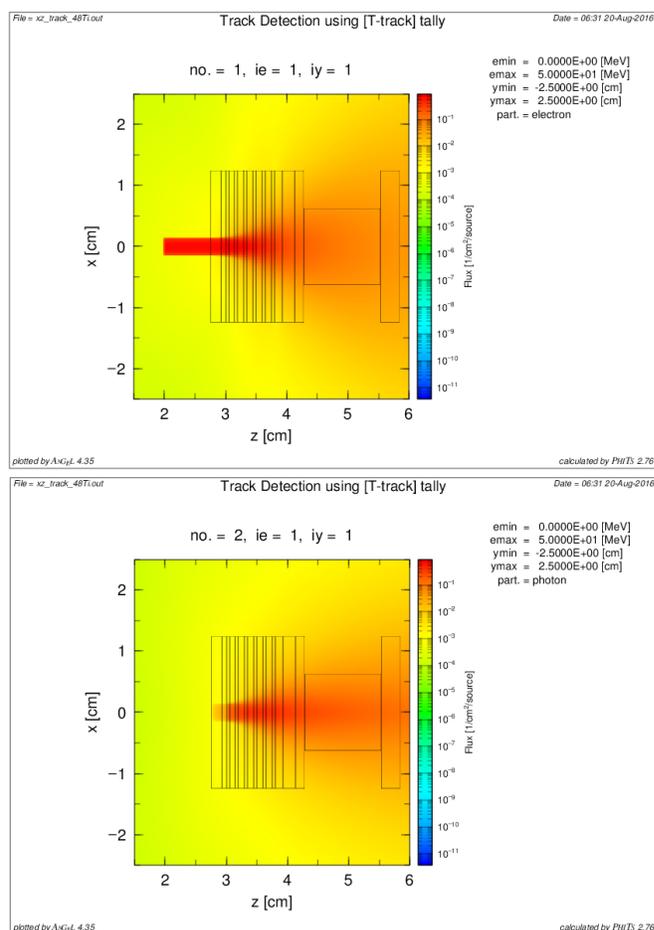
### RESULTS AND ACCOMPLISHMENTS

In FY 2016, preliminary irradiation of natural titanium dioxide ( $\text{TiO}_2$ ) and Ti metal targets demonstrated the photonuclear production of  $^{47}\text{Sc}$  and provided enough radioactive scandium to develop chemical processing methodologies. Through photonuclear reactions, we produced small quantities (<10 millicuries/experiment) of  $^{47}\text{Sc}$  at Argonne's LEAF, using the LINAC, and compared production yields with theoretical simulations. These results have carried over to our efforts toward  $^{225}\text{Ac}$  production.

**Scandium-47.** The first irradiation was performed in order to prepare an in-house stock of radios scandium for development of a purification method. A water-cooled tungsten or tantalum converter was used to convert the incident electrons to photons. Two natural Ti foils and natural  $\text{TiO}_2$  were irradiated for 3 hours with an electron-beam energy of 35 MeV and a power of 2 kW. Post-irradiation, the  $\text{TiO}_2$  was analyzed with a high-purity germanium (HPGe) detector, and the Ti plates were scanned by a gamma scanner to verify beam position. A small portion of the  $\text{TiO}_2$  sample was dissolved and gamma counted to verify initial analyses.

Radioscandiums were separated and purified from the Ti target material by extraction chromatography. Radioscandiums were eluted from the column with >98% recovery. The product was analyzed with the HPGe detector and inductively coupled plasma/mass

spectrometry (ICP-MS). The ICP-MS data demonstrated excellent purification of scandium with only environmental impurities (sodium, boron, silicon, and iron) present. Subsequent irradiations were performed to verify results, perfect chemical processing methodologies and to irradiate samples with well defined geometries to enable simulations (Figure 1). Specific activities of >7 curies per gram were achieved in these trials, and simulation of the production yield of  $^{47}\text{Sc}$  was in good agreement with the experimental data.



**Figure 1.** Monte-carlo simulations (using PHITS software) for the production of Bremsstrahlung photons and isotopes at the electron linear accelerator. **Top:** the simulated incident electron beam and electron scattering upon interaction with tantalum converters (3 cm – 4 cm). **Bottom:** the resulting photons interact with the target material (4.25 cm – 5.5 cm) to produce the isotopes of interest via photonuclear reactions.

$^{225}\text{Ac}$ : We are investigating the  $^{226}\text{Ra}(\gamma, n)^{225}\text{Ra} \rightarrow ^{225}\text{Ac} + \beta^-$  production route. We have carried out high-level yield simulations and thermal calculations for the compact converter target geometry. We predict that we will be able to produce one curie of  $^{225}\text{Ac}$  per five-day irradiation at 10-kW beam power, resulting in an annual production rate of isotopically pure  $^{225}\text{Ac}$  that is 10 to 100 times greater than current production capabilities.

**PROPOSED FUTURE WORK**

The encouraging results of FY 2016 have encouraged us to continue scaling up the technology of  $^{47}\text{Sc}$  to produce larger quantities. Proof of the production scalability may allow performing chelation studies and ultimately advancing the isotope to clinical trials. We are also in possession of enriched Ti target material, which will augment the yields of  $^{47}\text{Sc}$  as well as the purity and specific activity; the target material will be irradiated, provided trials using natural Ti are successful. In addition, we are investigating various forms of Ti to enhance production yields. Furthermore, in FY 2017, we plan on conducting a pilot irradiation to produce  $^{225}\text{Ac}$ .

## Additive Manufacturing for Nuclear Energy Applications

2016-159-NO

Abdellatif Yacout, Peter Kozak, Kun Mo, and Michael Pellin

**PROJECT DESCRIPTION**

Recently, significant attention has been focused on additive manufacturing (AM) as a tool to produce precise and complex forms and/or structures, with the potential for application to large-scale manufacturing. Also referred to as three-dimensional (3D) printing, AM involves manufacturing a part by depositing material layer by layer. Compared to injection molding or machining and/or subtractive technologies, AM has several advantages, some of which can be of particular benefit to nuclear energy applications. Those advantages include the ability to form complex shapes, the reduction and/or elimination of waste scrap during manufacturing, and the ability to produce new and/or improved material with better performance through organizing the microstructure at the mesoscale level. The main objectives of this project are to (1) demonstrate the possible role of AM in improving the processes of material and components production for nuclear energy applications, (2) consider a demonstration focus area, and (3) establish a base for this technology at Argonne. The main application considered here is the application to nuclear fuel (i.e., actinide) materials. AM can be applied to achieve innovations in actinide materials as well as improvements in the manufacturing of components. Other institutions are pursuing printing of actinide materials using AM techniques that require expensive metal 3D printing technologies (e.g., direct sintering of powder through the use of a laser or electron beam). That approach can limit scale-up to the commercial scale, especially given the controlled environment that is required for handling actinide materials. This project considers two independent methods for low-cost,

scalable 3D printing of metal for nuclear fuel applications: use of metal-impregnated filament and metallic paste and/or slurry. Both of these techniques will require post-processing to remove the plastic matrix material and to sinter the part, and both methods will involve the challenges of porosity mitigation and dealing with dimensional changes during sintering.

**MISSION RELEVANCE**

The application of AM to produce uranium molybdenum (U-Mo) foils, which are difficult to fabricate using conventional methods, will benefit the DOE National Nuclear Security Administration's material minimization efforts and activities related to the conversion of U.S. high-power research reactors from the use of highly enriched uranium to low enriched uranium, as it can lead to major cost savings and reduction in waste associated with the fabrication process. The developed technology will be transferred to fuel fabricators (e.g., Babcock & Wilcox Nuclear Energy, Inc.) to produce the foils. Development of the capability to produce fuel material with controlled structure using AM can lead to production of advanced reactor fuels with superior properties (e.g., higher thermal conductivity, controlled porosity, and/or improved irradiation resistance). This capability will benefit the wider advanced-reactors fuel development programs that are supported by the light water reactor community and DOE Office of Nuclear Energy campaigns such as the Advanced Fuels Campaign (AFC), Nuclear Energy Enabling Technologies (NEET), and Advanced Reactor Technologies (ART).

**RESULTS AND ACCOMPLISHMENTS**

Two independent methods for low-cost, scalable 3D printing of metal for nuclear fuel applications are being considered: use of metal-impregnated filament and metallic paste and/or slurry. The following is a summary of the activities related to the implementation of each technology for 3D printing using non-actinide materials. Work with actinide materials will be pursued once the printing methodology is established.

**Route 1: Metal Powder-Impregnated Plastic Filament**

A compact fused deposition modeling (FDM) 3D printer was used with a copper impregnated filament having a stated copper content of 87.75%. Preliminary tests showed that this material is quite easy to work with and prints very cleanly. A small test object (Figure 1a) was successfully printed. Salient characteristics of this unsintered green part are visible in scanning electron microscope (SEM) images showing the striations due to the print layers (Figure 1b) and the spherical metal particles in the

polymer matrix (Figure 1c). Gaps between the printing layers (150-micron layers were used in this case) can be minimized by printing in thinner layers or, in the case of a macro-scale object, sanding the exposed surfaces to a smooth finish.

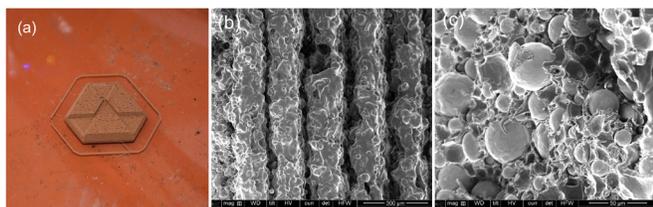


Figure 1. (a): First test print of Argonne logo using 87.75 wt% copper filament (in poly(lactic acid)) from The Virtual Foundry; (b) SEM image showing ~150-micron-layer striations in printed part using copper-loaded filament; and (c) SEM image showing copper particles embedded in the polymer matrix.

## Route 2: Metal Powder as Paste and/or Slurry

A printer was acquired that takes a standard Luer-lock syringe and can thus use a variety of tips, including blunt-tip stainless steel needles and plastic nozzles of varying inside diameters. Preliminary tests to explore printer functionality and control of the extrusion system have been performed. Generation of metal paste (or pre-ink) according to a published formulation continues. Preliminary testing indicated that it will be challenging to select a pre-ink that is thick enough not to ooze from the nozzle or sag on printing, but which can still be forced through the syringe at an acceptable rate. Additional related factors are selecting an appropriate syringe diameter and length and optimizing print settings. In the first attempt to formulate the pre-ink using copper, the shape of the printed components was not well controlled because of the inhomogeneity of the ink during printing. While some difficulty has been encountered in maintaining a consistent viscosity, progress is being made by adding small amounts of hydroxypropyl methylcellulose as a thickener. It is anticipated that testing will first be conducted using molybdenum oxide, aluminum, copper, or other metals of interest to understand the procedure and optimize the process before moving the printer to a glovebox and working with radioactive materials.

SEM examinations were performed on four different 3D-printed specimens to evaluate their microstructures and porosities. The pre-ink consisted of copper powder mixed with poly(lactic-co-glycolic acid) (PLGA) or another plastic solution. The pros and cons of different solutions were reviewed on the basis of the SEM examinations. Figure 2 shows the microstructures of the four samples. The first sample (Figure 2a) was printed with a pre-ink produced by mixing copper powders with a proprietary plastic formula. The printed samples show large pores, and the connections between the particles are not firm.

The plastic and/or glue seems not to hold the copper particles very well. In contrast, the other two samples (Figures 2b and 2c), printed with a pre-ink produced by mixing copper powders with PLGA, are more promising. The particles are well merged into the PLGA, and no pores are visible.

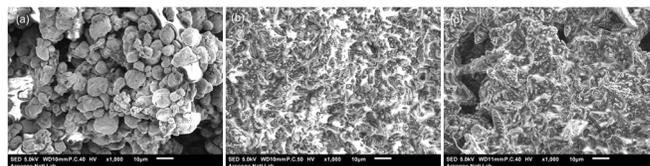


Figure 2. Microstructures of 3D printed samples made from three different pre-ink formulations: (a) Sample printed using paste formulated from hydroxypropyl methylcellulose and dichloromethane (DCM) solvent; (b) Sample printed using paste formulated from poly(lactic co-glycolic acid), with poly(lactic acid) structure supporting the paste material; (c) Sample printed using paste formulated from poly(lactic co-glycolic acid), without poly(lactic acid) structure supporting the paste material. The poly(lactic acid) structure used as supporting materials was found to be able to better preserve the shape and integrity of the paste materials during 3D printing.

## PROPOSED FUTURE WORK

In FY 2017, we will continue working to improve both of the above-described printing processes. Meanwhile, we plan to start working with radioactive materials after moving the printers into a glovebox located in a radiological area. Specific tasks are as follows:

1. Print U-Mo/UCO<sub>2</sub> or other actinide powder green bodies.
2. Optimize the annealing of green bodies to form foils similar to those produced with conventional methods.
3. Explore increasing the foil density, if needed, using additional steps.
4. Print a second layer on top of actinide foils and fabricate micro-plates for testing, if possible.



# **LDRD PRIME – UNIVERSE AS A LAB (ULAB)**

## Detectors for CMB Experiments

2016-143-NO

Clarence Chang, Valentine Novosad, Gensheng Wang, and Volodymyr Yefremenko

### PROJECT DESCRIPTION

This project involves fabricating, modeling and characterizing different detector architectures for use in next-generation Cosmic Microwave Background (CMB) experiments with the goal of understanding the fabrication and performance advantages and trade-offs associated with different detector designs. The primary context for this work is research and development in preparation for a major role in detector fabrication for the upcoming CMB-S4 experiment. It will be the definitive, ground-based, CMB experiment, involving over 150 scientists across multiple national labs and university groups, and mapping the sky to levels near the fundamental limit. The scientific goal of CMB-S4 is to use precision measurements of the CMB to study the quantum nature of inflation and to explore neutrino physics.

CMB-S4 scientific requirements present a unique challenge for detector design. Requirements include: 1) observing over half the sky, which requires operating multiple platforms from at least two geographic sites, 2) unprecedented sensitivity, which requires mass producing ~500,000 superconducting detectors, and 3) unprecedented capability for foreground removal, which requires a large operating bandwidth of ~40–300 GHz. It is unlikely that a single detector design will be optimal for all of these requirements and the best approach will be to use multiple architectures, each optimized for a subset of experiment requirements. For this project, we will explore how different detector architectures can be implemented and optimized to provide a suite of technologies that meet the broad requirements of CMB-S4. Candidate structures include broadband lenslet-coupled sinuous antenna detectors, detectors with phased antenna arrays, and detectors coupling through 3D feeds. We will design, fabricate and characterize test versions of detectors where the design has been varied and optimized using commercially available simulation packages coupled with our measured superconducting material properties. By fabricating different detector designs using the same underlying materials and fabrication processes, we can directly evaluate the impact of detector architecture on device performance and fabrication yield.

This project is a collaboration among Argonne's High Energy Physics and Material Science Divisions, its Center for Nanoscale Materials, the University of Chicago, and the Fermi National Accelerator Laboratory to simulate, fabricate and test new CMB detector concepts. Argonne provides the resources and expertise in superconducting materials and nanofabrication. Fermilab provides resources for detector simulation using commercially available packages like Ansys HFSS and Sonnet. The University provides resources for spectral characterization of detector arrays through a custom-built Fourier Transform Spectrometer and cryogenic test bed. The results of our work will directly impact the design of CMB-S4 detectors providing valuable input regarding the optimum suite of detector technologies. The technical expertise gained from this project will also establish a foundation in detector design and fabrication enabling Argonne to meet the challenge of CMB-S4 detector development and production.

### MISSION RELEVANCE

This project is relevant to DOE's basic science mission and directly addresses the mission of the Office of High Energy Physics (HEP). CMB science is part of the HEP core particle physics research program as echoed in Recommendation 18 of the Report of the Particle Physics Project Prioritization Panel (P5), which states, "Support CMB experiments as part of the core particle physics program. The multidisciplinary nature of the science warrants continued multiagency support." The CMB-S4 experiment was one of the recommended priorities in this report. Its science is relevant to and supported by DOE, NSF and NASA.

### RESULTS AND ACCOMPLISHMENTS

The first year of this project focused on fabricating and characterizing Argonne's first multi-chroic antenna-coupled CMB detector arrays. Measurements included thermal transport properties, polarization properties and spectral response. We also examined the detector mechanical-thermal architecture using a new laser scanning confocal microscope (see Figure 1). The spectral response of the detectors was simulated with model parameters coming from our measured superconducting materials properties. Figure 2 compares the measured spectral response of this detector array with the predictions from these simulations. The Argonne-fabricated detectors perform well and are in good agreement with the predictions from simulations. We have fabricated and characterized multiple arrays making small variations in materials properties from which we can evaluate the robustness of the fabrication

process. Our detector fabrication is sufficiently reliable for current generation CMB experiments, but the small variations in parameters (e.g., superconducting critical temperature and dielectric thickness) will need to be improved for future experiments. Changes in detector design and choice of materials may provide the necessary improvement for an experiment like CMB-S4.

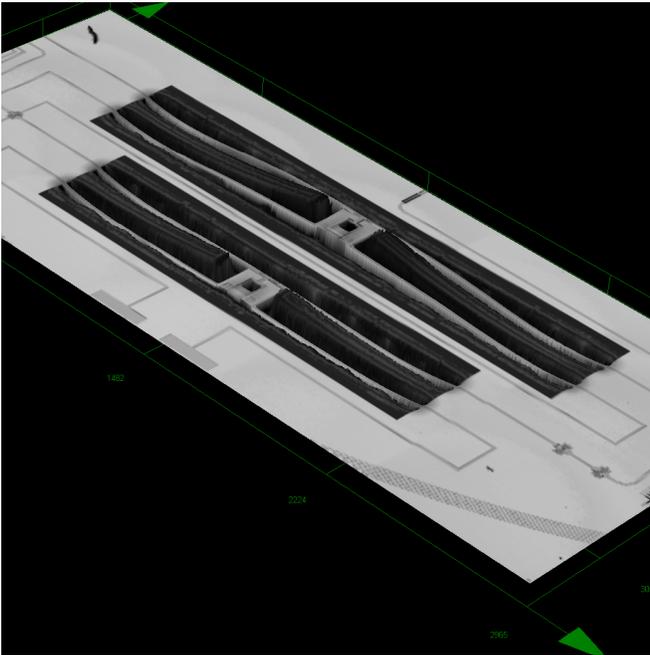


Figure 1. Bolometer islands from CMB detector arrays fabricated at Argonne. The structures are suspended by four SiN beams. Image was taken using a new laser scanning confocal microscope.

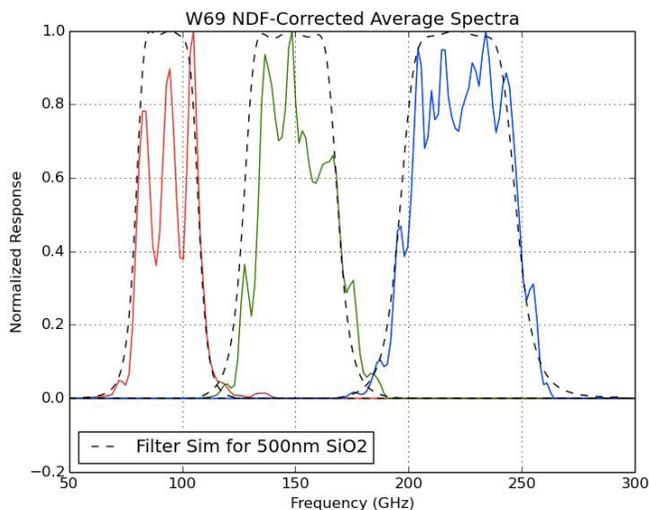


Figure 2. Spectral data for an Argonne-fabricated multi-chroic detector array. Colored lines correspond to measurements of each of the three optical passbands. The ripples in the data are artifacts typical in these mm-wave spectral measurements. Dashed lines correspond to simulated passbands showing good agreement between predicted and measured performance.

## PROPOSED FUTURE WORK

The next step in this work is to improve the design of the multi-chroic antenna-coupled detectors by implementing small changes to the fabrication process to improve fabrication reliability. We will also develop simulations of the detector antenna pattern using commercially available numerical solvers of electromagnetic structures. After completing our studies of this multi-chroic structure, we will repeat the process with other architectures including designs using 3D feedhorn structures.

## Data-Intensive Computing and the Cosmic Frontier

2016-163-N0

Ravi K. Madduri and Daniel Murphy-Olson

### PROJECT DESCRIPTION

This project is exploring new computational technologies to deliver a dedicated data-intensive computational infrastructure that can be used for analyzing datasets from cosmological surveys and large-scale cosmological simulations. Our working hypothesis is that any practical implementation of a data-intensive system should consider managing data as a first-class design principle along with enhancements in advances in processor speeds and density. The basis of this capability is the Argonne-led Portal for Data Analysis services for Cosmological Simulations (PDACS). PDACS will be tuned to handle large-scale observational data streams and, very importantly, allow for joint analysis of observational and simulation datasets. PDACS will also provide a centralized index of collections of cosmology data across the DOE complex. Additionally, working with domain experts we will improve upon and extend analysis workflows available in PDACS. A key feature is the integration of software container technology, which will enable collaborative software development, and improve software development and deployment process efficiency, and ease of integration of domain expert knowledge in high performance scientific software. As an important application, South Pole Telescope (SPT) workflows and analysis tasks will be integrated into PDACS. Finally, we will explore generalizing these tools so they can be leveraged in other science domains.

### MISSION RELEVANCE

This project supports DOE's mission in fundamental science. Data-intensive computing is an area of increasing interest to DOE's Office of Advanced Scientific Computing Research (ASCR) and to the other DOE Office of Science

programs. The recent ASCR/High Energy Physics (HEP) Exascale Requirement Review highlighted the need for joint efforts by the two offices in this direction. This project will be a pathfinder for a new set of capabilities for HEP's Cosmic Frontier projects. Additionally, it will be of great interest to a number of other research communities, including DOE Basic Energy Sciences.

## RESULTS AND ACCOMPLISHMENTS

- *The beta release of the PDACS portal was deployed.* The portal uses Globus service to authenticate users. PDACS also uses Globus for the reliable, secure transfer of cosmological simulation data from various supercomputing centers. We added support for data movement from the National Center for Supercomputing Applications (NCSA) Blue Waters and Argonne's Mira systems. The PDACS portal is deployed as a Docker container, increasing the portability of the system to multiple supercomputing resources. Two important visualization capabilities were added to the portal. Cosmological datasets can be visualized, like the results from halo finders (analysis tools that search simulation datasets for locally over-dense clumps of matter, called halos). Currently, Friends-of-Friends (FOF), and Spherical Over Density (SOD) halo finders are supported. Halo mass distributions can be plotted using a JavaScript-based gnu plot tool. We also enabled support to launch Jupyter notebooks so one can interactively analyze data and create reusable iPython notebooks for common data wrangling.
- *Globus Transfer was enabled.* Globus transfer has been enabled on the cluster and tools were developed on the PDACS portal to make it easy to move large cosmological simulations datasets from other supercomputing centers using the Globus. This capability is essential for large-scale data analysis of future simulations and surveys. A demonstration of this capability was presented at Supercomputing 2016.
- *An HPC cluster dedicated to this project was deployed—the Jupiter cluster.* We designed an initial tailored operating environment. We currently have 82 total nodes online, with a subset (currently 64) available in production mode. A beta release of the environment is in place. This effort included upgrading the operating systems on all the nodes to CentOS 7.3, upgrading all the software packages needed for the science groups, deploying a computational job manager, SLURM (developed at LLNL), that executes analysis codes on computational nodes, and deployed the necessary infrastructure for creating and running Docker and Shifter containers. Initial users from cosmology groups and the SPT are utilizing the

system. We are also working on creating reusable recipes using Puppet to deploy a homogenous computational infrastructure across the cluster. We deployed check\_mk for monitoring. Baseline hardware monitoring is currently in place. We are in the process of adding monitoring for the workflow system and the application servers.

- *Hardware updates were specified and implemented.* Now that we have the system in beta mode, we have a better understanding of requirements and will be able to make informed decisions about needed hardware upgrades. In FY 2016, we procured four additional Compute Servers, which will be used to run services that require reliable hardware. Also, these nodes can support the latest Nvidia graphics processing units. We also procured approximately 400 TB of additional storage capacity. This storage system is a higher density design than the current standard low-cost solutions we employ. This new design will enable more efficient large-scale storage deployments. As part of this project we are developing processes, procedures and tools for this new design.
- *Production support infrastructure was deployed.* The centralized logging infrastructure has been deployed, and all logs flowing to it have been deployed using rsyslog. All base infrastructure logs are flowing to the central syslog server. Comprehensive and easy-to-follow documentation is the key for software adoption. We created an initial set of documentation that can be followed to leverage Jupiter resources and the PDACS portal.

## PROPOSED FUTURE WORK

- We plan to add support for execution using Docker containers. This work will involve creating containers for all the PDACS-based analysis tools, including the halo finders and mass functions. The goal of this work is to create a deployment of PDACS and the tools such that they are portable across various supercomputing centers.
- We plan to create a data catalog that allows querying for data using various cosmological parameters across multiple sites. This tool will use Globus transfer to move data to Jupyter for further analysis.
- We plan to add support for data visualization using ParaViewWeb.
- We plan to add additional cosmological tools based on identified needs.

- A ticket system has been deployed, leveraging the Computing, Environment, and Life Sciences Directorate's existing JIRA infrastructure. JIRA is issue tracking and project management software by Atlassian, commonly used on software projects. We will begin evaluating this system internally. We anticipate using this system to facilitate communications with PDACS users once the system begins to move to production.
- We plan to enhance the documentation in the coming months.
- We plan on configuring application-level logs from PDACS to flow to the central syslog server.

## Superconducting Materials for Using the Universe as Our Laboratory

2016-167-NO

Valentine Novosad, Clarence Chang, Gensheng Wang, and Volodymyr Yefremenko

### PROJECT DESCRIPTION

This project aims to advance the science and technology of superconducting materials and detectors. Superconducting detectors are the favored technology for astrophysical measurements of radiation at sub-millimeter (sub-mm) and mm wavelengths. This spectral range encompasses the majority of the measurable extragalactic radiation making superconducting detectors a key technology for utilizing the universe as a laboratory (ULab) for fundamental science. The short-term focus of this project is developing materials and technology relevant for next-generation, transition edge sensor (TES) bolometer arrays utilizing superconducting microstrip transmission lines.

### MISSION RELEVANCE

This project directly addresses two DOE science missions: first, it advances the cosmic frontier of high energy physics (HEP) through advancing the CMB experiment; and second, it addresses the materials sciences and engineering (MSE) of the DOE Office of Science, Basic Energy Sciences (BES) through the development of superconducting materials with novel structures, functions, and properties. The scope of this proposal is also well aligned with the goals of Argonne's ULab Focus Area and directly addresses ULab's key topic area of CMB and leadership in CMB-S4.

### RESULTS AND ACCOMPLISHMENTS

In our first year of work, we have configured, procured, installed, and tested a dedicated thin-film deposition system. The new instrument is required to achieve full control over the film growth parameters and to minimize cross contamination from other processes. We created a 6-in., wafer-capable, ultra-high vacuum tool equipped with an oversized cryo-pump and internal bake-out heaters. It has a low-voltage, gridless hollow cathode-ion source plumbed with argon (Ar), oxygen (O<sub>2</sub>), and nitrogen (N<sub>2</sub>) for *in situ* wafer cleaning and ion-beam-assisted sputter deposition (see Figure 1). The deposition sources include a six-pocket e-beam evaporator, and six sputtering heads powered by direct current (DC), pulse DC, and radio frequency (RF) power supplies. The sample heating stage is both rotatable and tiltable *in situ*. The tool has an automated, turbo-pumped, five-position load-lock chamber. This unique configuration is ideal for the thin film research and development (R&D).

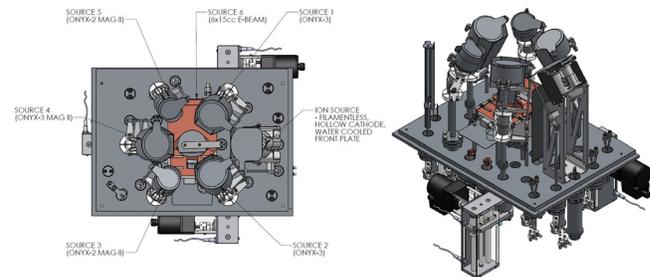


Figure 1. Ion, e-beam, and sputter deposition sources layout

### PROPOSED FUTURE WORK

In our second year, we will begin fabrication and characterization of new low critical transition temperature ( $T_c$ ) superconducting materials and superconducting nitrides. Then, we will utilize our existing CMB detector technology to develop new measurement techniques to rapidly characterize relevant properties of superconducting materials and layered structures. Finally, the focus will shift to integrating new materials into complete CMB detector arrays and assessing the stability and consistency of the detector fabrication using these new materials.

# Cross-Correlating Ground-Based Optical Surveys with the Cosmic Microwave Background

2016-170-NO

Katrin Heitmann, Lindsey Bleem, Sebastian Bocquet, Samuel Flender, and Vinu Vikraman

## PROJECT DESCRIPTION

The aim of this project is to build a strong connection between datasets from the cosmic microwave background (CMB) and the large-scale structure (LSS) distribution of galaxies as measured by ongoing and upcoming surveys. This work needs to include a strong simulation component to understand systematic errors, investigate possible detections of hints of new science, and predict signals and signal strength(s) from new physics. The project has three major science components: (1) the investigation of a new sample of clusters of galaxies observed by the South Pole Telescope (SPT), in particular strong lensing, the thermal Sunyaev-Zel'dovich effect, and follow-up observations of the SPT cluster sample; (2) improved synthetic sky catalogs for the Dark Energy Spectroscopic Instrument; and (3) CMB lensing maps. All three involve the melding of observational and simulated data. They will lead to new cosmological constraints from current data and synthetic sky maps to help guide the development of next-generation surveys.

## MISSION RELEVANCE

This project is relevant to DOE's science mission and particularly to its programs in high-performance computing. Our simulation capabilities position us to complete the CMB effort at Argonne by adding an analysis and theory component that can take full advantage of the upcoming data. They also enable us to create the best simulated maps of the universe, which are essential for extracting the science from the surveys. Our project addresses key areas in the DOE Office of Science High Energy Physics (HEP) Cosmic Frontier research area, and it touches on related questions in the Intensity Frontier research area, especially with regard to our study of the mass of the neutrino.

## RESULTS AND ACCOMPLISHMENTS

As part of the South Pole Telescope Sunyaev-Zel'dovich (SPT-SZ) effect survey, we have been working on different aspects of analyzing the observed cluster sample. This work includes several different tasks. A series of validation cross-checks of the analysis pipeline were conducted that were ultimately used to publish the first cosmological constraints from galaxy cluster counts using the data of the full 2500 deg<sup>2</sup> SPT-SZ survey. We are leading the next cluster cosmology analysis using the SPT-SZ data to obtain constraints on the cosmic growth of structure. The next step in cluster cosmology with the SPT-SZ sample is to incorporate measurements of the weak gravitational lensing (WGL) shear that results from dark matter halos. We are using our analysis pipeline to relate the WGL measurements to the SPT-SZ sample to improve our knowledge of cluster astrophysics and cosmology.

A new cluster catalog has been assembled from SPTpol data and is being analyzed. We are using new CMB data from SPTpol in combination with optical data from the Dark Energy Survey (DES) to select the best targets for follow-up observations.

We have conducted an observational campaign using the new Parallel Imager for Southern Cosmology Observations (PISCO) on the 6.5-m Magellan Telescope to obtain uniform, high-resolution, deep imaging of all of the SPT clusters to allow us to identify strong lenses in the SPT cluster sample. Further observations with the IMACS and LDSS3 spectrographs allow us to characterize the newly discovered distant lensed galaxies. There have been numerous imaging and spectroscopic runs over the past year to collect data for this project. We have observed on all three of the PISCO observing runs, and thus far, we have imaged 40% of the SPT sample. Current efforts are to reduce this imaging data and conduct the spectroscopic follow-up of lensed systems.

## PROPOSED FUTURE WORK

We will continue our work on cross-correlating measurements from the DES and SPT to obtain cosmological constraints. We will create a detailed multi-wavelength map based on our large simulations that will be essential for this work. As more data become available, we will sharpen our constraints on dark energy.

# Synthetic Sky Catalogs for Space-Based Cosmology Missions

2016-171-N0

Lindsey Bleem, Salman Habib, Katrin Heitmann, and Eve Kovacs

## PROJECT DESCRIPTION

This project targets the science of two proposed National Aeronautics and Space Administration (NASA) cosmology missions—WFIRST, the Wide Field Infrared Survey Telescope, and SPHEREx, the Spectro-Photometer for the History of the Universe, Epoch of Reionization and Ices Explorer. WFIRST will explore the nature of dark energy, modified gravity, primordial fluctuations, dark matter properties, and neutrino masses, carrying out a wide field near-infrared space mission. Our main interest in the SPHEREx mission concerns cosmological studies. The primary focus of this project, is to build realistic synthetic sky catalogs for both missions. NASA awarded grants for WFIRST Science Investigation Teams in December 2015. Argonne is part of the only team focusing on cosmological studies with the WFIRST High Latitude Survey (HLS). The development of synthetic catalogs is a key element underlying Argonne’s contribution. NASA selected the SPHEREx mission for a 1-year Phase A study to compete with two other mission concepts for a SMEX (Small Explorers) Mission. Argonne is a member institution of SPHEREx and is currently developing forecasts for cluster studies with SPHEREx, as well as tailored galaxy sky catalogs. Although SPHEREx was not selected for the SMEX mission, NASA is still considering it as a Medium Explorer (MIDEX) candidate.

## MISSION RELEVANCE

This project is relevant to DOE’s mission in basic science research, specifically in High Energy Physics (HEP). Within DOE’s current HEP program [1], dark energy and dark matter are two of the five science drivers. Understanding the nature of cosmic acceleration—the problem of dark energy—is the most important problem in cosmology. In addition, probing the primordial fluctuations that led to the current structure of the universe is another foundational issue, another pillar of the DOE HEP research program. The cosmological relevance of WFIRST is driven primarily by its study of dark energy, whereas SPHEREx is a probe of the primordial fluctuations. For both missions, it is important to make forecasts and synthetic sky catalogs to test analysis methods and control systematics. In addition, we must determine whether the surveys can be used for science tasks that were not part of the original design

(e.g., kinematic Sunyaev-Zel’dovich effect measurements using SPHEREx combined with cosmic microwave background measurements). The tasks performed in this project involve analysis of large-scale simulations run on supercomputers at DOE facilities. A key aspect of this work lies in data management and running workflows on parallel computing platforms, an area of major interest in addressing future DOE needs across a number of program offices.

## RESULTS AND ACCOMPLISHMENTS

Building synthetic galaxy catalogs for both surveys relies on the ability to post-process data from large-scale cosmological simulations. Structure in the universe forms when dark matter collapses to form localized clumps called halos. Galaxies form and live within halos. After forming, halos evolve smoothly, as well as interact with each other, and halo mergers tracked in time define merger trees (Figure 1). The final halo is shown in the upper right corner of the figure, and the dark circles show the “backbone” of the halo, the link-up of the heaviest progenitor across time-steps. This visualization combines a temporal and spatial view of the halo—it shows the spatial regions over which the halo evolved in the x- and y-axis and the temporal evolution by showing the halo progenitors at 100 time snapshots. The merger trees described here follow the evolution of the main halos. In order to produce consistent merger trees, especially those with very large numbers of branches (in the tens of thousands), very carefully constructed analysis code is needed, which we have developed. An important part of the work in this project lies in taking these merger trees and using different models of galaxy formation to construct galaxy catalogs.

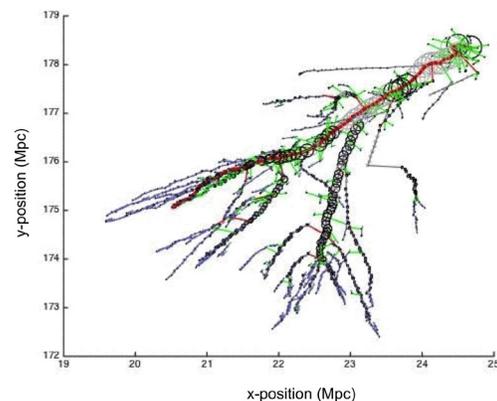


Figure 1. Spatial visualization of a merger tree. The final halo is in the upper right corner; the evolution of individual branches over time is shown in different colors and symbols.

In order to place galaxies in halos, a number of different models are used, ranging from empirical models to fairly complex semi-analytic models of galaxy formation (represented, for example, by the Galacticus code). In both cases, researchers need to be able to place candidate galaxies within the halos. Typically, this effort involves knowing the positions of smaller halos that fall into larger ones. The usual approach uses subhalo finders that look for signatures of sub-clumps within the main halos. However, there are several problems with this method given that subhalos can be destroyed easily by tidal forces, whereas the galaxies they host remain relatively stable. We have introduced a new method called core-tracking that solves this problem. With this technique, we can build statistical models for placing galaxies within halos that follow the actual spatial distribution of the infalling objects. This information is now being used to build galaxy catalogs that are highly relevant for WFIRST, focusing on emission line galaxies. In order to build these targeted catalogs, our co-investigators have included the relevant information in Galacticus, including dust modeling, to allow for tracking of this particular class of galaxies. The model predicts galaxy colors while taking into account the dust around the galaxies, thereby including the reddening attributable to extinction in different color bands. We applied the new dust model to a downscaled simulation and measured the extinction in different bands. We are currently validating the new model and its implementation.

Forecasts for SPHEREx included predictions for the number of clusters that would be found independently by SPHEREx ( $\sim 30,000$  with a median redshift,  $z \sim 0.2$ ). An important major contribution would be the determination of cluster redshifts (Figure 2) of these and other clusters, such as those discovered by the mm-wave cluster surveys AdvACTpol and SPT-3G, and by eROSITA (X-ray). The simulations suggest that the precision of cluster redshifts from SPHEREx should equal or exceed that of current generation optical surveys to  $z < 0.6$ . Perhaps more importantly for future cosmological constraints, however, SPHEREx data provide a useful cross-check of the redshifts—especially for clusters at redshifts near where the  $4000 \text{ \AA}$  break transitions between optical filters. For future surveys, ensuring low bias in redshifts (rather than improving the already excellent precision) will be important.

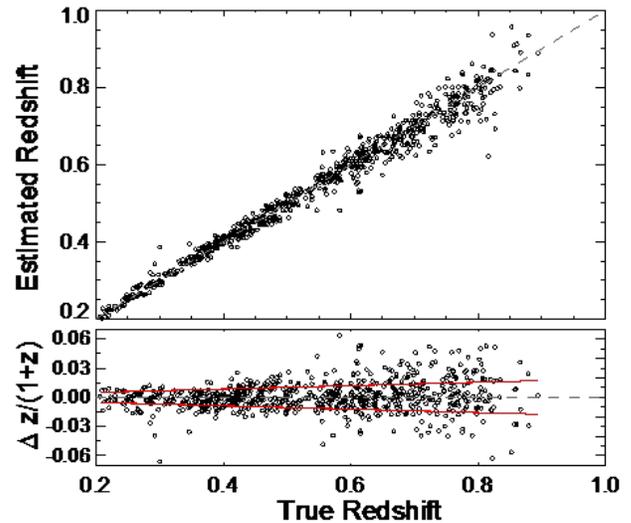


Figure 2. Simulation of redshifts ( $z$ ) estimated using SPHEREx data on a cluster sample.

SPHEREx observations would also play important roles in measurements of the pairwise kinematic Sunyaev-Zel'dovich effect, for which we previously made estimates. These results have been published in the SPHEREx science report.

### PROPOSED FUTURE WORK

We will focus on WFIRST science requirements. Tasks include predictions for galaxy distributions, intrinsic alignments, observational validation of synthetic catalogs, and new cross-correlation possibilities, in particular with cosmic microwave measurements. A number of new runs from the Mira-Titan set of cosmological simulations will be used to investigate the extraction of cosmological parameters from these cross-correlation studies.

[1] DOE HEP Research website, <https://science.energy.gov/hep/research/>

# Hydrodynamic Simulations with HACC on Next Generation Supercomputers

2016-172-NO

Salman Habib, Sebastian Bocquet, and Nicholas Frontiere

## PROJECT DESCRIPTION

This project targets the implementation of a hydrodynamics component of the HACC (Hardware/Hybrid Accelerated Cosmology Code) framework. In particular, we focus on the next-generation systems Theta and Aurora at the Argonne Leadership Computing Facility (ALCF), and Summit at the Oak Ridge Leadership Computing Facility (OLCF). The plan is to carry out two major hydrodynamics simulations—one to study the intrinsic alignment of galaxies on the sky and the second to study clusters of galaxies, a powerful probe of dark energy. We are preparing HACC for the new hydrodynamics capability. This effort includes the development and implementation of a new Smoothed-Particle Hydrodynamics (SPH) kernel, the extension of HACC to enable the evolution of multiple particle species (including changes to both the initializer and the main code), and the implementation of subgrid models. At the end of this project, we will have developed an initial version of the hydro-HACC code, and begun studies of the subgrid physics that needs to be implemented to address the two science cases outlined above.

## MISSION RELEVANCE

All ongoing and upcoming dark energy surveys will soon be limited by our understanding of systematic errors. In particular, cosmological probes that target small-scale structures, such as weak lensing or clusters of galaxies, will rely on the availability of large, accurate simulations including detailed baryonic physics. Thus, this project targets one of the top priorities of DOE's High Energy Physics Cosmic Frontier Program—the understanding of dark energy. In addition, the implementation of HACC in a way that lets it be easily ported between different architectures is of great interest to DOE's Advanced Scientific Computing Research programs for next-generation architectures. This new development within HACC will be very important for the next and next-to-next (exascale) generation of high-performance computing platforms.

## RESULTS AND ACCOMPLISHMENTS

The work in this project consists of developing the hydrodynamics capability needed to run simulations that study a number of important cosmological effects which must be taken into account for precision cosmology analyses. These include baryonic effects on weak lensing, intrinsic galaxy alignments that affect the measurement of cosmic shear, and multiple cluster physics probes at resolutions and scales that have not been possible so far. The computer time needed to run these simulations has been awarded at ALCF and OLCF under the Early Science Projects program. The primary milestone for the first year was to implement the new hydrodynamics solver in HACC. The major development of the new Conservative Reproducing Kernel SPH (CRKSPH) scheme has been finished, and a paper has been completed and accepted for publication.

The key advantage of CRKSPH in cosmological applications is the much improved treatment of mixing, a major historical deficiency of SPH codes. This advantage of CRKSPH can be seen in multiple tests. Figures 1, 2, and 3 show the improved performance of CRKSPH in handling the triple-point shock test with vorticity. In this test, a special initial condition is imposed with a high-density and high-pressure material (region I (blue), Figure 1) driving a shock to the right in a direction parallel to a density discontinuity between regions II (light blue) and III (red), with the sound speed in region II being larger than in region III (the colors do not represent densities). As the shock propagates to the right, it seeds vorticity in the interface between regions II and III, rolling up the interface region. There is a strong interplay between shock hydrodynamics and instability growth (both Kelvin-Helmholtz and Richtmyer-Meshkov), with the boundaries in the problem causing the shocks to repeatedly reflect and interact, as depicted in Figure 2, run with with CRKSPH. Figure 3 compares the CRKSPH results with other methods—two SPH schemes and a Lagrangian mesh method (ReALE); the results have been reflected (top-bottom and left-right) to allow the four different cases to be viewed at the same time. The shock fronts show good agreement, while the CRKSPH results clearly improve on the other SPH methods and show the distortion of the main vortex and secondary instabilities (Kelvin-Helmholtz) in front of the expanding plume. These results are in good agreement with those from an Eulerian adaptive-mesh refinement calculation carried out by our collaborators at Lawrence Berkeley National Laboratory. The HACC framework is now being refactored to allow for multiple particle species (dark matter plus baryons) and for changes in how the initial conditions are handled in order to be able to include the new hydro solver. The work on the initial-conditions code is very close to completion.

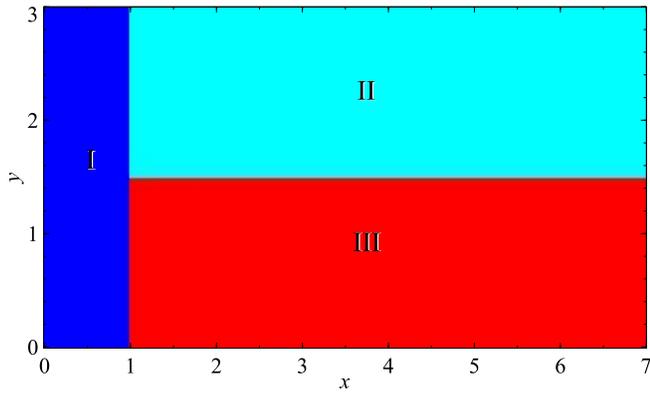


Figure 1. The initial conditions for the triple-point test. Region I (blue) represents a high-density and high-pressure material that drives a shock to the right in a direction parallel to a density discontinuity (regions II (light blue) and III (red), with the sound speed in region II being larger than in region III. The colors do not represent densities.

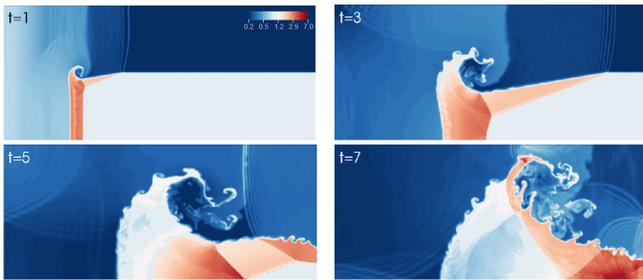


Figure 2. Time sequence of the mass density evolution with the initial condition as depicted in Figure 1 showing the complex reshocking and vertical interactions present in the test problem. The interface between regions II and III rolls up due to the different sound speeds and the shock front progresses from left to right. Density is shown on a logarithmic scale.

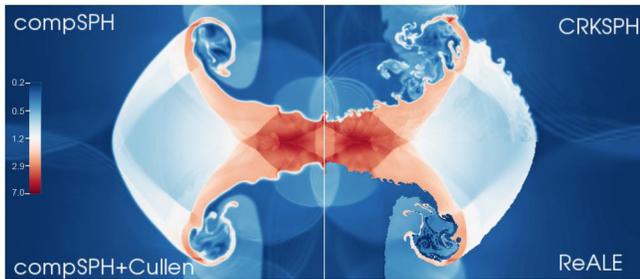


Figure 3. Comparison of CRKSPH with other methods. The orientation of the compSPH result (top left quadrant) follows that of Figure 2. The other results have been flipped left-right and top-bottom for ease of comparison. Note that the shock-dominated regions are in very good agreement, but CRKSPH clearly shows the most evolution in terms of tracking the Kelvin-Helmholtz instabilities, including the front of the expanding plume (note the spiral-like structures).

### PROPOSED FUTURE WORK

Proposed future work will be related to the validation of the simulation framework against cluster observations, as well as observations of the Lyman alpha forest. This data-based validation is needed for properly fixing the parameters in subgrid models. These models include methods for including star formation, homogeneous and inhomogeneous photo-ionization heating, active galactic nuclei and supernova feedback, and cooling mechanisms. The first applications of the new capability will be to measurements of the thermal and kinematic Sunyaev-Zeldovich effects in galaxy clusters, made by the South Pole Telescope (SPT). We will use recent and upcoming SPT measurements, as well as publicly available X-ray measurements, for these validation tasks. In addition, we will use data from Lyman alpha observations with both medium- and high-resolution spectrographs for validation at higher redshifts.



# **DIRECTOR'S GRAND CHALLENGE – DATA-DRIVEN SCIENCE**

# Integrating Simulation and Observation: Discovery Engines for Big Data

2013-165-R3

Ian T. Foster, Jonathan D. Almer, Rachana Ananthakrishnan, Ben Blaiszik, Kyle Chard, Lin X. Chen, Peter Chupas, Emil M. Constantinescu, Hal Finkel, Nicholas Frontiere, Ben Gutierrez, Salman Habib, Katrin Heitmann, Guy Jennings, Raj Kettimuthu, Eve Kovacs, Ravi K. Madduri, Tanu Malik, Ray Osborn, Adrian Pope, Esteban Rangel, Stephan Rosenkranz, Hemant Sharma, David Tiede, Tom Uram, Peter van Gemmeren, Venkatram Vishwanath, Michael Wilde, Justin Wozniak, and Peter Zapol

## PROJECT DESCRIPTION

This project was part of the Argonne Big Data Strategic Initiative. We sought problems that were important to science, relevant to Argonne and DOE projects, and tractable, given the state of the technology and our specific expertise. This perspective led us to adopt a dual focus for the project: namely, research problems in cosmology and materials science that involve coupling experiment and modeling, and accelerating end-to-end workflows in our research.

In cosmology, we sought to build new methods capable of exploiting observational data from increasingly high-precision digital sky surveys—for example, the Sloan Digital Sky Survey, Dark Energy Survey, Dark Energy Spectroscopic Instrument, Large Synoptic Survey Telescope, and South Pole Telescope. These methods use high-resolution cosmological simulations run on supercomputers, such as the Blue Gene/Q (Mira), to both determine the cosmological parameters and quantitatively evaluate the validity of the modeling process itself. In materials science, the goal was to manage big data on the Advanced Photon Source (APS) beamlines and to generate scientific models using computational simulation and other statistical techniques. A particular focus was to determine complex defect structures derived from single-crystal diffuse scattering experiments.

While cosmology and materials science differ widely in their scales and scientific foci, they share concerns that make interactions between these two efforts fruitful. In particular, they share a need to contend with the substantial complexity of analysis (both must collect, organize, and manage data from many experiments, instruments, simulations, and analyses); the scale of analysis (both must perform complex analysis on large datasets, solve large statistical inverse problems, and manage big data); and the deployment of new methods in the workflows of experimental and/or observational

facilities. In both domains, scientific progress can be accelerated by creating new discovery engines that enable the rapid and collaborative acquisition, exploration, integration, and analysis of large quantities of observational and simulated data.

## MISSION RELEVANCE

Big data problems are pervasive across the DOE science mission. For example, extreme data volumes are encountered at DOE experimental facilities, such as light sources; in supercomputer simulations conducted at leadership computing facilities; in the digital sky surveys used in cosmology; and in high-energy physics experiments. Furthermore, dramatically larger data volumes and velocities are expected from new light source detectors and exascale simulations. The need to integrate a challenging variety of data arises in biology, materials science, and sky surveys.

## RESULTS AND ACCOMPLISHMENTS

Work in the first three years produced new methods for processing light source data, running cosmological simulations, and performing big data science. Using the infrastructure shown in Figure 1, we developed new end-to-end, high-performance, APS data processing pipelines for two quite different experimental modalities (diffuse scattering and near- and far-field high-energy diffraction microscopy [HEDM]), which involved engaging successfully with ten APS sectors in various ways, and explored two new analysis methods that integrate theory with experiment. We ran some of the world's largest cosmological simulations, producing a multi-petabyte simulation dataset that is larger, in terms of raw size, than any contemporary observational dataset; and we developed new algorithms for analyzing those data (for density estimation, merger tree, and sub-halo tracking). We defined an overall data services architecture; developed new services to track complex, end-to-end activities; developed the concept for a Materials Data Facility; and informed the design of data publication and discovery services, which other disciplines are already adopting.

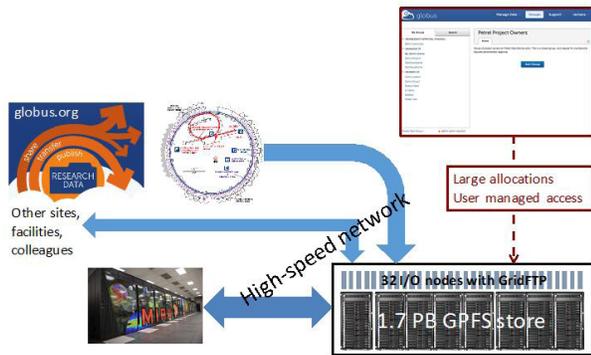


Figure 1. The research data infrastructure developed as part of this project, and its connection with other Argonne research infrastructure including the Advanced Photon Source ring at center, the Petrel data server at lower right, and the Mira supercomputer at lower left. (Also see the report of project 2014-182-R2 elsewhere in this volume.)

In the final three months of this project (Q1 of FY 2016), we completed the functional initial data facilities and explored further applications, as follows:

**Cosmology**

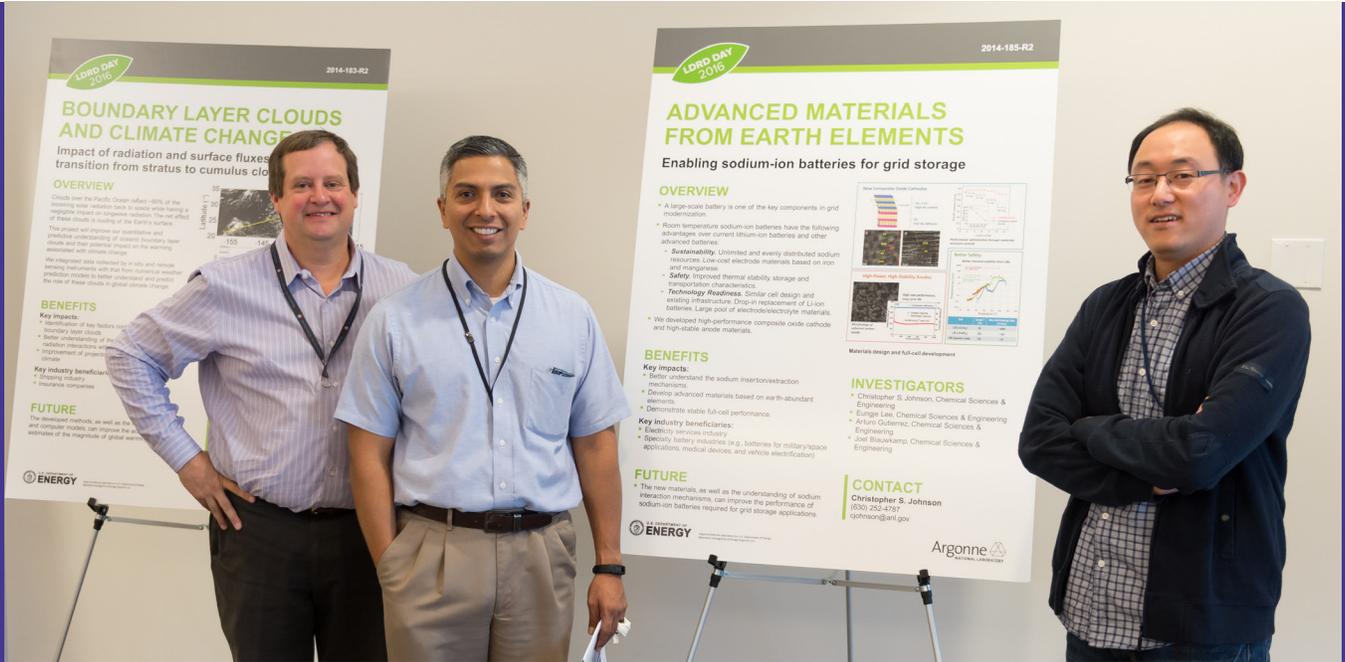
- We completed and/or optimized the suite of algorithms.
- We released the first production version of the software-as-a-service cosmology portal for analyzing simulation data.
- We implemented the databases.
- We carried out science analyses that exercised the full system, including the observational data.

**Materials**

- We evaluated research models, deployments, and applications developed during years one through three, and collecting data for publication.
- We started developing scripts that handle other X-ray techniques within the APS and multiple techniques across different facilities.

**Data and Workflow**

- We completed the work on user-defined analyses and capturing derived data products.



# OTHER NOVEL R&D

## Enabling Sodium-Ion Batteries for Grid Storage

2014-185-R2

Christopher Johnson, Joel Blauwkamp, Arturo Gutierrez, and Eungje Lee

### PROJECT DESCRIPTION

Sodium-ion batteries (SIBs) that operate at ambient temperatures present a great opportunity for the development of new grid-scale energy storage systems. One of the important opportunities in SIBs is that sodium (Na) electrochemistry enables utilization of several high-performance, low-cost electrode materials that have not been successful for lithium-ion batteries (LIBs), giving SIBs a wealth of possibilities and versatility. In addition, the similarity between Na and Li) electrochemistry will enable rapid testing of the SIB system through the use of benchmarks of current LIBs and the usage of existing equipment for electrode materials, electrodes, and cell fabrication. In addition to SIBs' advantages of low-cost electrode materials, a wide temperature window for applications, and the suitability of an inexpensive propylene carbonate solvent electrolyte system.

Currently, there are no Na-ion-based grid-scale energy storage systems operating at ambient temperatures anywhere. However, we do not see this as a barrier to the technology. On the technical side, our Battery Performance and Cost Model (BatPaC) calculation indicates that a cathode with 200 mAh/g specific capacity coupled to a high-capacity anode (500 mAh/g) with a cell voltage of 3.0 V will produce a pack-level energy density of 220 Wh/kg. Considering the burdened weight of the pack, the maximum cell-level energy density can be 400–600 Wh/kg.

### MISSION RELEVANCE

A key mission of the DOE is large-scale grid regulation. In addition, there is a focus on increasing the use of renewable fuels and decreasing the use of fossil fuels to lower our carbon footprint and begin curtailing global warming. The rise of renewables like solar energy and wind power will require associated energy storage because of the intermittent nature of renewable power generation. Thus, the DOE Office of Electricity Delivery and Energy Reliability pays attention to developments in energy storage for electricity grids. The SIB research and development effort in this project is well aligned with this energy mission.

The excellent safety and durability of SIBs will interest the U.S. Department of Defense and the National Aeronautics

and Space Administration. Also, because of their robust chemistry, SIBs can be shipped in a zero-energy stored state without deterioration of the cells' performance. This feature is an advantage over LIBs for non-regulated air transport.

### RESULTS AND ACCOMPLISHMENTS

In FY 2015, we synthesized, developed, and demonstrated a superior operating anode material, SnO-carbon composite, for SIBs. The SnO anode features very reversible electrochemistry in Na half-cells with 500 mAh/g specific capacity at a 10 h cycling rate at a 0.4-V average voltage. Rate tests have also demonstrated a >200-mAh/g specific capacity at 6 minute sustained discharge and charge. This anode meets our objective.

On the cathode side, our intergrowth Li-doped  $\text{Na}_y\text{Ni}_{1-x}\text{Mn}_x\text{O}_2$  layered oxide that was developed in FY 2014 and yielded specific capacities of 130 mAh/g at an average discharge voltage of 3.1 V. The cycling stability was good, but this value is too low for our targets. For the low capacity and low voltage reasons, we have studied a new phase of  $\text{NaCoPO}_4$ , which is expected to possess high voltages above 4.0 V versus sodium metal which should lead to higher energy densities.

In FY 2016, we focused on  $\text{NaCoPO}_4$  framework polyanions, since they have higher voltages than layered phases. However, we decided to pursue a different, untested, Red-phase of  $\text{NaCoPO}_4$ , which should possess a voltage above 4.0 V, i.e., above Na, and a theoretical capacity of 216 mAh/g. Replacement of the layered cathode with the polyanion compound could boost the energy density of the grid storage battery by 20%, to 260–280 Wh/kg.

This new  $\text{NaCoPO}_4$  polymorph (Red-NCP) was synthesized for the first time, using a rapid microwave-assisted solvothermal process. The synthesis process was complex and much of the year was devoted to optimizing it for high purity and good yield. The polymorph was investigated for use as a cathode material in SIBs. It was determined that two separate redox events, at around 4.1 and 4.4 V, occur during cycling as a result of the presence of two distinct cobalt sites within the structure. In addition, analysis of electrodes at different states of charge revealed that the  $\text{Co}^{2+/3+}$  redox couple is active during cycling. Moreover, it was demonstrated that the crystal structure undergoes reversible changes during cycling. However, the capacities are too low and the polycrystalline powder requires optimization through nanosizing and carbon coating. Otherwise the Red-phase is one of a very few high-voltage cathodes currently available for SIBs.

## Conversion of C<sub>2</sub> and C<sub>3</sub> Paraffins into Liquid-Phase Products

2015-174-R1

Christopher L. Marshall and Jeffrey C. Bunquin

### PROJECT DESCRIPTION

In this project, we are attempting to create tandem catalysts for converting gas-phase molecules directly into higher-value liquids. The work couples two successes with atomic layer deposition (ALD) synthesis at Argonne: (1) ALD overcoating of metallic catalysts, and (2) high-precision synthesis of controlled acidic functions to create a tandem catalyst that will convert light gases directly into C<sub>4</sub> to C<sub>6</sub> liquids. ALD overcoating will be used to stabilize the catalytic metal nanoparticles and to boost the yield of heavier olefins. By designing a bimetallic catalyst composed of a primary alumina coating and a secondary silica coating, an acidic site will be created inside the catalytic pore capable of polymerizing olefins. The catalysts' uniform and restricted pore dimensions will limit olefin oligomerization to C<sub>4</sub> to C<sub>6</sub> olefins with little or no coking. The modular design of the catalyst will allow the system to have high transportability and can thus be used to monetize stranded and remote resources that are not easily accessible to large commercial plants, which currently must be built adjacent to vast gas fields.

### MISSION RELEVANCE

This project is relevant to DOE's basic energy sciences (BES) mission for the development of fundamental scientific principles enabling rational catalyst design and chemical transformation control. The BES emphasis is on the atomistic understanding of the reaction mechanism enabling proper identification, understanding, and control of catalytic active sites. The research focuses on the synthesis of new catalytic materials that are selective to a single product. The project utilizes advanced synthesis techniques (ALD) to make tandem functional sites on catalysts that are within molecular distances of each other to allow interactions to yield a catalyst that is a combination of both sites.

### RESULTS AND ACCOMPLISHMENTS

In the first year of the project, we conducted planning and ordered materials for the work that was to be performed in FY 2016. The work also included training on the integrated ALD synthesis-catalysis (I-ALD-CAT) unit that was expected to be used for the project. Training on the ALD batch unit was also conducted. It was anticipated

that each unit could be used for this project. Training included how to maintain proper conditions for correct metal deposition (T, P, time of deposition). During training, however, we discovered that a downstream valve was not operating properly and was (in fact) preventing correct deposition of the metals of interest. Thus, the remainder of FY 2015 was spent repairing this problem.

The I-ALD-CAT unit was down for much of FY 2016. Modifications are currently under way to bring the unit back to operation; but it will still have limited time available for this LDRD project in FY 2017. ALD overcoating on this project has been carried out on the "batch scale" ALD unit with catalytic testing being conducted in a separate plug flow reactor. The ALD overcoating shows promise for stabilizing the catalyst for both sintering and coking. Palladium (Pd) catalysts were synthesized using three different supports (TiO<sub>2</sub>, ZnO, and Al<sub>2</sub>O<sub>3</sub>) on the batch-scale ALD unit. Each Pd catalyst was then overcoated with Al<sub>2</sub>O<sub>3</sub>. Subsequent reaction testing was conducted in a separate plug flow unit. ALD overcoated samples showed minimal coking for materials with 10 or more overlayers calcined at 500°C or higher. The largest yield was for Pd on Al<sub>2</sub>O<sub>3</sub>, with the selectivity limited to the ethylene from ethane and propylene from propane. The use of SiO<sub>2</sub> as an overcoat will be tested in FY 2017. It is anticipated that the charge differential between the support and the overcoat should increase the acidity near the Pd site, thereby facilitating olefin coupling. If coupling still is not observed, it might be that the concentration of two or more olefins near the acidic site is not sufficiently high to support the coupling reaction.

### PROPOSED FUTURE WORK

In FY 2017, we will investigate the use of silica as an overcoating material. The charge imbalance between Al<sup>+3</sup> and Si<sup>+4</sup> should provide a site for a Brønsted acid that could promote coupling. If olefin coupling continues to show limited promise, the remainder of FY 2017 will be dedicated to reacting the intermediate olefin (ethylene or propylene) with water to form the alcohol (either ethanol or propanol). Alcohol products are also of interest within this project scope, because their boiling points are significantly above that of the paraffinic feed, and therefore could easily be separated from a methane feed stream. Initial work with the water feed will concentrate on the catalysts previously synthesized. Further work, as time allows, will concentrate on other overcoats which should have different acidities. In addition, the effect of the calcination temperature will be studied, given that earlier work has shown that the temperature of calcination has a dramatic effect on the pore structure of the overcoat.

# Fine Resolution Reconstruction of Large Volumes of a Brain

2015-181-R1

Narayanan Kasthuri

## PROJECT DESCRIPTION

The purpose of this project is to explore imaging of the fine structure of the brain research using both electron and high-energy X-ray microscopy. There is a current push to develop approaches to map all of the neurons and connections at the nanometer (nm) scale in a large volume of a brain and also to accomplish the same advances for entire brains (connectomics). The current approach is to use serial section electron microscopy. We will continue that approach along with determining how synchrotron-based, high-energy X-ray microscopy of the same brains can complement and extend the capabilities for connectomics. The Advanced Photon Source (APS) is ideal for carrying out such experiments. Technical objectives for this project include producing: (1) a map of an entire mouse brain at sub-micron resolution ( $\sim 100$ -nm voxels), where the goal is to map all the cells in a brain, their long-distance projections, and the blood vessels that supply their energy and remove their waste; (2) a map of a functional module of a single brain at nanometer scale ( $\sim 10$  nm/voxel over a cubic millimeter [ $\text{mm}^3$ ]), where the goal is to find every neuronal connection in that volume; and (3) the creation of both maps in the same brain.

The long-term goal of this project is to provide a wiring diagram for brains that will significantly improve our computational models of brain processing and eventually lead to better algorithms for real-world objectives (e.g., face recognition, novel object detection in scenes) based on how brains process similar information. Similar data will eventually be collected from “pathological” brains (i.e., brains marked by disease conditions, especially structural and functional changes produced by diseases such as autism or schizophrenia) to determine whether miswiring of neurons contributes to the pathological behavior of those diseases. Ultimately, they will serve as targets for therapy. In the near term, the successful pursuit of the project will yield insights into how brains develop and age. Finally, mapping the brain at nanometer resolution will entail large amounts (hundreds to thousands of terabytes’ worth) of data and developing new algorithms to analyze and manage such large datasets.

## MISSION RELEVANCE

The National Strategic Computing Initiative (NSCI) Executive Order promotes a whole-of-government approach to bringing the unique national computing capabilities of DOE to transform how a partner agency executes its mission. The study of the brain, perhaps unlike any other biological system, requires perhaps the largest datasets and simulation capacities to obtain a fuller understanding. In this project, by partnering with multiple academic researchers nationwide, we will be leveraging the high-performance computing (HPC), big data analytics, and machine learning tools of the national labs with the domain knowledge and instrumentation experience of our academic partners to create a unique national resource for mapping neuronal circuits in brains in healthy and diseased states. The problems are hard but will have considerable impact on multiple DOE programs including neuromorphic and low-energy computing. An exciting possibility is that exascale-assisted brain mapping will reveal new generations of software and hardware architectures for future national lab computing resources well beyond the exascale.

## RESULTS AND ACCOMPLISHMENTS

In FY 2015, we hired personnel and found collaborators at APS and ALCF for both acquisition and analyses parts of our pipeline.

In FY 2016, we had several accomplishments:

1. We developed protocols with the Advanced Photon Source for imaging entire mouse brains. (This effort led to the submission of a scientific paper to *E-Life*.) In addition, we have now mapped an entire mouse brain and are preparing a second manuscript for submission.
2. We have developed the infrastructure for performing brain mapping, including:
  - a. Obtaining, validating, and training on equipment for electron microscopy (EM) and X-ray brain mapping, including a scanning electron microscope for brain imaging.
  - b. Developing and deploying automated algorithms based on machine learning in concert with the Argonne Leadership Computing Facility (ALCF). These algorithms will be used for automatically tracing neurons and their connections, and they are now the fastest and most powerful computational resources (potentially) for performing brain mapping in the United States.

**PROPOSED FUTURE WORK**

We plan two main endeavors. The first is to map entire mouse brains with synchrotron radiation at a submicron level of resolution. This effort will allow us to reconstruct every neuron, blood vessel, and long-range projection in single brains. The second is to map sub-volumes of entire mouse brains at nanometer-scale resolution. This effort will map every connection between every neuron in a biologically relevant volume. This dataset will also serve as a reference atlas that will ultimately enable comparison with diseased brains, young and/or aged brains, etc.

## New Thin-Film Oxide, Chalcogenide, and Oxy-Chalcogenide Materials Discovery

2016-120-NO

Supratik Guha

**PROJECT DESCRIPTION**

This project investigates new materials and exploratory devices for low-power, high-efficiency neuromorphic computing, including artificial neurons, synapses, nonvolatile memory, and interconnects. Increased data intensive workloads and the slowing of Moore's Law have led to increased interest in non-traditional forms of computing, among them computing where the processor has a denser interplay with memory elements, and neuromorphic or "brain-inspired" computing, which follows interest in developing information processing hardware that can harness neural network and related algorithms more efficiently. This requires new materials and devices that are similar to the synaptic and neuronal functions of the brain. There has been very little fundamental materials science and experimental physics work in this area, which is the subject of this project. Specifically, we are developing new types of materials and nanostructured approaches to make materials and structures appropriate for such neurons and synapses.

Future materials/device technologies are increasingly relying on the availability of low-power devices with unique characteristics. These devices include the more near-term nonvolatile memory elements that are increasingly trending toward crossbar geometries in order to accommodate ultrahigh densities close to the processor, as well as longer-term neuromorphic-type devices. In particular, there is tremendous interest in low-voltage (and low-power) devices that, besides

being useful for energy-efficient computing, open the door for neural prosthetics—where man-made neurons and synaptic devices can be inserted within neuronal networks. For this insertion to occur, the turn-on voltages must be in the 100- to 200-mV range, below the 1+ volts in today's devices.

**MISSION RELEVANCE**

This project seeks new alternative computing approaches beyond von Neumann computing. It is relevant to DOE's science mission because it addresses both the recent slowing of the acceleration of computing speed relative to Moore's Law and the emergence of new data-intensive workloads. The DOE is particularly interested in this emerging area and it recently held the Neuromorphic Computing Workshop in April 2016 in order to assess the status and opportunities. It is expected that there will be a significant number of new programs in this area going forward.

**RESULTS AND ACCOMPLISHMENTS**

Our research efforts encompass two main areas: low-voltage-threshold devices using defective oxides and low-voltage artificial neurons using feedback-engineered insulator-to-metal transition (IMT) devices.

**Low-Voltage-Threshold Devices Using Defective Oxides**

Our initial experiments have been on solid-state electrochemical Cu(or Ag)/HfO<sub>2</sub>/inert electrode devices for threshold switches and analog memories.

During FY 2016, we designed, fabricated, and characterized a HfO<sub>2</sub>-based cross-point selector switch array fabricated by atomic layer deposition (ALD). Some of our key findings are listed below.

- We verified nano-ionic filamentary conduction with an ON/OFF ratio of 10<sup>4</sup>: the essential mechanism for switching is provided by the ionic transport and electrochemical redox reactions.
- We demonstrated tunable hysteresis and ON/OFF ratio by post-fabrication annealing, and achieved improved ON-state current density and less than 1-volt switching by doping with Cu. Because switching voltage is mainly determined by activation energy for the chemical reaction and ionic diffusion constant, a pre-doped matrix facilitates low-voltage switching.

- We demonstrated low-temperature switching. As temperatures decrease, the thermal energies of oxygen, vacancies and ions are reduced. Therefore, it is expected that a stronger electric field is needed to form or rupture the conductive filament. We did not find such an increase in the electric field when switching was observed down to 20 K. There are indications that the conduction mechanism at cryogenic temperatures could be variable-range hopping, rather than the nearest-neighbor hopping observed at room temperature.
- We achieved current-driven self-healing in a resistive switching device. After repeated cycling in memory devices, the low resistivity state remains and the device cannot be switched. We show that by passing a high current through the device once it is stuck in its failed state, the device spontaneously recovers to its high-resistance state, indicating dissolution of a conducting filament and thus self-healing. The underlying mechanism involved in such behavior is still under investigation.

#### Low-Voltage Artificial Neuron Using Feedback-Engineered Insulator-to-Metal Transition Devices

Vanadium oxide ( $\text{VO}_2$ ) has a phase transition close to room temperature ( $66^\circ\text{C}$ ). The basic experimental structure in this study is a two-terminal  $\text{VO}_2$  strip (resistor) with a variable resistivity associated with the  $\text{VO}_2$  phase transition. The strength of the IMT is defined as the ratio of the resistivity at room temperature (high-state resistivity) and at 400 K (low-state resistivity), and is denoted by  $R_H/R_L$ . The strength of the IMT can be controlled by varying the deposition conditions and the substrates being used. This strength is related to the oxygen stoichiometry in the  $\text{VO}_2$  films. Three samples (A, B, and C) with IMT strength varying from  $8 \times 10^4$  to  $2 \times 10^1$  have been synthesized. The high-resistivity states play a critical role in achieving low-voltage operation. Ti/Au (10/150 nm) contacts are deposited by e-beam evaporation and a lift-off process. The gap of the two contacts defines the length  $L$  of the  $\text{VO}_2$  strip.

Staircase voltage sweep is applied between two terminals to test the IMT and the reverse metal-to-insulator transition. To avoid excess heating after the IMT, the current through the IMT is limited to 5 mA. Device length and width are  $0.5\mu\text{m}$  and  $2.5\mu\text{m}$ , respectively. Figure 1 shows the measured hysteresis loop for  $\text{VO}_2$  devices on samples A, B, and C. The hysteresis is observed in all three samples.

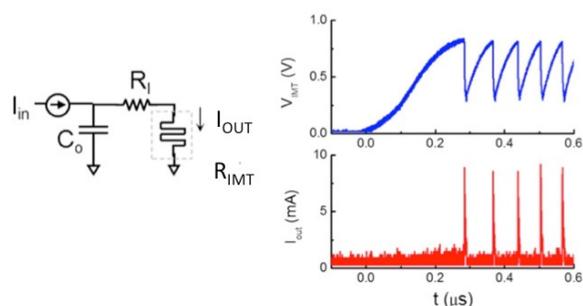


Figure 1. Left, circuit schematics of combining IMT (dashed box) with capacitance and current source for demonstrating artificial firing neurons. A resistor is connected in series to limit the current through the IMT and measure current output. Right, measured waveforms for this circuit: (blue) voltage across the IMT and (red) current through the IMT for sample C.

To understand the fabricated IMT device characteristics, we developed a one-dimensional (1D) simulation that self-consistently couples the physics of resistivity heating and heat transfer, as well as abrupt switching in the IMT. The model matches well with experimental results.

#### PROPOSED FUTURE WORK

##### Low-Voltage-Threshold Devices

1. Development of high-throughput process flow for nanometer-scale cross-point arrays.
2. Exploration of low-voltage resistive switching in systems involving organic molecules.
3. Exploration of low-forming-voltage anode and improvement of cycling endurance.

##### Low-Voltage Artificial Neuron

1. Use of  $\text{VO}_2$  as a precursor material.
2. Demonstration of a sub-200-mV artificial neuron.

## Plasmonic Grating-Launched Nanoscale Light Source for Optical Spectroscopy on Atomically Resolved Systems

2016-121-N0

Jeffrey R. Guest and Aftab Ahmed

#### PROJECT DESCRIPTION

The purpose of this project is to develop a nano-focused light source at the end of a scanning tunneling microscope (STM) tip in an ultrahigh vacuum (UHV) environment for nanoscale laser spectroscopy. Scanning tunneling microscopy provides atomic-scale topographical and electronic information on systems under investigation; however, alone, this approach fails to provide chemically

resolved information. This work will integrate the molecular and crystal structural information obtained from optical Raman spectroscopy with the excellent spatial resolution of STM.

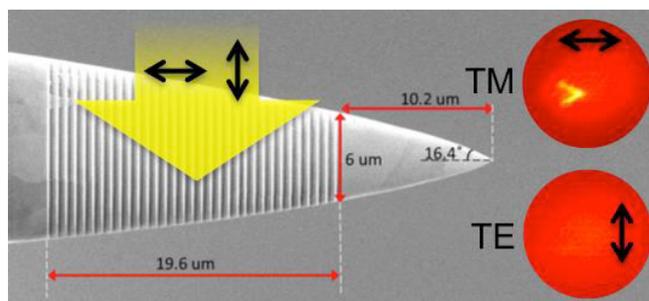
This deep sub-wavelength light source will be realized by coupling light through a nanofabricated grating to surface plasmon polaritons on a plasmonic STM probe and then launching them toward the tip's apex. Enhanced electromagnetic fields at the apex of the tip will allow for enhanced excitation and scattering from the sample at nanometer spatial resolution. Furthermore, this ultrahigh-spatial-resolution laser spectroscopy will be correlated with an understanding of structure and electronic properties of atomically controlled and resolved nanoscale systems using UHV STM. In addition, Raman spectroscopy is extremely sensitive to local charge; this approach may provide a powerful window into charge transfer processes in nanoscale and molecular systems.

### MISSION RELEVANCE

This project supports the DOE mission of use-inspired fundamental science. The investigations will allow imaging and chemical recognition at the single-molecule level, providing new potential to explore molecules at sub-nanometer length scales. Furthermore, this nanoscale light source will be beneficial for exploring many other light-matter interactions on nanometer length scales, including photocatalysis, photophysics, and optoelectronic materials. The development of this capability within Argonne's Center for Nanoscale Materials will provide a unique resource for high-impact user projects, leveraging our effort for the benefit of the Nanoscale Science Research Centers, DOE, Argonne, and the user community.

### RESULTS AND ACCOMPLISHMENTS

Work in FY 2016 has focused first on developing the plasmonic grating tips. Using numerical modeling, we have optimized the design of the gratings on our gold tips for the most efficient conversion of light into plasmons and transmission of plasmons to the tip apex; the grating can be seen in the image at the left side of Figure 1. We have fabricated these tips and have demonstrated that they effectively couple light into plasmons that propagate to the end of the STM tip, where they convert back into emitted light. This transfer can be seen clearly from the far-field optical microscopy images in the figure. When light polarized in the correct orientation (transverse-magnetic or TM) couples to the grating, the end of the STM tip lights up, whereas the orthogonal polarization (transverse-electric or TE) fails to couple to a plasmon and the end of the tip remains dark.



**Figure 1.** Fabricated gold tip along with images of the tip when excited by TM or TE polarized white light. The arrows show the polarization of the incident field with respect to the grating. The microscopic images (red insets) show that only TM-polarized light couples to the grating and launches a plasmon to light up the tip.

In order to perform nanoscale spectroscopy, we have modified the UHV STM by adding *in situ* optics for effective illumination of the plasmonic grating and collection of the emitted light. We have set up and optimized far-field Raman spectroscopy and are currently testing it on 2D materials in anticipation of Raman spectroscopy with the plasmonic tips. In order to explore the strongly enhanced optical field in the tip-substrate gap, we have also prepared atomically flat, plasmonically active gold (Au) samples with the goal of measuring a rectified optical field electronically. The plasmonic substrate will significantly increase the local field and reduce the spatial extent of the plasmonic field in the gap, further improving the sensitivity and spatial resolution of Raman measurements.

### PROPOSED FUTURE WORK

This project was approved as a one-year project. In related efforts, we are currently investigating the behavior of these plasmonic tips in the UHV STM; we have been able to achieve atomic-scale imaging, and are investigating their optical properties as correlated with local structure. Future experiments will investigate the potential rectification of the plasmonic optical field in the tip-sample gap due to the nonlinear tip-sample conductance and will explore the optical field enhancement to improve Raman measurements on nanometer length scales.

# Development of a Pre-Conceptual Design of a New Tracking System for CLAS12 Detector

2016-179-NO

Kawtar Hafidi and Whitney Armstrong

## PROJECT DESCRIPTION

The goals of this project are to identify the luminosity limitations of the Continuous Electron Beam Accelerator Facility (CEBAF) Large Acceptance Spectrometer “CLAS12” at DOE’s Thomas Jefferson National Accelerator Facility and to propose a new tracking detector that will allow the machine to run at luminosities an order of magnitude higher than what is achievable now. This effort will require a detailed simulation to understand the limitations of the current design and how it can be improved.

## MISSION RELEVANCE

This project is relevant to DOE’s mission in basic science. The current CLAS12 configuration has large-area wire drift-chamber detectors that are used to reconstruct particle tracks. When the rates of particles through the drift chambers are very high, the track reconstruction efficiency drops owing to uncorrelated hits and multiple tracks going through the same region of the detector (see Figure 1). Increasing the luminosity, and thus the particle rates, will allow a rapid completion of the backlog which, at current luminosity limitations, consists of roughly nine years’ worth of approved CLAS12 experiments. Therefore, improving the detectors to handle higher rates will dramatically increase the scientific throughput of the CLAS12 physics program over the next decade.

## RESULTS AND ACCOMPLISHMENTS

Our accomplishments in FY 2016 included the following:

- We developed a full Geant4 simulation of CLAS12 with an optimization for accurately extracting the drift chamber wire hit occupancies (see Figure 2).
- We developed a realistic event generator and cross-validated it with Geant4 results. This event generator allows for a fast and efficient simulation by only producing events that will land in the CLAS12 detectors. The main contribution of background events comes from Moller electron scattering. Other sources of background include electron-proton elastic scattering and inclusive pion production. All of these processes,

and more, are included in the event generator to produce a realistic sample of events.

- We have identified the small scattering angles as the location for high drift chamber occupancies. This will be the initial region we select to improve with an initial design that can mitigate the high rates and maintain a high tracking efficiency.

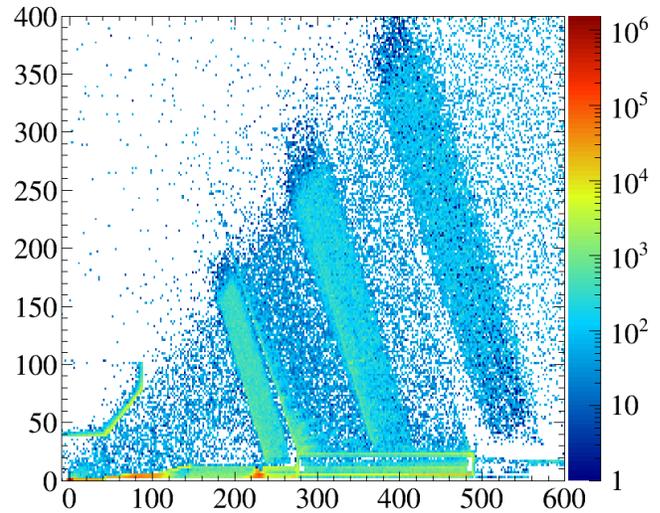


Figure 1. The simulated origins of tracks producing background hits in the drift chamber. Shown is a slice of the x-z coordinates where the three tilted chambers can be seen clearly.

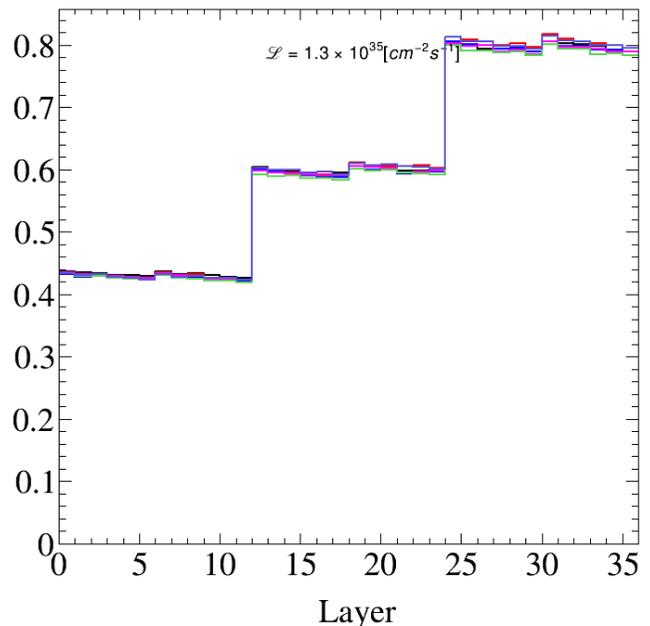


Figure 2. The simulated drift chamber hit occupancy for each layer, where each chamber consists of 12 layers of wires.

**PROPOSED FUTURE WORK**

Activities for FY 2017 will include the following:

- We will continue to improve the simulation to further understand the background sources.
- We will begin simulating new designs for a supplemental tracking detector at small scattering angles. This effort will include exploring various technologies such as gaseous electron multipliers (GEMs) and Micro-MEsh GASEous structure (Micromegas) detectors.
- We are planning to complete the full simulations and develop an initial design proposal to submit to DOE in coordination with Jefferson Lab management.
- We will begin to outline and highlight the scope of new physics accessible with these improvements. This activity will consist of developing new simulations and proof of concept around measurements of rare processes such as exclusive J/psi electro-production.

## Highly Anisotropic Magnetic Materials for Microwave Applications

2016-189-NO

Xing Chen

**PROJECT DESCRIPTION**

This project aims to expand existing Argonne capabilities in nanofiber fabrication, increase understanding of magnetic properties of nanofiber assemblies, and pursue precision coating of such materials by atomic layer deposition for applications in microwave devices such as circulators, filters, and phase shifters. Specifically, we will address proof-of-concept evaluation of new materials to determine their compatibility in gallium nitride (GaN) devices.

In a separate endeavor, the materials produced by this project will be available for evaluation by our industrial partner, Qorvo, a leading microwave solutions company, under a cooperative research and development agreement (CRADA).

**MISSION RELEVANCE**

The new materials and technology developed will enable much smaller and more energy-efficient devices for microwave and electronic applications. This project is therefore related to DOE's energy security mission. The enabling of more sensitive devices for microwave

applications implies relevance to the Department's national security mission as well.

**RESULTS AND ACCOMPLISHMENTS**

Argonne technology was used to produce highly oriented magnetic nanofibers that were coated using atomic layer deposition: specifically, we synthesized high-anisotropy Fe-Co magnetic nanofiber cores, with diameters ranging from 8–30 nm and lengths exceeding 1 cm, coated with 3–6 nm aluminum oxide shells. The materials produced were evaluated for compositional purity and consistency. To facilitate handling and subsequent processing, the nanofibers were broken up and sized to approximately 10–100  $\mu\text{m}$  lengths in an ultrasonic bath. Magnetic analysis and determination of GaN compatibility of the materials were outsourced to the industrial partner with whom we plan future development work. The results indicated that the dielectric and magnetic properties of the materials developed using Argonne technology are suitable for microwave applications and specifically for frequencies in the 1–10 GHz range.

**PROPOSED FUTURE WORK**

We will engage our industrial partner, Qorvo, to implement the high-anisotropy magnetic nanowire technology for microwave applications. The work will continue under two projects funded by the Defense Advanced Research Projects Agency (DARPA), as well as the CRADA with the industrial partner.

## Hybrid Silicon Nanolasers

2016-190-NO

Chad Husko

**PROJECT DESCRIPTION**

In this project, our team will demonstrate a hybrid silicon nanolaser. While silicon has excellent electrical properties, its optical properties have proven much more challenging to master. Specifically, silicon is a very poor light emitter because of its indirect bandgap. The solution to overcoming silicon's intrinsic limitation is to create a hybrid structure in which the light emission is provided by a complementary direct gap emitter material.

The project started in February 2016. The goals for the first year were as follows:

1. *Nano-cavity resonators.* Fabrication and characterization of the silicon resonators using existing nanofabrication techniques.

2. *Light emitter.* Development of a scalable transfer technique for the light-emitting material.
3. *Optical lasing.* Demonstration of the optically pumped hybrid silicon nanolaser.

Note: This project is part of the University of Chicago's FACCTS program (France and Chicago Collaborating in the Sciences) (<http://fcc.uchicago.edu/FACCTS>). Our collaborator in France where nanofabrication was done is affiliated with the Institut d'Electronique Fondamental located at the Université Paris-Sud. Collaborators at Northwestern University focused on synthesis of the emitter.

### MISSION RELEVANCE

This project is relevant to DOE's basic science mission. The primary focus of the work here is to build a hybrid nanomaterial composed of silicon and an emitter material. The specific embodiment of this concept is a silicon nanolaser. Nanolasers offer the possibility of a near-zero energy threshold and are widely regarded as critical elements for next-generation integrated circuits, which incorporate both optical and electronic devices in a single system. From an energy standpoint, they have very low thresholds, which allow for scaling of optical devices. From a broader perspective, nanolasers have clear relevance to increased information signal processing capabilities (i.e., supercomputing), as well as to compact opto-electronics in applications for the U.S. Department of Defense.

### RESULTS AND ACCOMPLISHMENTS

To date, we have accomplished the first two goals: (1) delivery of a test batch of silicon nano-cavity resonators; and (2) measurement of the photoluminescence of the emitter with Northwestern researchers.

Toward goal (3), we combined the two materials to make our first hybrid devices and made very promising initial measurements showing cavity-enhanced emission. Figure 1 shows these first results. We note that these experiments were at room temperature and under ambient environmental conditions, which are not ideal. Further, a visible-wavelength optical pump was used and likely caused additional absorption in the silicon. Nonetheless, these initial successes highlight a clear path forward. Achieving goal (3) would actually constitute a success not only for this project, but for the field.

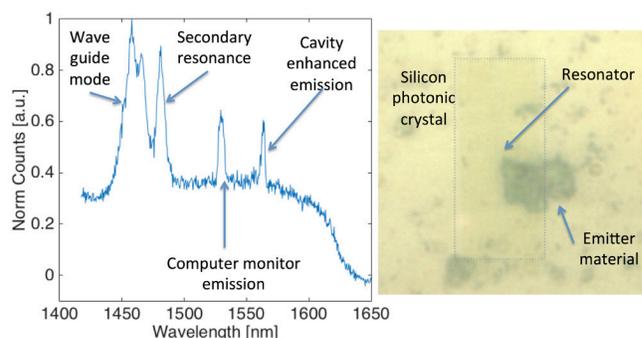


Figure 1. (Left) Resonant-enhanced optical emission from the emitter material on silicon pumped with a visible laser in normalized arbitrary units. (Right) Optical microscope image from a 100 $\times$  objective. The box is 10  $\times$  4  $\mu$ m in size and represents the photonic crystal.

### PROPOSED FUTURE WORK

In recent months, the setup has been improved so that the sample can simultaneously be in vacuum and at cryogenic temperatures. Further, piezo controls and a more suitable pump diode were obtained and are being commissioned. We expect improved and likely publishable results in FY 2017. After our first year, we believe the future scope of the work should involve further characterizing the performance of the nanolaser (linewidth, coherence, threshold, carrier dynamics, and quantum efficiency) in lieu of targeting electrical pumping. We will pursue both thrusts simultaneously, although it is likely that measurements of laser performance will be performed first.

# **PROGRAM ASSESSMENT**

## PERFORMANCE METRICS

The LDRD Program Office collects statistical data on current and completed LDRD projects. The data cover various items such as inventions and publications (see appendix to this report), follow on sponsorship, and the enhancement of staff by post-doctoral appointees and new hires. Although these data are of little value on a project-by-project basis, in the aggregate, they do provide a picture of overall program productivity. Summaries of the most recently collected data are provided here in

Tables 1 and 2. The first table displays project outcomes realized only during FY 2016 but derived from projects active in any year or years from FY 2013 forward. The data in Table 1 are subdivided by LDRD Program component. For the same prior and currently active projects, the second table displays those metrics for which cumulative results are monitored, with no restriction as to when the accomplishments occurred.

**Table 1. Aggregate FY 2016 Outcomes for Recently Completed and Current Projects**

Most Recent Project Year LDRD Component	Number of Refereed Publications	Number of Students/ Postdocs Supported	Number of New Staff Hires	Number of Non-Publication Copyrights	Number of Invention Disclosures	Number of Patents Issued/ Pending
<b>2013</b>						
Competitive Grants	6	0	0	0	1	1
Strategic Initiative	20	0	5	0	0	4
<b>2014</b>						
Competitive Grants	0	0	0	0	0	1
Strategic Initiative	3	0	0	0	0	0
<b>2015</b>						
Competitive Grants	14	0	1	0	0	2
Strategic Initiative	26	0	0	0	0	6
<b>2016</b>						
Innovate	35	42	2	0	3	4
Named Fellows	14	10	0	2	3	1
Swift	0	1	0	0	0	0
Prime*	100	152	22	1	22	7
<b>Totals: 265 Projects</b>	<b>218</b>	<b>205</b>	<b>30</b>	<b>3</b>	<b>29</b>	<b>26</b>

\* Data for the Director's Grand Challenge component is included in the Prime data.

**Table 2. Aggregate Outcomes for All Years of Recently Completed and Current Projects (2013–2016)**

Most Recent Project Year	Number of Projects Receiving Follow-on Funds	Number of Proposals Submitted to Sponsors	Number of Intellectual Property Events	Number of External Reviews*
2013	32	202	53	12 DOE 9 Other 83 UofC
				<b>104 Total</b>
2014	13	89	39	7 DOE 2 Other 20 UofC
				<b>29 Total</b>
2015	19	99	46	10 DOE 3 Other 35 UofC
				<b>48 Total</b>
2016	35	188	85	10 DOE 8 Other 52 UofC
				<b>70 Total</b>
<b>Totals: 265 Projects</b>	<b>99</b>	<b>578</b>	<b>223</b>	39 DOE 22 Other 190 UofC
				<b>251 Total</b>

\* UoC refers to UChicago Argonne, LLC.

## LDRD PROJECT CHARACTERISTICS

### MISSION RELEVANCE

Evaluating the relevance of LDRD projects with respect to DOE mission areas is of utmost importance during the review and selection process. All LDRD projects have demonstrable ties to one or more of the science, energy, environment, and national security missions, and many are also relevant to the missions of other federal agencies that sponsor work at Argonne. Figure 1 represents the number of FY 2016 LDRD projects supporting one or more of the four DOE mission areas.

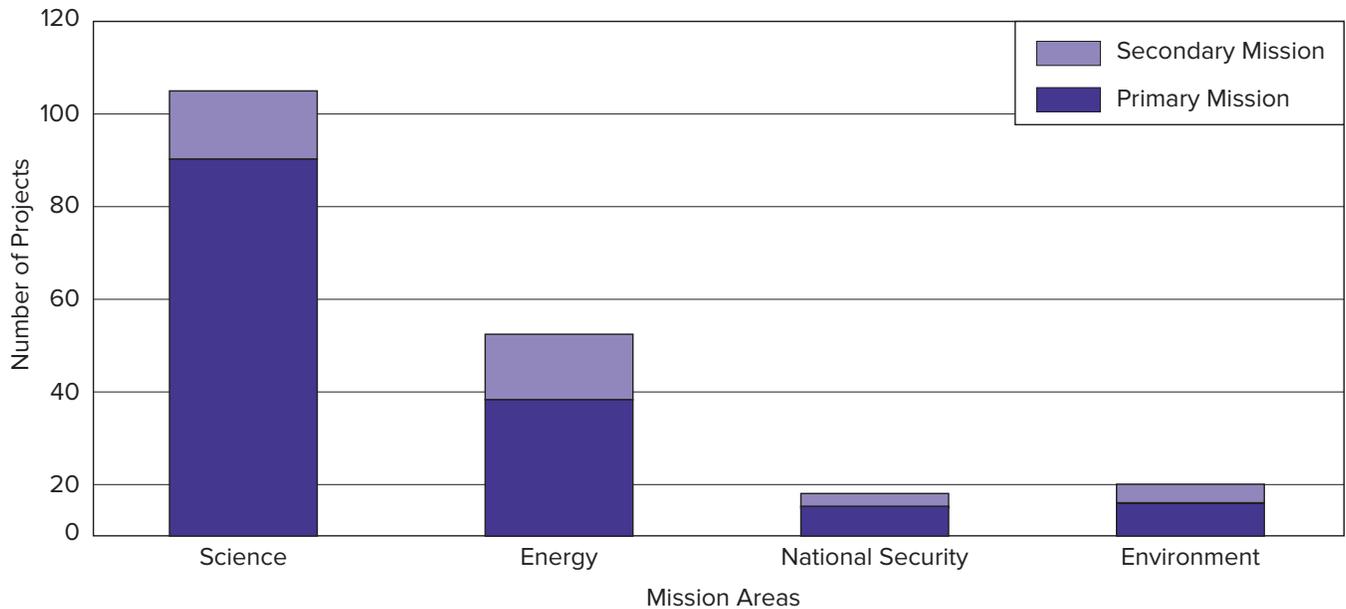


Figure 1. Number of LDRD Projects Supporting the DOE Mission Areas

### LEVEL OF FUNDING

Figure 2 depicts the funding distribution for the 135 projects funded in FY 2016. Around 65% of the projects were in the \$101K to \$300K range, with a little more than 9% receiving \$100K or less. About 21% of the projects received between \$301K and \$500K, while only 4% of projects were in the range of \$501K to \$1M. About 1% of projects received more than \$1M. The average funding level of projects in FY 2016 was approximately \$250K.

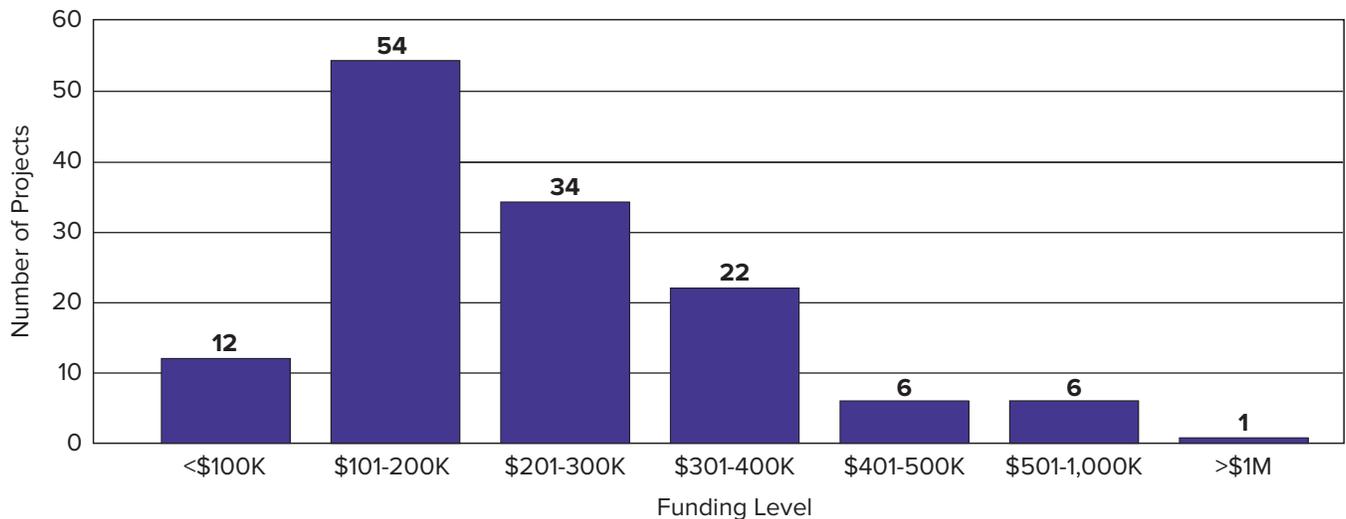


Figure 2. Number of Projects and Levels of Funding

## FY 2017 LDRD PROGRAM UPDATE

DOE approved Argonne's FY 2017 LDRD Plan and program expenditures not to exceed \$36.0M. A list of projects begun so far in FY 2017, organized by component/Focus Area and title, is provided at the end of this section.

For FY 2017, we have continued implementing changes begun in FY 2016 to the structure of the program's components. The Strategic Initiative component was renamed "LDRD Prime." The Director's Competitive Grants component was renamed "LDRD Innovate." The focus of each component remains essentially the same; however, some revised criteria are being applied. New LDRD Innovate projects are limited to a duration of no more than two years with funding not to exceed \$250K per year. The two-year limit, although not strictly required for new LDRD Prime projects, is encouraged, with exceptions requiring a strong justification. Also, for FY 2017, the previous Director's Grand Challenge component will have been phased out.

We initiated a new "LDRD Swift" component under which projects are limited to one-year efforts expending up to \$150K. These projects focus primarily on the applied sciences and respond to a specific potential near-term follow-on funding opportunity. LDRD Swift also includes proof-of-concept projects for early career researchers. Finally, the existing Argonne Fellowship program has been incorporated into LDRD as the LDRD Named Fellows component, which continues in FY 2017. The Fellowship

program has and will continue to attract highly talented early career scientists and engineers to Argonne.

The LDRD Program Office also instituted a weekly seminar series to give each principal investigator of an active LDRD project the opportunity to showcase the new science and technologies that are being developed in support of Argonne's Focus Areas and the DOE missions.

For FY 2017, we also are employing a Prime advisory committee to review how we manage the annual call for proposals; the submission, review, and evaluation of proposals; and the selection of LDRD Prime proposals for funding. The committee will make recommendations that improve those processes and procedures across all Focus Areas under the LDRD Prime component, including the new Focus Area added in FY 2017, Institute for Molecular Engineering.

Finally, we continue to refine our use of electronic tools to communicate with investigators and reviewers and to collect and document performance information on LDRD projects. Based on user feedback and other forms of input, we are improving our web-based applications and creating new tools as necessary. One such example is a recent modification to our online proposal submission system to accept Innovate *pre*-proposals, that is, brief accounts of ideas for new projects that can garner reviewer feedback before full proposals are submitted.

## LDRD PROJECTS BEGUN IN FY 2017

### LDRD INNOVATE

- Atomic Layer Deposition of Silicon Carbide for Nuclear Applications
- BOLT: OpenMP over Lightweight Threads
- Bonding Dissimilar Materials using Nanoparticles/ Nanofilm as Eutectic Compounds
- A Continuously Refinable Mesh, Limited Area Atmospheric Model
- Developing Superconducting MgB<sub>2</sub> films on Copper Radio-Frequency Accelerating Structures
- Engineered Interfaces for Gallium Oxide Power Semiconductor Devices
- Integrating High Throughput Computation and Wet-chemistry Synthesis for Functional Supercrystals
- The Missing Link in XTIP: Synergy of Experiments and Theory for Argonne's Global Leadership
- New Techniques to Manipulate Rare Isotopes using Adaptive Optics

- A Novel Method of Longitudinal Bunch Shaping by Double Emittance Exchange
- Realizing a Gate Tunable Kinetic Inductance for a Transmon Qubit using SrTiO<sub>3</sub>

### LDRD NAMED FELLOWS

- Beehive: A Dynamic Execution Environment for Performance, Power, and Resilience on Extreme-Scale Computing Systems
- Combining Electrochemistry and Ultrafast Spectroscopies: Real Time Characterization of Multi-Electron/Proton Intermediates in Hydrogen and Oxygen Evolving Catalysts
- Ecological Organic Photovoltaics using Water-borne Semiconductor Nanoparticles
- Microstructural Simulations of Stable Conjugated Polymer Glasses
- Novel Devices and Systems for Neuromorphic Computing

- On the Colloidal Suspension of Lithium Clusters in Molten Lithium Chloride
- A Universal Data Analytics Platform for Science

#### **LDRD SWIFT**

- Application of Combined Rheology and X-ray Scattering to Paint Industry for Optimizing Formulation Processes
- Building a Battery Recycling Model within GREET and BatPaC
- Enhancing Computational Tools for Polynomial Optimization Problems Relevant to Networked Systems
- FOXHUNT Proof of Concept DEMO
- High-Entropy Alloys for Advanced Nuclear Reactors
- Multiscale Modeling to Understand Ion-diffusion-induced Degradation in Photovoltaics
- Towards the Reduction of U.S. Petroleum Consumption by Fueling Light-duty Engines with Propane
- X-ray Investigation of the Potential of Pressure-Assisted Atomization Technology for Medical Inhaler Sprays

#### **LDRD PRIME**

##### **APPLIED ENERGY AND SUSTAINABLE TRANSPORTATION**

- Advancing Additive Manufacturing of Metal Alloys; from Fundamental Principles to Durable Components
- Improving Cost and Energy Efficiency of Nontraditional Water Desalination through Innovative Material and Process Integration
- Metal Additive Manufacturing Modeling

##### **BIOLOGICAL AND ENVIRONMENTAL SCIENCES CAPABILITY DEVELOPMENT**

- Integrating Atmospheric, Ecological, and Biogeochemical Monitoring in Wetlands
- Linking Climate to Water: Implementing a 4KM Regional Climate Model with Hydrologic Model Coupling (WRF-Hydro) Using Argonne's HPC Resources

##### **HARD X-RAY SCIENCES**

- COHED: Coherence for High-Energy Diffraction
- Developing Advanced Coherent Surface Scattering Reconstruction Method Incorporating Dynamical Scattering Theory
- Development of a Compact Accelerator for A High Repetition Rate Free-Electron Laser
- Soft Matter Visualization and Characterization by Electron Optical Beam Lines
- Universal Superconducting Undulator

##### **INSTITUTE FOR MOLECULAR ENGINEERING**

- Quantum Optics with Phonons
- Self-assembling Soft Nanostructures with Ultra-Slow Dissociation Kinetics

##### **MATERIALS AND MOLECULES TO MANUFACTURING**

- Advanced Materials for the Energy-Water Nexus
- Catalysts Modeled After Nature's Enzymes
- Developing Hierarchical Multi-functional Hybrid Polymer-Proteins Structures for Energy Applications
- Integrated Imaging
- Oxides for Novel Computational Approaches
- Towards an Artificial Neuron—Non-Covalent Synaptic Assemblies

##### **NATIONAL AND GLOBAL SECURITY**

- Miniaturized High-Efficiency RF Energy Harvesting
- Understanding Resilient Infrastructure Dependencies and Interdependencies through Advanced Optimization and Simulation

##### **NEXT GENERATION COMPUTING**

- Enabling Multidimensional X-ray Nano-Tomography
- End-to-End Genome Annotation and Phenotype Prediction with Deep Learning
- An Exascale Application for Simulating Urban Boundary Layers
- The Perfect Thermodynamics of Imperfect Materials
- SLIK-D: Scalable Machine Learning Infrastructure for Knowledge Discovery

##### **NUCLEAR ENERGY SCIENCE AND TECHNOLOGY**

- Conceptual Design of a Flexible Spectrum Test Reactor (FSTR)
- Development of Molten-Salt Reactor Analysis Computation Tools to Support Emerging Markets
- Technological Improvements to Increase Scalability of Ex-Vessel Melt Coolability and Concrete Interaction Experiments

##### **UNIVERSE AS THE LAB (ULAB)**

- Exploring the Universe: Large Scale Structure to the First Stars
- A Strategic Scientific Program to Establish Argonne Leadership in the Development of the Future Electron-Ion Collider
- Superconducting Detectors for Future CMB Experiments

# APPENDIX

# INTELLECTUAL PROPERTY EVENTS OCCURING IN FY 2016

(As a Result of LDRD Projects and Subsequent Related Sponsored Research)

## INVENTION DISCLOSURES

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**2006-137**

**PATENT GRANTED**

Zhang, Z., K. Amine, and Z. Chen. "Non-Aqueous Electrolytes for Lithium-Air Batteries." Patent No. 9,362,599 granted June 2016. [ANL-IN-08-073]

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**2009-070**

**PATENT APPLICATION**

Pokkuluri, P.R., M. Schiffer, R. Wilton, and A. Joachimiak. "Stabilization of Rubisco Activase for Enhanced Photosynthesis and Crop Yields." Patent Application No. 62/402,227 filed September 2016. [ANL-IN-12-007] [Also see 2013-013.]

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**2009-097**

**PATENT GRANTED**

Laible, P.D. and S.W. Snyder. "Engineered Photosynthetic Bacteria, Method of Manufacture of Biofuels." Patent No. 9,441,248 granted September 2016. [ANL-IN-12-007]

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**2010-117**

**PATENT GRANTED**

Lopez, D., I-W. Jung, J. Wang, D. Mukhopadhyay, D. Walko, and G. Shenoy. "Diffraction Leveraged Modulation of X-ray Pulses using Mems-based X-ray Optics." Patent No. 9,412,480 granted August 2016. [ANL-IN-12-047]

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**2010-158**

**INVENTION DISCLOSURE**

Shui, J., C. Chen, and D.-J. Liu. "Nanofibrous Electrocatalysts." Invention report disclosed May 2016. [ANL-IN-12-063B] [Also see 2010-185 and 2014-051.]

**PATENT APPLICATION**

Shui, J., C. Chen, and D.-J. Liu. "Nanofibrous Electrocatalysts." Patent Application No. 15/144,650 filed May 2016. [ANL-IN-12-063B] [Also see 2010-185 and 2014-051.]

**PATENT GRANTED**

Liu, D.-J., C. Chen, and J. Shui. "Nanofibrous Electrocatalysts." Patent No. 9,350,026 granted May 2016. [ANL-IN-12-063] [Also see 2010-185.]

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**2010-185**

**INVENTION DISCLOSURE**

Shui, J., C. Chen, and D.-J. Liu. "Nanofibrous Electrocatalysts." Invention report disclosed May 2016. [ANL-IN-12-063B] [Also see 2010-158 and 2014-051.]

**PATENT APPLICATION**

Shui, J., C. Chen, and D.-J. Liu. "Nanofibrous Electrocatalysts." Patent Application No. 15/144,650 filed May 2016. [ANL-IN-12-063B] [Also see 2010-158 and 2014-051.]

**PATENTS GRANTED**

Liu, D.-J., C. Chen, and J. Shui. "Nanofibrous Electrocatalysts." Patent No. 9,350,026 granted May 2016. [ANL-IN-12-063] [Also see 2010-158.]

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**2010-188**

**PATENT GRANTED**

Johnson, C.S., T. Rajh, E. Shevchenko, and B. Koo. "Hollow Nanoparticle Cathode Materials for Sodium Electrochemical Cells and Batteries." Patent No. 9,391,319 granted July 2016. [ANL-IN-13-024]

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**2010-197**

**PATENT GRANTED**

Pellin, M.J., M. Stan, and A. Yacout. "Design Porosity Materials in Nuclear Reactor Components." Patent No. 9,437,335 granted September 2016. [ANL-IN-12-043] [Also see 2013-152.]

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**2010-202**

**INVENTION DISCLOSURE**

Miller, J.T., B. Hu, N.M. Schweitzer, and A.S. Hock. "Selective Alkane Activation with Single Site Atoms on Amorphous Support." Invention report disclosed November 2015. [ANL-IN-12-114B]

**PATENT APPLICATION**

Miller, J.T., B. Hu, N.M. Schweitzer, and A.S. Hock. "Selective Alkane Activation with Single Site Atoms on Amorphous Support." Patent Application No. 14/946,453 filed November 2015. [ANL-IN-12-114B]

**PATENT GRANTED**

Miller, J.T., B. Hu, N.M. Schweitzer, and A.S. Hock. "Selective Alkane Activation with Single Site Atoms on Amorphous Support." Patent No. 9,192,919 granted November 2015. [ANL-IN-12-114]

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**2010-203**

**PATENT GRANTED**

Zhang, L., F.R. Brushett, Z. Chen, A.N. Jansen, and J.T. Vaughey. "Organic Non-aqueous Cation-based Redox Flow Batteries." Patent No. 9,300,000 granted March 2016. [ANL-IN-09-054]

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**2011-012**

**PATENT GRANTED**

Benmore, C.J., and J.R. Weber. "Containerless Synthesis of Amorphous and Nanophase Organic Materials." Patent No. 9,327,264 granted May 2016. [ANL-IN-10-011]

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**2011-060**

**PATENT GRANTED**

Liu, D.J., G. Goenaga, and S. Yuan. "Electrocatalysts Using Porous Polymers and Method of Preparation." Patent No. 9,406,943 granted August 2016. [ANL-IN-09-109B]

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**2011-147**

**INVENTION DISCLOSURE**

Novosad, V. and E.A. Rozhkova. "Ferromagnetic Particles as Ultra-sensitive Non-linear Response Labels for Magnetic Particles Imaging (MPI) and Sensing Applications." Invention report disclosed August 2016. [ANL-IN-16-045]

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**2012-087****PATENT APPLICATION**

Katsoudas, J., C. Segre, D. Singh, and E.V. Timofeeva. "Rechargeable Nanoelectrofuel Electrodes and Devices for High Energy Density Flow Batteries." Patent Application No. 14/889,939 filed November 2015. [ANL-IN-12-122]

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**2013-013****PATENT APPLICATION**

Pokkuluri, P.R., M. Schiffer, R. Wilton, and A. Joachimiak. "Stabilization of Rubisco Activase for Enhanced Photosynthesis and Crop Yields." Patent Application No. 62/402,227 filed September 2016. [ANL-IN-12-007] [Also see 2009-070.]

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**2013-100****PATENT GRANTED**

Martinson, A.B., R. McCarthy, M.S. Weimer, and A.S. Hock. "Oxygen-free Atomic Layer Deposition of Indium Sulfide." Patent No. 9,382,618 granted July 2016. [ANL-IN-14-022]

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**2013-152****PATENT GRANTED**

Pellin, M.J., M. Stan, and A. Yacout. "Designed Porosity Materials in Nuclear Reactor Components." Patent No. 9,437,335 granted September 2016. [ANL-IN-12-043] [Also see 2010-197.]

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**2013-154****PATENT APPLICATIONS**

Elam, J.W., J.A. Libera, A.U. Mane, and A. Yanguas-Gil. "Refractory Solar Selective Coatings." Patent Application No. 15/017,548 filed February 2016. [ANL-IN-15-016]

Elam, J.W., J.A. Libera, A.U. Mane, and A. Yanguas-Gil. "Refractory Solar Selective Coatings." Patent Application No. 15/017,618 filed February 2016. [ANL-IN-15-016B]

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**2013-156****PATENT APPLICATION**

Urgun Demirtas, M., X. Chen, P. Ignacio-de Leon, R.W. Brotzman, and E.J. Rabe. "Magnetic Nanotube Composite Membranes." Patent Application No. 15/000,801 filed January 2016. [ANL-IN-15-030] [Also see 2014-169.]

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**2013-208****PATENT APPLICATION**

Murphy-Olson, D., R. Audelott, and S. Boisvert. "Systems and Methods for Metric Driven Deployments to Cloud Service Providers." Patent Application No. 62/402,959 filed September 2016. [ANL-IN-15-073]

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**2014-051****INVENTION DISCLOSURES**

Chong, L. and D.-J. Liu. "Low Platinum Catalyst and Method of Preparation." Invention report disclosed January 2016. [ANL-IN-15-143]

Shui, J., C. Chen, and D.-J. Liu. "Nanofibrous Electrocatalysts." Invention report disclosed May 2016 [ANL-IN-12-063B] [Also see 2010-158 and 2014-051.]

**PATENT APPLICATIONS**

Chong, L. and D.-J. Liu. "Low Platinum Catalyst and Method of Preparation." Patent Application No. 15/203,083 filed July 2016. [ANL-IN-15-143]

Shui, J., C. Chen, and D.-J. Liu. "Nanofibrous Electrocatalysts." Patent Application No. 15/144,650 filed May 2016. [ANL-IN-12-063B] [Also see 2010-158 and 2014-051.]

**2014-137****PATENT APPLICATION**

Welp, U., I. Kesgin, M. Kasa, Y. Ivanyushenkov, and C.L. Doose. "Continuous Winding Magnets Using Thin Film Conductors without Resistive Joints." Patent Application No. 14/962,251 filed December 2015. [ANL-IN-15-054]

**2014-161****INVENTION DISCLOSURES**

Chan, H., S. Sankaranarayanan, B. Narayanan, and M.J. Cherukara. "Machine Learning Technique to Identify Grains in Polycrystalline Materials Samples." Invention report disclosed September 2016. [ANL-IN-16-126] [Also see 2015-149.]

Sankaranarayanan, S., K. Wu, and X-M. Lin. "Nanoscale Membranes for Removing Trace Organic Contaminant in Water." Invention report disclosed September 2016. [ANL-IN-16-134]

**2014-169****INVENTION DISCLOSURES**

Chen, X. and Z. Zhou. "Magneto Dielectric Composite Materials and Microwave Applications Thereof." Invention report disclosed May 2016. [ANL-IN-16-067]

Chen, X. "Nanostructured Transverse Thermoelectric Materials." Invention report disclosed April 2016. [ANL-IN-16-044]

Zhou, Z. and X. Chen. "Magnetic Nanofiber Composite Materials and Devices using Same." Invention report disclosed September 2016. [ANL-IN-16-066]

**PATENT APPLICATIONS**

Chen, X. and Z. Zhou. "Magneto Dielectric Composite Materials and Microwave Applications Thereof." Patent Application No. 15/279,867 filed September 2016. [ANL-IN-16-067]

Chen, X. and Z. Zhou. "Tunable Broadband Microwave Absorber." Patent Application No. 15/082,901 filed March 2016. [ANL-IN-14-097]

**2014-181****NON-PUBLICATION COPYRIGHT**

Di, S. and F. Cappello. "AID: Adaptive Impact Driven Protection." Software copyright issued June 2016. [ANL-SF-16-103]

Di, S. and F. Cappello. "Error Bounded Lossy HPC Data Compressor." Software copyright issued June 2016. [ANL-SF-16-105]

**2014-185****INVENTION DISCLOSURE**

Johnson, Christopher S. "Environment Sensing Cell Phone/Consumer Device with Split Battery." Invention report disclosed January 2016. [ANL-IN-15-145]

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**2014-187****PATENT APPLICATION**

Darling, S.B., A. Lee, J.W. Elam, and J.A. Libera. "Hydrophilic, Light Active Coatings for Membranes." Patent Application No. 15/002,102 filed January 2016. [ANL-IN-15-102]

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**2014-194****NON-PUBLICATION COPYRIGHT**

North, M., P. Sydelko, I. Martinez-Moyano, and B. Friedman. "ASDM." Software copyright issued September 2016. [ANL-SF-16-130]

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**2015-121****PATENT APPLICATION**

Wang, P., J. Li, L.B. Guzowski, R.T. Muehleisen and Y. Sun. "Continuous Flow Synthesis of VO<sub>2</sub> Nanoparticles or Nanorods by Using a Capillary Based Microreactor." Patent Application No. 62/323,343 filed April 2016. [ANL-IN-15-033]

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**2015-149****INVENTION DISCLOSURE**

Chan, H., S. Sankaranarayanan, B. Narayanan, and M.J. Cherukara. "Machine Learning Technique to Identify Grains in Polycrystalline Materials Samples." Invention report disclosed September 2016. [ANL-IN-16-126] [Also see 2014-161.]

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**2015-151****INVENTION DISCLOSURES**

Elam, J.W. and A.U. Mane. "*In situ* Nanostructure Growth Method to Fabricate Functional Filaments for 3D Printing." Invention report disclosed March 2016. [ANL-IN-16-038]

Elam, J.W. and A.U. Mane. "Scheme to Create Thin Film Secondary Electron Generation Layer/Membrane on Electron Amplification Devices." Invention report disclosed March 2016. [ANL-IN-16-042]

Libera, J.A., A.U. Mane and J.W. Elam. "Atomic Layer Deposition Methods for Making Thin Films Metal Fluorides Using Metal Tert-Butoxide and Metal Fluoride Recursors." Invention report disclosed March 2016. [ANL-IN-16-037]

Mane, A.U. and J.W. Elam. "Etching/Removal of Thin Films by Metal Fluoride Vapors." Invention report disclosed August 2016. [ANL-IN-16-119]

Mane, A.U. and J.W. Elam. "Scheme to Fabricate Neutron Sensitive Structures for Neutron Detection Devices." Invention report disclosed March 2016. [ANL-IN-16-041]

Mane, A.U. and J.W. Elam. "Systems and Methods for Metal Layer Adhesion." Invention report disclosed April 2016. [ANL-IN-16-031]

Yanguas-Gil, A. "3D Architectures for Neuomorphic Computing." Invention report disclosed February 2016. [ANL-IN-16-051]

Yanguas-Gil, A. and J.W. Elam. "Method for Enhanced Isolation and Defect Reduction of Power Semiconductor Devices." Invention report disclosed September 2016. [ANL-IN-15-119]

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**2016-054****INVENTION DISCLOSURE**

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Bakhtiari, S., A. Heifetz, and R.B. Vilim. "Transmission of Information by Acoustic Communication along Metal Pathways in Nuclear Facilities." Invention report disclosed April 2016. [ANL-IN-16-050]

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Xie, J., J.W. Elam, H. Nicholson, M.J. Pellin, R.G. Wagner, J. Wang, A.U. Mane, and L. Xia. "3D Printed Boron Enriched Capillary Array for Thermal Neutron Absorption and Detection." Invention report disclosed August 2016. [ANL-IN-16-104]

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**INVENTION DISCLOSURE**

Acik, M. and S.B. Darling. "One-Step *in situ* Solution Growth Method for Methyllammonium Lead Perovskite Crystals." Invention report disclosed August 2016. [ANL-IN-16-118]

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**2016-186**

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Schaller, R.D. and B. Diroll. "Systems and Methods for Ultrafast Plasmonic Response in Doped, Colloidal Nanostructures." Invention report disclosed May 2016. [ANL-IN-16-072]

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**INVENTION DISCLOSURE**

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Chen, X. and Y. Ciu. "A Micro-packaged Miniature RF Circulator Based on Highly Anisotropic Magnetic Nanofiber." Invention report disclosed June 2016. [ANL-IN-16-084]

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## 2014-054-R2

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## 2014-077-R2

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**2014-081-R2****REFEREED PUBLICATIONS**

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## 2014-084-R2

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## 2014-095-R2

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## 2014-108-R2

### REFEREED PUBLICATION

Michalska, K., A.D. Steen, G. Chhor, M. Endres, A.T. Webber, J. Bird, K.G. Lloyd and A. Joachimiak (2015). “New Aminopeptidase from “Microbial Dark Matter” Archaeon.” *The Journal of the Federation of American Societies of Experimental Biology* **29**(9): 4071–4079.

### PRESENTATIONS

Michalska, K., A. Steen, G. Chhor, M. Endres, A.T. Webber, J. Bird, K. Lloyd and A. Joachimiak (2016). “Microbial Degradation of Biopolymers—Structural Biology Insights.” University of Tennessee, Knoxville, TN, October 19, 2015.

Michalska, K., A. Steen, G. Chhor, K.M. Fayman, M. Endres, G. Babnigg, K. Lloyd, R. Jedrzejczak and A. Joachimiak (2014). “Discovery of Proteins from ‘Microbial Dark Matter’” NIH Structural Biology Horizons Workshop, Bethesda, MD, December 9–10, 2013.

Michalska, K., A. Steen, G. Chhor, K. M. Fayman, M. Endres, G. Babnigg, K. Lloyd, R. Jedrzejczak and A. Joachimiak (2014). “Structural Genomics of Sedimentary Archaea in Postgenomic Era.” DOE Joint Genome Institute 9th Annual Genomics of Energy & Environment Meeting, Walnut Creek, CA, March 18–20, 2014.

Michalska, K., A. Steen, G. Chhor, K. Fayman, M. Endres, G. Babnigg, K. Lloyd, R. Jedrzejczak and A. Joachimiak (2014). “Structure and Specificity of Novel Aminopeptidase from Marine Sediment Archaea.” 23rd Congress and General Assembly of the International Union of Crystallography, Montreal, Quebec, Canada, August 5–13, 2014.

Steen, A., K. Michalska, G. Chhor, M. Endres, J. Vazin, K. Lloyd, S.W. Wilhelm and A. Joachimiak (2014). “Strategies to Assess the Biochemical Properties of Extracellular Hydrolases in Aquatic Environments.” Goldschmidt 2014 Conference, Sacramento, CA, June 8–13, 2014.

## 2015-078- R1

### REFEREED PUBLICATIONS

Benseman, T.M., H. Yang, V.K. Vlasko-Vlasov, U. Welp, A.E. Koshelev, W.-K. Kwok, R. Divan, C. Keiser, C. Watanabe and K. Kadowaki. “High-Resolution Thermal Micro-Imaging Using Europium Chelate Luminescent Coatings.” *Journal of Visualized Experiments*. (To be published.)

Benseman, T.M., A.E. Koshelev, V. Vlasko-Vlasov, Y. Hao, W.K. Kwok, U. Welp, C. Keiser, B. Gross, M. Lange, D. Kölle, R. Kleiner, H. Minami, C. Watanabe and K. Kadowaki (2015). “Current Filamentation in Large  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  Mesa Devices Observed via Luminescent and Scanning Laser Thermal Microscopy.” *Physical Review Applied* **3**(4): 044017.

### NON-REFEREED PUBLICATIONS

Benseman, T., A. Koshelev, V. Vlasko-Vlasov, U. Welp, W.-K. Kwok, Y. Hao, B. Gross, M. Lange, D. Koelle, R. Kleiner and K. Kadowaki (2016). “The Cavity Resonance Mode of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  Mesa Terahertz Source as Probed by Scanning Laser Thermal Microscopy.” 2016 March Meeting of the American Physical Society, Baltimore, MD, March 14–18, 2016.

Hao, Y., U. Welp, A. Koshelev, V. Vlasko-Vlasov, W.-K. Kwok, K. Kadowaki and T. Benseman (2016). “Artificially Induced Hotspots in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  Mesa Terahertz Sources.” 2016 March Meeting of the American Society, Baltimore, MD, March 14–18, 2016.

### PRESENTATIONS

Benseman, T.M., A.E. Koshelev, V. Vlasko-Vlasov, Y. Hao, W.-K. Kwok, U. Welp, C. Keiser, B. Gross, M. Lange, D. Koelle, R. Kleiner and K. Kadowaki (2015). “Comparison of Luminescent and Scanning Laser Thermal Micro-imaging of Self-heating in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  Mesa THz Sources.” American Physical Society March Meeting, San Antonio, TX, March 2–6, 2015.

Benseman, T.M., A.E. Koshelev, V. Vlasko-Vlasov, Y. Hao, U. Welp, W.-K. Kwok, B. Gross, M. Lange, D. Koelle, R. Kleiner and K. Kadowaki (2015). “Terahertz Radiation from  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+6}$  Interlayer Josephson Junctions: Progress and Future Strategies.” AMN-7: Advanced Materials and Nanotechnology Conference, Nelson, New Zealand, February 8–12, 2015.

Benseman, T.M., A.E. Koshelev, V. Vlasko-Vlasov, Y. Hao, U. Welp, W.-K. Kwok, B. Gross, M. Lange, D. Koelle, R. Kleiner and K. Kadowaki (2015). “Terahertz Radiation from  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+6}$  Interlayer Josephson Junctions: Progress and Future Strategies.” City of University of NY-Queens College Colloquium, New York, NY, February 25, 2015.

Hao, Y., T.M. Benseman, A.E. Koshelev, V. Vlasko-Vlasov, W.-K. Kwok, U. Welp, C. Keiser, B. Gross, M. Lange, D. Koelle, R. Kleiner and K. Kadowaki (2015). “The Stability of Current Filaments in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+6}$  Observed Via Luminescent Thermal Microscopy.” American Physical Society March Meeting, San Antonio, TX, March 2–6, 2015.

Welp, U., T. Benseman, Y. Hao, A.E. Koshelev, V. Vlasko-Vlasov, W.-K. Kwok, H. Minami, C. Watanabe, K. Kadowaki, B. Gross, M. Lange, D. Koelle and R. Kleiner (2015). “Current Filamentation in Large  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+6}$  Mesas Observed by Luminescent and Scanning Laser Thermal Microscopy.” Plasma 2014, Kyoto, Japan, November 30–December 3, 2014.

### 2015-091- R1

#### REFEREED PUBLICATIONS

Zou, J., L. Chong, D.-J. Liu, X. Zeng, L. Peng and W. Ding (2016). “Wrapped By Graphene: An Efficient Way to Achieve High Capacity, Reversible Hydrogen Storage Through Nanoencapsulated Hydride.” *Science* **351**(6278): 1223.

Chong, L., X. Zeng, W. Ding, D.-J. Liu and J. Zou (2015). “ $\text{NaBH}_4$  in ‘Graphene Wrapper’: Significantly Enhanced Hydrogen Storage Capacity and Regenerability through Nanoencapsulation.” *Advanced Materials* **27**(34): 5070–5074.

#### PRESENTATIONS

Liu, D.-J. (2015). “Recent Developments in New Materials and Characterization Techniques for Energy Storage and Conversion.” University of Illinois at Chicago, Chicago, IL, February 26, 2015. (Also see 2014-051.)

Liu, D.-J. (2015). “Recent Developments in New Materials and Characterization Techniques for Energy Storage and Conversion.” University of Nebraska, Lincoln, NE, October 20, 2014. (Also see 2014-051.)

### 2015-096-R1

#### REFEREED PUBLICATIONS

Benmore, C.J., L.B. Skinner, B. Lee, J.R. Weber, J.B. Parise and M.A. Williamson (2016). “Topological Ordering in Liquid  $\text{UO}_2$ .” *Journal of Physics: Condensed Matter* **28**(1): 015102. (Also see 2015–136.)

Guthrie, M., C.J. Benmore, L.B. Skinner, O.L.G. Alderman, J.K.R. Weber, J.B. Parise and M. Williamson (2017). “Thermal Expansion in  $\text{UO}_2$  Determined by High-energy X-ray Diffraction.” *Journal of Nuclear Materials* **479**: 19–22. (Also see 2015-136.)

Skinner, L.B., C.J. Benmore, J.R. Weber, M.A. Williamson, A.J. Tamalonis, A.S. Hebden, T. Wiencek, O.L.G. Alderman, M. Guthrie, L. Leibowitz and J.B. Parise (2015). “Molten Uranium Dioxide Structure and Dynamics.” *Science* **346**(6212): 984–987. (Also see 2015-136.)

Weber, J.K.R., A.J. Tamalonis, C.J. Benmore, O.L.G. Alderman, S. Sendelbach, A. Hebden and M.A. Williamson (2016). “Aerodynamic Levitator for *in situ* X-ray Structure Measurements on High Temperature and Molten Nuclear Fuel Materials.” *Review of Scientific Instruments* **87**(7): 073902–073902. (Also see 2015-136.)

### 2016-001-NO

#### PRESENTATION

Sen, A., K.L. Reid and S.T. Pratt (2016). “Circular Dichroism of Angular Distributions (CDAD) by Using Velocity Map Photoelectron Imaging.” Advanced Particle Imaging Techniques: 1986–2016 And Beyond, Telluride, CO, August 8–12, 2016.

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**2016-010-NO****REFEREED PUBLICATIONS**

Galda, A. and V.M. Vinokur (2016). “Parity-time Symmetry-breaking in Magnetic Systems.” *Physical Review B: Condensed Matter* **94**(2): 020408(R).

Tripathi, V., A. Galda, H. Barman and V.M. Vinokur (2016). “Parity-time Symmetry-breaking Mechanism of Dynamic Mott Transitions in Dissipative Systems.” *Physical Review B: Condensed Matter* **94**(4): 041104.

**PRESENTATIONS**

Vinokur, V.M. (2016). “Parity-time Symmetry and Dynamic Phase Transitions.” Transport in Interacting Disordered Systems—2016, Granada, Spain, August 21–25, 2016.

Vinokur, V.M. (2016). “Parity-time Symmetry and Dynamic Phase Transitions.” 12th International Conference on Superconductivity and Magnetism, Coma Ruga, Spain, July 4–7, 2016.

Vinokur, V.M. (2016). “Parity-time Symmetry and Dynamic Phase Transitions.” Superstripes-2016, Ischia, Italy, June 23–29, 2016.

Vinokur, V.M. (2016). “Parity-time Symmetry and Dynamic Phase Transitions.” 5th International Conference on Superconductivity and Magnetism, Fenthieye, Turkey, April 24–30, 2016.

Vinokur, V.M. (2016). “Parity-time Symmetry Mechanism of Out-of-Equilibrium Phase Transitions.” Superconducting and Magnetic Systems, Natal, Brazil, September 3–6, 2016.

Vinokur, V.M. (2016). “Vortex Mott Transition: Experiment and Theory.” International Conference on Quantum Condensed Matter, Engelberg, Switzerland, February 10–12, 2016.

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**2016-027-NO****PRESENTATION**

Wang, J., A.U. Mane, S. Liao, R.G. Wagner, J.W. Elam and D. Haskel (2016). “X-ray Polarization Analysis with Gas-Filled Microchannel Plates: GF-MCP.” 65th Annual Conference on Applications of X-ray Analysis, Rosemont, IL, August 1–5, 2016.

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**2016-054-NO****REFEREED PUBLICATION**

Sampson, M.D., J.S. Park, R.D. Schaller, M.K.Y. Chan and A.B.F. Martinson (2017). “Transition Metal-Substituted Lead Halide Perovskite Absorbers.” *Journal of Materials Chemistry A: Materials for Energy and Sustainability* **5**(7): 3578–3588.

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**2016-069-NO****REFEREED PUBLICATIONS**

Kinaci, A., B. Narayanan, F.G. Sen, M.J. Davis, S.K. Gray, S.K.R.S. Sankaranarayanan and M.K.Y. Chan (2017). “Unraveling the Planar-Globular Transition in Gold Nanoclusters through Evolutionary Search.” *Scientific Reports* **6**: 34974.

Sun, C., T. Paulauskas, F.G. Sen, G. Lian, J. Wang, C. Burma, M.K.Y. Chan, R.F. Klie and M.J. Kim (2016). “Atomic and Electronic Structure of Lomer Dislocations at CdTe Bicrystal Interface.” *Scientific Reports* **6**: 27009.

Wang, H., J. Wen, D.J. Miller, Q. Zhou, M. Chen, H.N. Lee, K.M. Rabe and X. Wu (2016). “Stabilization of Highly Polar BiFeO<sub>3</sub>-like Structure: A New Interface Design Route for Enhanced Ferroelectricity in Artificial Perovskite Superlattices.” *Physical Review X* **6**(1): 011027.

**PRESENTATIONS**

Chan, M. (2016). “Theory Meets Reality: Combined First Principles Modeling and Characterization Studies of Renewable Energy Materials.” Massachusetts Institute of Technology, Cambridge, MA, April 7, 2016.

Chan, M. (2016). “Theory Meets Reality: Combined First Principles Modeling and Characterization Studies of Renewable Energy Materials.” Nano and Advanced Materials Institute Limited, Hong Kong, December 2, 2015.

Chan, M. (2016). “Where are the atoms and what do they do? Using Computational Modeling to Understand and Improve Renewable Energy Materials.” White House Office of Science and Technology Policy, March 2, 2016

Schwenker, E., F. Sen, T. Paulauskas, C. Sun, J. Wen, M. Kim, R.F. Klie and M. Chan (2016). “Prediction of Atomic Structure of Interfaces Using Electron Microscopy and Atomistic Simulations.” 3rd International Congress on 3D Materials Science (3DMS), St. Charles, IL, July 10–13, 2016.

Sen, F.G., C. Buurma, T. Paulauskas, C. Sun, M. Kim, S. Sivananthan, R.F. Klie and M.K.Y. Chan (2016). “First Principles Modeling of Grain Boundaries in CdTe.” The 43rd IEEE Photovoltaic Specialists Conference, Portland, OR, June 5–10, 2016.

Wen, J. (2016). “Amplitude Contrast High Resolution Electron Microscopy of A-site Associated Oxygen Octahedral Rotations in Artificial Perovskite Superlattices: Stabilization of Highly Polar BiFeO<sub>3</sub>-like Structure.” XXV International Materials Research Congress, Cancun, Mexico, August 14–19, 2016.

## 2016-082-NO

### REFEREED PUBLICATIONS

Cherukara, M.J., B. Narayanan, A. Kinaci, K. Sasikumar, S.K. Gray, M.K.Y. Chan and S.K.R.S. Sankaranarayanan (2016). “*Ab initio*-Based Bond Order Potential to Investigate Low Thermal Conductivity of Stanene Nanostructures.” *Journal of Physical Chemistry Letters* **7**(19): 3752–3759. (Also see 2014-161, 2015-149 and 2016-082.)

Das, S., M.K. Bera, S. Tong, B. Narayanan, G. Kamath, A. Mane, A.P. Paulikas, M.R. Antonio, S.K. R.S. Sankaranarayanan and A.K. Roelofs (2016). “A Self-Limiting Electro-Ablation Technique for the Top-Down Synthesis of Large-Area Monolayer Flakes of 2D Materials.” *Scientific Reports* **6**: 28195. (Also see 2014-161, 2015-149 and 2016-082.)

Sumant, A.V., D. Berman, S. Deshmukh, B. Narayanan, S.K.R.S. Sankaranarayanan, Z. Yan, A. Balandin, A. Zinovev and D. Rosenmann (2016). “Metal-induced Rapid Transformation of Diamond into Single and Multilayer Graphene on Wafer Scale.” *Nature Communications* **7**: 12099. (Also see 2014-161, 2015-149 and 2016-082.)

### PRESENTATION

Narayanan, B., M.J. Cherukara, A. Kinaci, K. Sasikumar, S.K. Gray, M.K.Y. Chan and S.K.R.S. Sankaranarayanan (2017). “Bond Order Potential for 2D Stanene to Probe Thermal Transport Using Molecular Dynamics Simulations.” 2016 Pacific Rim Meeting on Electrochemical and Solid-State Science—Joint Meeting 230 Electrochemical Society, 2016 Electrochemical Society of Japan, 2016 Fall Korean Electrochemical Society, Honolulu, HI, October 2–7, 2016.

## 2016-092-NO

### REFEREED PUBLICATIONS

Ding, J., P. Lapa, S. Jain, T. Khaire, S. Lendinez, W. Zhang, M.B. Jungfleisch, C.M. Posada, V.G. Yefremenko, J.E. Pearson, A. Hoffmann and V. Novosad (2016). “Spin Vortex Resonance in Non-planar Ferromagnetic Dots.” *Scientific Reports* (6): 25196.

Stebliy, M.E., S. Jain, A.G. Kolesnikov, A.V. Ognev, A.S. Samardak, A.V. Davidenko, L.A. Chetbotkevich, J. Ding, J. Pearson, V.V. Khovaylo and V. Novosad. “Vortex Dynamics and Frequency Splitting in Vertically Coupled Nanomagnets.” *Scientific Reports*. (To be published.)

### PRESENTATIONS

Ding, J., P.N. Lapa, S. Jain, T. Khaire, S. Lendinez, W. Zhang, M.B. Jungfleisch, C.M. Posada, V.G. Yefremenko, J.E. Pearson, A. Hoffmann and V. Novosad (2017). “Controlling of Gyrotropic Frequency in Ferromagnetic Dots Using Nanoscale Vortex Barrier.” 61st Annual Conference on Magnetism and Magnetic Materials, New Orleans, LA, October 31–November 4, 2016.

Ding, J. (2016). “Vortex Gyrotropic Motion in patterned Ferromagnetic Dots.” American Physical Society March Meeting 2016, Baltimore, MD, March 14–18, 2016.

Novosad, V. (2016). “Dynamic Control of Interacting Mesoscale Ferromagnets.” 2016 International Conference on Nanomaterials: Application and Properties, Lviv, Ukraine, September 14–19, 2016.

Novosad, V. (2016). “Dynamic Control of Interacting Spin Vortices.” 2016 Materials Research Society Spring Meeting and Exhibit, Phoenix, AZ, March 28–April 1, 2016.

Novosad, V. (2016). “Geometrical Confinement and Spin Vortex Resonance.” 2016 Materials Research Society Spring Meeting and Exhibit, Phoenix, AZ, March 28–April 1, 2016.

Novosad, V. and E.A. Rozhkova (2016). “Magnetic Particles: Applications and Properties.” 2016 International Conference on Nanomaterials: Application & Properties, Lviv, Ukraine, September 14–19, 2016.

## 2016-098-NO

### REFEREED PUBLICATIONS

Carrillo-Serrano, M.E., W. Bentz, I.C. Cloet and A.W. Thomas (2016). “Baryon Octet Electromagnetic Form Factors in a Confining NJL Model.” *Physics Letters B* **759**: 178–183.

Hutauruk, P.T.P., I.C. Cloet and A.W. Thomas (2016). “Flavour Dependence of the Pion and Kaon Form Factors and Parton Distribution Functions.” *Physical Review C: Nuclear Physics* **94**(3): 035201.

### PRESENTATIONS

Cloet, I.C. (2016). “Dyson-Schwinger Equation Approaches to TMDs.” Parton Transverse Momentum Distributions at Large X: A Window into Parton Dynamics in Nucleon Structure within QCD, Trento, Italy, April 11–15, 2016.

Cloet, I.C. (2016). “The EMC Effect: Exposing the Partonic Structure of Nuclei.” Next Generation Nuclear Physics with JLab12 and EIC, Florida International University, Miami, FL, February 10–13, 2016.

Cloet, I.C. (2016). “Hadron and Nuclear Structure from the DSEs.” A New Era for Hadro-Particle Physics, Newport News, VA, June 23–24, 2016.

Cloet, I.C. (2016). “Nucleon Transverse Structure from the DSEs.” Probing Transverse Nucleon Structure at High Momentum Transfer, Trento, Italy, April 18–22, 2016.

Cloet, I.C. (2016). “PVDIS and QCD in Nuclei.” Physics Beyond the Standard Model and Precision Nucleon Structure Measurements with Parity-violating Electron Scattering, Trento, Italy, August 1–5, 2016.

Cloet, I.C. (2016). “Role of DCSB in the Pion & Nucleon.” 26th International Nuclear Physics Conference, Adelaide, Australia, September 9–11, 2016.

Cloet, I.C. (2016). “Toward Continuum QCD Quark Fragmentation Functions.” From 1D Fragmentation Towards 3D Correlated Fragmentation, Trento, Italy, October 26–30, 2015.

## LDRD NAMED FELLOWS

### 2016-180-NO

#### REFEREED PUBLICATION

Acik, M. and S.B. Darling (2016). “Graphene in Perovskite Solar Cells: Device Design, Characterization and Implementation.” *Journal of Materials Chemistry A: Materials for Energy and Sustainability* **4**(17): 6185–6235.

#### PRESENTATIONS

Acik, M. and S.B. Darling (2017). “*In situ* Growth and Degradation Mechanisms in Hybrid Lead Halide Perovskite/Graphene Solar Cells.” 2016 Pacific Rim Meeting on Electrochemical and Solid-state Science—Joint Meeting 230th ECS Prime Meeting, 2016 Fall Electrochemical Society of Japan, 2016 Fall Korean Electrochemical Society, Honolulu, HI, October 2–7, 2016.

Acik, M. and S.B. Darling (2017). "Stability Factors in Graphene-Based Perovskite Solar Cells Studied By *in situ* Spectroscopy." 2016 Pacific Rim Meeting on Electrochemical and Solid-state Science - Joint Meeting 230th ECS Prime Meeting, 2016 Fall Electrochemical Society of Japan, 2016 Fall Korean Electrochemical Society, Honolulu, HI, October 2–7, 2016.

Acik, M. and S.B. Darling (2016). "*In situ* Characterization of Perovskite Formation in Graphene-based Perovskite Solar Cells." XXV International Materials Research Congress, Cancun, Mexico, August 14–19, 2016.

Acik, M., S.B. Darling and M.M. Segovia Monrroy (2016). "Interfaces in Graphene-organolead Halide Nanohybrid Perovskite Solar Cells Examined by *in situ* Spectroscopy." Materials Research Society Spring Meeting, Tucson, AZ, March 28–April 1, 2016.

Acik, M. and S.B. Darling (2016). "Spectroscopic Evolution of *in situ* Perovskite Film Growth on Reduced Graphene Oxide for Graphene-Perovskite Solar Cells." 2016 APS/CNM Users Meeting, Argonne, IL, May 9–12, 2016.

Acik, M. and S.B. Darling (2016). "Unraveling Degradation Mechanisms in Graphene-based Perovskite Solar Cells by *in situ* Spectroscopy." XXV International Materials Research Congress, Cancun, Mexico, August 14–19, 2016.

#### 2016-181-NO

##### REFEREED PUBLICATIONS

Ghimire, N.J., D. Phelan, H. Zheng and J.F. Mitchell (2016). "Magnetotransport of Single Crystalline YSb." *Journal of Physics: Condensed Matter* **28**(23): 235601.

He, J., C. Zhang, N.J. Ghimire, T. Liang, C. Jia, J. Jiang, S. Tang, S. Chen, Y. He, S.-K. Mo and J.F. Mitchell (2017). "Distinct Electronic Structure for The Extreme Magnetoresistance in YSb." *Physical Review Letters* **117**(26): 267201.

#### 2016-182-NO

##### REFEREED PUBLICATION

Zhou, Z., G.L. Grocke, P. Ignacio-de Leon and X. Chen (2016). "CoFe<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/PMNPT Multiferroic Heterostructure by Atomic Layered Deposition." *Applied Physics Letters* **108**(18): 182907.

#### 2016-184-NO

##### REFEREED PUBLICATION

Plaza, M., X. Huang, J.Y.P. Ko, M. Shen, B.H. Simpson, J. Rodriguez-Lopez, N.L. Ritzert, K. Letchworth-Weaver, D. Gunceler, D.G. Schlom, T.A. Arias, J.D. Brock and H.D. Abruna (2016). "Structure of the Photo-catalytically Active Surface of SrTiO<sub>3</sub>." *Journal of American Chemical Society* **138**(25): 7816–7819.

##### PRESENTATIONS

Letchworth-Weaver, K., R. Sundararaman, C.K. Umbricht and T.A. Arias (2016). "Benchmarking Joint DFT Predictions of the Structure and Energetics of the Electrode/Electrolyte Interface." Materials Research Society Spring Meeting and Exhibit, Phoenix, AZ, March 28–April 1, 2016.

Letchworth-Weaver, K., D. Gunceler, X. Huang, M. Plaza, J. Rodriguez-Lopez, J.D. Brock, H.D. Abruna and T.A. Arias (2016). "Determining Operando Surface Structure: Combining First Principles Theory with Experimental Data." 2nd Functional Oxide Thin Films for Advanced Energy and Information Technology Conference, Cancun, Mexico, March 5–8, 2016.

Letchworth-Weaver, K. (2016). "Joint Density-Functional Theory: Atomically Detailed Structure of the Electrode-Electrolyte Interface." Lawrence Livermore National Laboratory, Livermore, CA, August 11, 2016.

Letchworth-Weaver, K. (2016). "Joint Density-Functional Theory: Atomically Detailed Structure of the Electrode-Electrolyte Interface." University of California Berkeley, Berkeley, CA, August 10, 2016.

Letchworth-Weaver, K. (2016). “Joint Density-Functional Theory: Atomically Detailed Structure of the Electrode-Electrolyte Interface.” Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, CA, January 19, 2016.

Letchworth-Weaver, K., C.K. Umbright, M. Chan, P. Fenter and T.A. Arias (2016). “Joint Density-Functional Theory for the Electrode/Electrolyte Interface: Benchmarking Liquid Structure with Experiment and *ab initio* Molecular Dynamics.” American Physical Society March Meeting, Baltimore, MD, March 14–18, 2016.

Letchworth-Weaver, K., R. Warburton, J. Greeley, C.K. Umbright, T.A. Arias and M.K.Y. Chan (2016). “Joint Density-Functional Theory Investigations of Atomic-Scale Structure and Energetics at the Solid-Liquid Interface.” 28th Annual Workshop on Recent Developments in Electronic Structure Theory, Albuquerque, NM, June 26–29, 2016.

Letchworth-Weaver, K., R. Sundararaman, M.K.Y. Chan, P. Fenter, J.D. Brock, H.D. Abruna and T.A. Arias (2016). “Joint Density-Functional Theory for Multiscale Modeling of the Electrode-Electrolyte Interface.” Gordon Research Conference on Electrochemistry, Ventura, CA, January 10–15, 2016.

Letchworth-Weaver, K. (2016). “The Role of Liquids in Clean Energy Technology.” Argonne Outloud Public Lecture, Argonne, IL, September 15, 2016.

Letchworth-Weaver, K., R. Warburton, J. Greeley, C. Umbright, T.A. Arias and M.K.Y. Chan (2016). “Theoretical Investigations of Atomic-Scale Structure and Energetics at the Solid/Liquid Interface.” Nanoscale Materials Users Meeting, Argonne National Laboratory, May 9–12, 2016.

## 2016-185-NO

### REFEREED PUBLICATIONS

Brawand, N., M.B. Goldey, M. Vörös and G. Galli (2017). “Defect States and Charge Transport in Quantum Dot Solids.” *Chemistry of Materials* **29**(3): 1255–1262.

Brawand, N., M. Vörös, M. Govoni and G. Galli (2017). “Generalization of Dielectric-Dependent Hybrid Functionals to Finite Systems.” *Physical Review X* **6**(4): 041002. (Also see 2014-192.)

Galli, A., T. Demján, M. Vörös, G. Thiering, E. Cannuccia and A. Marini (2016). “Electron-vibration Coupling Induced Renormalization in the Photo-emission Spectrum of Diamondoids.” *Nature Communications* **7**: 11327.

Kroupa, D.M., M. Vörös, N.P. Brawand, B.W. McNichols, E.M. Miller, J. Gu, A.J. Nozik, A. Sellinger, G. Galli and M.C. Beard. “Tuning Colloidal Quantum Dot Band Edge Positions through Solution-Phase Surface Chemistry Modification.” *Nature Communications*. (To be published.)

Vörös, M., N. Brawand and G. Galli (2017). “Hydrogen Treatment as a Detergent of Electronic Trap States in Lead Chalcogenide Nanoparticles.” *Chemistry of Materials*. 10.1021/acs.chemmater.6b04126

Wang, L., N. Brawand, M. Vörös, P.D. Dahlberg, J.P. Otto, N. Williams, D.M. Tiede, G. Galli and G.S. Engel. “Excitations Partition into Two Distinct Populations in Bulk Perovskites Due to Polaron Formation.” *Energy & Environmental Science*. (To be published.)

Wippermann, S., Y. He, M. Vörös and G. Galli (2017). “Novel Silicon Phases and Nanostructures for Solar Energy Conversion.” *Applied Physics Reviews* **3**(4): 040807.

### PRESENTATIONS

Vörös, M., N. Brawand and G. Galli (2016). “Ligand Engineering of the Optoelectronic Properties of PbS Nanoparticles.” National Renewable Energy Laboratory, Golden, CO, December 21, 2015.

Vörös, M. (2016). “Molecular Design of Nanocrystals for Third Generation Photovoltaics Using First Principles Simulations.” University of Wisconsin, Madison, WI, December 9, 2015.

Vörös, M. (2016). “Molecular Engineering of Nanoparticle Solar Cells.” American Physical Society March Meeting, Baltimore, MD, March 14–18, 2016.

#### 2016-186-NO

##### REFEREED PUBLICATIONS

B.T. Diroll, P.G., R.P.H. Chang, R.D. Schaller (2017). “Large Transient Optical Modulation of Epsilon-Near-Zero Colloidal Nanocrystals.” *ACS Nano* **10**(11): 10099–10105.

Chang, A.Y., Y.-J. Cho, K.-C. Chen, C.-W. Chen, A. Kinaci, M.K.Y. Chan, B.T. Diroll, M.J. Wagner, H.-W. Lin and R.D. Schaller (2016). “Slow Organic-to-Inorganic Sub-Lattice Thermalization in Methylammonium Lead Halide Perovskites Observed by Ultrafast Photoluminescence.” *Advanced Energy Materials* **6**(15): 1600402.

Diroll, B.T., R.D. Schaller, D. Talapin, V. Srivastava and E. Janke (2016). “Facile, Economic and Size-Tunable Synthesis of Metal-Arsenide Nanocrystals.” *Chemistry of Materials* **28**(18): 6797–6802.

Diroll, B.T., R.D. Schaller and P.T. Darancet (2016). “Surface-Area-Dependent Electron Transfer Between Isoenergetic 2D Quantum Wells and a Molecular Acceptor.” *Journal of the American Chemical Society* **138**(35): 11109–11112.

Guo, P., R.D. Schaller, L.E. Ocola, B.T. Diroll, J.B. Ketterson and R.P.H. Chang (2016). “Large Optical Nonlinearity of Indium Tin Oxide Nanorods for Sub-Picosecond All-Optical Modulation of the Full-Visible Spectrum.” *Nature Communications* **7**: 12892.

#### 2016-187-NO

##### REFEREED PUBLICATIONS

Liu, Y., P.P. Lopes, W. Cha, R. Harder, J. Maser, E. Maxey, M. J. Highland, N. Markovic, S. Hruszkewycz, G.B. Stephenson, H. You and A. Ulvestad (2017). “Stability Limits and Defect Dynamics in Ag Nanoparticles Probed by Bragg Coherent Diffractive Imaging.” *Nano Letters* **17**(3): 1595–1601.

Ulvestad, A., M.J. Welland, W. Cha, Y. Liu, J.W. Kim, E. Maxey, J.N. Clark, M.J. Highland, H. You, P. Zapol, S. Hruszkewycz and G.B. Stephenson (2017). “Three-dimensional Imaging of Dislocation Dynamics During the Hydriding Phase Transformation.” *Nature Materials* doi:10.1038/nmat4842.

Ulvestad, A., M.J. Welland, S. Collins, R. Harder, E. Maxey, J. Wingert, A. Singer, S. Hy, P. Mulvaney, P. Zapol and O.G. Shpyrko (2016). “Avalanching Strain Dynamics During the Hydriding Phase Transformation in Individual Palladium Nanoparticles.” *Nature Communications* **6**: 10092.

Ulvestad, A., A. Tripathi, S.O. Hruszkewycz, W. Cha, S.M. Wild, G.B. Stephenson and P.H. Fuoss (2016). “Coherent Diffractive Imaging of Time-Evolving Samples with Improved Temporal Resolution.” *Physical Review B: Condensed Matter* **93**(18): 184105. (Also see 2015-167.)

Ulvestad, A., K. Sasikumar, J.W. Kim, R. Harder, E. Maxey, J.N. Clark, B. Narayanan, S. Deshmukh, N. Ferrier, P. Mulvaney, S.K.R.S. Sankaranarayanan and O.G. Shpyrko (2016). “*In situ* 3D Imaging of Catalysis Induced Strain in Gold Nanoparticles.” *Journal of Physical Chemistry Letters* **7**(15): 3008–3013. (Also see 2015-149.)

#### 2016-188-NO

##### REFEREED PUBLICATIONS

Berthou, B., D. Binosi, N. Chouika, M. Guidal, C. Mezrag, H. Moutarde, F. Sabatie, P. Sznajder and J. Wagner. “PARTONS: PARTonic Tomography of Nucleon Software.” *European Physical Journal C: Particles and Fields*. (To be published.)

Mezrag, C., H. Moutarde and J. Rodriguez-Quintero (2016). “From Bethe-Salpeter Wave Functions to Generalized Parton Distributions.” *Few-Body Systems* **57**(9): 729–772.

## LDRD PRIME APPLIED ENERGY AND SUSTAINABLE TRANSPORTATION

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### 2014-120-R2

#### REFEREED PUBLICATIONS

Bessac, J., E. Constantinescu and M. Anitescu. "Stochastic Simulation of Predictive Space-Time Scenarios of Wind Speed Using Observations and Physical Models." *Annals of Applied Statistics*. (To be published.)

Botterud, A. (2017). "Enhanced Representations of Lithium-ion Batteries in Power Systems Models and their Effect on the Valuation of Energy Arbitrage Applications." *Journal of Power Sources* **342**: 279–291.

de Sisternes, F.J., J.D. Jenkins and A. Botterud (2016). "The Value of Energy Storage in Deep Decarbonization of the Electricity Sector." *Applied Energy* **175**: 368–379.

Krishnamurthy, D., C. Uckun, Z. Zhou, P. Thimmapuram and A. Botterud. "Energy Storage Arbitrage Under Day-Ahead and Real-Time Price Uncertainty." *IEEE Transactions on Power Systems*. (To be published.)

Li, N., C. Uckun, E. Constantinescu, J. Birge, K. Hedman and A. Botterud (2016). "Flexible Operation of Batteries in Power System Scheduling with Renewable Energy." *IEEE Transactions on Sustainable Energy* **7**(2): 685–696.

Wankmueller, F., P. Thimmapuram, K.G. Gallagher and A. Botterud (2017). "Impact of Battery Degradation on Energy Arbitrage Revenue of Grid-level Energy Storage." *Journal of Energy Storage* **10**: 56–66.

#### PRESENTATIONS

Botterud, A. (2016). "Flexible Operation of Batteries in Power System Scheduling with Renewable Energy." The Institute for Operations Research and the Management Sciences (INFORMS) Annual Meeting, Philadelphia, PA, November 1–4, 2015.

Botterud, A. (2016). "The Role of Energy Storage in Future Electricity Markets." Panel Session IEEE PES General Meeting, Boston, MA, July 17–21 2016.

Botterud, A. (2016). "The Role of Energy Storage in Future Electricity Markets." ETH Zürich, Zurich, Switzerland, April 12, 2016.

Botterud, A. (2015). "Energy Storage for Grid Integration of Renewable Energy." Next Generation Batteries 2015, San Diego, CA, April 22, 2015.

Botterud, A., C. Uckun, P. Thimmapuram, K. Gallagher, E. Constantinescu and J.R. Birge (2015). "Grid Level Energy Storage for Integration of Renewable Energy." The Institute for Operations Research and the Management Sciences (INFORMS) Annual Meeting, San Francisco, CA, November 9–12, 2014.

Botterud, A. (2015). "Integration of Renewable Energy, Possible Solutions, the Role of Storage." MITeI Symposium: Storage, Renewables and the Evolution of the Grid, Cambridge, MA, May 1, 2015.

Botterud, A. (2014). "Energy Storage for the Power Grid: A U.S. Perspective." Workshop on Energy Storage: From Technologies to Grids and Electricity Markets, Porto, Portugal, July 4, 2014.

Li, N., K. Hedman, A. Botterud, C. Uckun and J.R. Birge (2015). "Economic Assessment of Energy Storage in Systems with High Renewable Penetration." The Institute for Operations Research and the Management Sciences (INFORMS) Annual Meeting, San Francisco, CA, November 9–12, 2014.

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### 2014-169-R2

#### REFEREED PUBLICATION

Zhang, Y.J., M. Liu, B. Peng, Z.Y. Zhou, X. Chen, S.M. Yang, Z.D. Jiang, J. Zhang, W. Ren and Z.G. Ye (2016). "Controlled Phase and Tunable Magnetism in Ordered Iron Oxide Nanotube Arrays Prepared by Atomic Layer Deposition." *Scientific Reports* **6**: 18401.

**PRESENTATIONS**

Chen, X. (2016). “Functional Highly Anisotropic Nanostructures.” University of Denver, Denver, CO, October 16, 2015.

Chen, X. (2016). “High Anisotropic Magnetic Nanostructures for Microwave Applications.” University of Colorado, Boulder, CO, October 15, 2015.

Chen, X. (2015). “Fast Design Cycles and Concept Validation in a Multi-Discipline Laboratory.” COMSOL Midwest Meeting, Columbus, OH, July 22, 2015.

Chen, X. (2015). “Functional Highly Anisotropic Nanostructures.” Naval Research Laboratory, Washington, DC, April 21, 2015.

Chen, X. (2015). “Functional Highly Anisotropic Nanostructures.” Johns Hopkins University, Baltimore, MD, April 20, 2015.

Chen, X. (2015). “Functional Highly Anisotropic Nanostructures.” University of Arizona, Tucson, AZ, May 26, 2015.

Chen, X. (2015). “Functional Nanostructures by Electrospinning and Atomic Layer Deposition.” Northeastern University, Boston, MA, October 10, 2014.

**2015-151-R1****REFEREED PUBLICATIONS**

Babar, S., A.U. Mane, A. Yanguas-Gil, R. Haasch and J.W. Elam (2016). “Bandgap Tailoring of W:Al<sub>2</sub>O<sub>3</sub> Nanocomposite Thin Films Prepared by Atomic Layer Deposition.” *Chemistry of Materials* **120**(27): 14681–14689.

Biswas, M., J.A. Libera, S.B. Darling and J.W. Elam (2015). “Kinetics for the Sequential Infiltration Synthesis of Alumina in Poly(methyl methacrylate): An Infrared Spectroscopic Study.” *Journal of Physical Chemistry C* **119**(26): 14585–14592.

**PRESENTATIONS**

Elam, J.W. (2017). “Refractory Solar Selective Coatings Synthesized by Atomic Layer Deposition.” AVS 63rd International Symposium, Nashville, TN, November 6–10, 2016.

Elam, J.W. (2017). “Synthesis, Characterization, and Application of Tunable Nanocomposite Coatings Prepared by Atomic Layer Deposition.” 3rd International Conference on ALD Applications and 2016 China ALD Conference, Suzhou, China, October 16–19, 2016.

**2015-159-R1****REFEREED PUBLICATIONS**

Campos, E. and J. Wang (2016). “Numerical Simulation and Analysis of the April 2013 Chicago Floods.” *Journal of Hydrology* **531**(Part 2): 454–474.

Qiu, F., J. Wang, C. Chen and T. Jianzhong (2016). “Optimal Black Start Resource Allocation.” *IEEE Transactions on Power Systems* **31**(3): 2493–2494.

**2015-176-R1****NON-REFEREED PUBLICATION**

Karbowski, D., V. Sokolov and A. Rousseau (2016). “Vehicle Energy Management Optimization through Digital Maps and Connectivity.” 22nd ITS World Congress, Bordeaux, France, October 5–9, 2015.

**PRESENTATIONS**

Auld, J., D. Karbowski, V. Sokolov and N. Kim (2016). “A Disaggregate Model System for Assessing the Energy Impact of Transportation at the Regional Level.” 95th Annual Meeting of the Transportation Research Board, Washington, DC, January 10–14, 2016.

Luo, Q., J. Auld and V. Sokolov (2016). "Addressing Some Issues of Map-Matching for Large-Scale, High-Frequency GPS Data Sets." 95th Annual Meeting of the Transportation Research Board, Washington, DC, January 10–14, 2016.

Rousseau, A., P. Michel, D. Karbowski, J. Auld and V. Sokolov (2017). "Energy Impact of Connected and Automated Vehicles." ITS World Congress, Melbourne, Australia, October 10–14, 2016.

Rousseau, A., P. Michel, D. Karbowski, J. Auld and V. Sokolov (2016). "Impact of Connection and Automation on Electrified Vehicle Energy Consumption." SAE 2016 Hybrid & Electric Vehicle Technologies Symposium, Anaheim, CA, February 9–11, 2016.

Sokolov, V., J. Auld, N. Kim, D. Karbowski and A. Rousseau (2016). "Modeling Framework for Transportation Simulation and Energy Assessment." 22nd ITS World Congress, Bordeaux, France, October 5–9, 2015.

## 2016-126-NO

### REFEREED PUBLICATIONS

Larson, J. "Platoon Formation Maximization through Centralized Routing and Departure Time Coordination." *Transportation Letters: The International Journal of Transportation Research*. (To be published.)

Larson, J., T. Munson and V. Sokolov (2017). "Coordinated Platoon Routing in a Metropolitan Network." *Proceedings of the 2016 SIAM Workshop on Combinatorial Scientific Computing*, Albuquerque, NM, October 10–12, 2016: 10.

### PRESENTATION

Larson, J., T. Munson and V. Sokolov (2017). "Coordinated Platoon Routing in a Metropolitan Network." 2016 SIAM Workshop on Combinatorial Scientific Computing, Albuquerque, NM, October 10–12, 2016.

## 2016-152-NO

### NON-REFEREED PUBLICATION

Kuiper, J.A., Y. Demissie, R.W. Gentry, E. Yan, J. Wang and A.M. Jared (2016). "Quantifying and Informing Extreme Climate and Hydrologic Events." 2016 Society for Conservation GIS Annual Conference, Monterey, CA, June 22–25, 2016.

### PRESENTATIONS

Betrie, G., E. Yan and C. Clark (2017). "Simulating the Water Use of Thermoelectric Power Plants in the United States: Model Development and Verification." 2016 American Geophysical Union Fall Meeting, San Francisco, CA, December 12–16, 2016.

Kuiper, J., Y. Demissie, R.W. Gentry, A.M. Jared, J. Wang and E. Yan (2016). "Quantifying and Informing Extreme Climate and Hydrologic Events." 2016 Society for Conservation GIS Annual Conference, Monterey, CA, June 22–25, 2016.

Mahat, V. and E. Yan (2017). "Stream Water Temperature Model for Upper Mississippi River Basin." 2016 American Geophysical Union Fall Meeting, San Francisco, CA, December 12–16, 2016. (132997)

Wang, J., Z. Zhou, T. Veselka, F. Qui, A. Schreiber and E. Yan (2017). "Economic Assessment of Correlated Energy-water Impacts Using Computable General Equilibrium Modeling." American Geophysical Union Fall Meeting, San Francisco, CA, December 12–16, 2016.

Yan, E., T. Veselka, Z. Zhou, V. Koritarov, M. Mahalik, F. Qui, V. Mahat, G. Betrie and C. Clark (2017). "Integrated Modeling for Assessment of Energy-water System Resilience Under Changing Climate." 2016 American Geophysical Union Fall Meeting, San Francisco, CA, December 12–16, 2016.

Zhou, Z., Y. Xia, T. Veselka, G. Betrie, F. Qui and E. Yan (2017). "Modeling and Economic Analysis of Power Grid Operations in a Water Constrained System." American Geophysical Union Fall Meeting, San Francisco, CA, December 12–16, 2016.

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**2016-175-NO****REFEREED PUBLICATION**

Fischer, P., M. Schmitt and A. Tomboulides. “Recent Developments in Spectral Element Simulations of Moving-Domain Problems.” *Fields Institute Communications: Recent Progress and Modern Challenges in Applied Mathematics, Modeling and Computational Science*. (To be published.)

**NON-REFEREED PUBLICATIONS**

Giannakopoulos, G.K., C.E. Frouzakis, P.F. Fischer, A.G. Tomboulides and K. Boulouchos (2016). “Direct Numerical Simulation of the Flow in the Intake Pipe of an Internal Combustion Engine.” The 11th International ERCOFTAC Symposium on Engineering Turbulence Modelling and Measurements (ETMM11), Palermo, Italy, September 21–23, 2016.

Kodavasal, J., Y. Pei, K. Harms, S.A. Ciatti, A. Wagner, P.K. Senecal, M. Garcia and S. Som (2016). “Global Sensitivity Analysis of a Gasoline Compression Ignition Engine Simulation with Multiple Targets on an IBM Blue Gene/Q Supercomputer.” 2016 SAE World Congress, Detroit, MI, April 12–14, 2016.

Kodavasal, J., N. Van Dam, Y. Pei, K. Harms, K. Maheshwari, A. Wagner, M. Garcia, S. Ciatti, P.K. Senecal and S. Som (2016). “Sensitivity Analysis on Key CFD Model Inputs for GCI on an IBM BG/Q Supercomputer.” 2016 THIESEL Conference on Thermo-and Fluid Dynamic Processes in Direct Injection Engines, Valencia, Spain, September 13–16, 2016.

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**BIOLOGICAL AND ENVIRONMENTAL SCIENCE CAPABILITY DEVELOPMENT**

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**2014-141-R2****PRESENTATIONS**

Antonopoulos, D.A. (2016). “Rarity and Stability within Microbial Communities: A Spatial Tale.” Montana State University, Bozeman, Montana, April 12, 2016.

Flynn, T.M., J.C. Koval, K.M. Kemner and D.A. Antonopoulos (2016). “Niche and Neutral Community Dynamics in Parallelized Aerobic, Single Carbon-source Enrichment Cultures.” 7th Annual Argonne National Laboratory Soil Metagenomics Meeting, Lisle, IL, October 21–23, 2015.

Flynn, T.M., J.C. Koval, S.M. Greenwald, S.M. Owens, K.M. Kemner and D.A. Antonopoulos (2015). “Community Level Physiological Profiling of Diverse Environments Reveals Functional and Taxonomic Diversity within Aerobic, Single Carbon-source Enrichments.” 115th American Society of Microbiology General Meeting (ASM 2015), New Orleans, LA, May 30–June 2, 2015.

Flynn, T.M., J.C. Koval, S.M. Moormann, S.M. Owens, S.L. O’Brien, S. Alvarez-Clare, E.J. O’Loughlin, K.M. Kemner and D.A. Antonopoulos (2015). “Community Level Physiological Profiling of Diverse Soil Environments Reveals Functional and Taxonomic Diversity Within Aerobic, Single-carbon Source Enrichments.” 6th Annual Argonne National Laboratory Soil Metagenomics Meeting, St. Charles, IL, October 1–3, 2014.

Flynn, T.M., J.C. Koval, S.M. Moormann, S.M. Owens, S.L. O’Brien, S. Alvarez-Clare, E.J. O’Loughlin, K.M. Kemner and D.A. Antonopoulos (2014). “Community Level Physiological Profiling of Diverse Environments Reveals Functional and Taxonomic Diversity Within Aerobic, Single Carbon-Source Enrichments.” 2014 Ecological Society of America Annual Meeting, Sacramento, CA, August 10–15, 2014.

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**2014-145-R2****REFEREED PUBLICATIONS**

Dishaw, L.J., J. Flores-Torres, S. Lax, K. Gemayel, B. Leigh, D. Melillo, M.G. Mueller, L. Natale, I. Zucchetti, R. De Santis, M.R. Pinto, G.W. Litman and J.A. Gilbert (2014). “The Gut of Geographically Disparate *Ciona intestinalis* Harbors a Core Microbiota.” *PLoS ONE* **9**(4): e93386.

Gibbons, S.M., N.M. Scott, E. Jones, A. Bearquiver, F. Blackwolf, W. Roundstone, J. Hooker, R. Madsen, M. Coleman and J.A. Gilbert (2014). "Human and Environmental Impacts on River Sediment Microbial Communities." *PLoS ONE* **9**(5): e97435.

Gilbert, J.A. (2015). "Science is Innate!" *Genome Biology* **15**(9): 477.

Gilbert, J.A., J. Jansson and R. Knight (2014). "The Earth Microbiome Project: Successes and Aspirations." *BMC Biology* **12**(69).

Gilbert, J.A., O.U. Mason, N.M. Scott, A. Gonzalez, A. Robbins-Pianka, J. Baelum, J. Kimbrel, N. Bouskill, E. Prestat and S. Borglin (2014). "Metagenomics Reveals Sediment Microbial Community Response to Deepwater Horizon Oil Spill." *ISME Journal* **8**: 1464–1475.

Gilbert, J.A., D. Van Der Lelie and I. Zarraonaindia Martinez (2014). "Microbial *terroir* for Wine Grapes." *Proceedings of the National Academy of Sciences of the United States of America* **111**(1): 5–6.

Groer, M.W., A.A. Luciano, L.J. Dishaw, T.L. Ashmeade, E. Miller and J.A. Gilbert (2015). "Development of the Preterm Infant Gut Microbiome: A Research Priority." *Microbiome* **2**(38).

Hamada, Y., J.A. Gilbert, P.E. Larsen and M.J. Norgaard (2014). "Toward Linking Aboveground Vegetation Properties and Soil Microbial Communities Using Remote Sensing." *Photogrammetric Engineering and Remote Sensing* **80**(4): 311–321.

Handley, K.M., E.J. O'Loughlin, W.L. Trimble, K.A. Skinner, J.A. Gilbert, N. Desai, E.M. Glass, T. Paczian, A. Wilke, D.A. Antonopoulos, K.M. Kemner and F. Meyer (2015). "The Complete Genome Sequence for Putative H<sub>2</sub>- and S- Oxidizer *Candidatus* Sulfuricicum sp., Assembled *de novo* from an Aquifer-derived Metagenome." *Environmental Microbiology* **16**(11): 2443–3462.

Handley, K.M., K.C. Wrighton, C.S. Miller, M.J. Wilkins, J.A. Gilbert, R. Kantor, B.C. Thomas, K.H. Williams, P.E. Long and J.F. Banfield (2014). "Disturbed Subsurface Microbial Communities Follow Equivalent Trajectories Despite Different Structural Starting Points." *Environmental Microbiology* **17**(3): 622–636.

Kyrpides, N.C., P. Hugenholtz, J. Eisen, T. Woyke, M. Goeker, C.T. Parker, R. Amann, B.J. Beck, P.S.G. Chain, J. Chun, R.R. Colwell, A. Danchin, P. Dawyndt, T. Dedeurwaerdere, E.F. DeLong, J.C. Detter, P. De Vos, T.J. Donohue, X.-Z. Dong, D.S. Ehrlich, C. Fraser, R. Gibbs, J.A. Gilbert, P. Gilna, F.O. Glöckner, J.K. Jansson, J.D. Keasling, R. Knight, D. Labeda, A. Lapidus, J.-S. Lee, W.-J. Li, J. MA, V. Markowitz, E.R.B. Moore, M. Morrison, F. Meyer, K.E. Nelson, M. Ohkuma, C.A. Ouzounis, N. Pace, J. Parkhill, N. Qin, R. Rossello-Mora, J. Sikorski, D. Smith, M. Sogin, R. Stevens, U. Stingl, K.-i. Suzuki, D. Taylor, H.M. Tiedje, B. Tindall, M. Wagner, G. Weinstock, J. Weissenbach, O. White, J. Wang, L. Zhang, Y.-G. Zhou, D. Feld, W.B. Whitman, G.M. Garrity and H.-P. Klenk (2014). "Genomic Encyclopedia of Bacteria and Archaea: Sequencing a Myriad of Type Strains." *PLoS ONE* **12**(8): e1001920.

LaBelle, E.V., C.W. Marshall, J.A. Gilbert and H.D. May (2015). "Influence of Acidic pH on Hydrogen and Acetate Production by an Electrosynthetic Microbiome." *PLoS ONE* **9**(10): e109935.

Lax, S., D.P. Smith, J. Hampton-Marcell, S.M. Owens, K.M. Handley, N.M. Scott, S.M. Gibbons, P. Larsen, B.D. Shogan, S. Weiss, J.L. Metcalf, L.K. Ursell, Y. Vazquez-Baeza, W. Van Treuren, N.A. Hasan, M.K. Gibson, R. Colwell, G. Gantas, R. Knight and J.A. Gilbert (2014). "Longitudinal Analysis of Microbial Interaction Between Humans and the Indoor Environment." *Science* **345**(6200): 1048–1052.

Nielsen, S.F., T. Minchin, S. Kimber, L. van Zwieten, J.A. Gilbert, P. Munroe, S. Joseph and T. Thomas (2014). "Comparative Analysis of the Microbial Communities in Agricultural Soil Amended with Enhanced Biochars or Traditional Fertilizers." *Agriculture, Ecosystems & Environment* **191**: 73–82.

Parfey, L.W., W. Walters, C.L. Lauber, J.C. Clemente, D. Berg-Lyons, C. Teiling, C. Kodira, M. Mohiuddin, J. Brunelle, M. Driscoll, N. Fierer, J.A. Gilbert and R. Knight (2014). "Communities of Microbial Eukaryotes in the Mammalian Gut Within the Context of Environmental Eukaryotic Diversity." *Frontiers in Microbiology* **5**(298).

Peer, X., J.A. Gilbert and G.C. An (2014). “Examining the Microbial Ecological Dynamics of Clostridium Difficile Infections and the Efficacy of Fecal Microbiome Transplant (FMT) Using an Agent-based Model.” *Journal of Surgical Research* **186**(2): 689.

Pfister, C.A., J.A. Gilbert and S.M. Gibbons (2015). “The Role of Macrobiota in Structuring Microbial Communities Along Rocky Shores.” *PeerJ* **2**(631).

Piombino, P., A. Genovese, S. Esposito, L. Moio, P.P. Cutolo, A. Chambery, V. Severino, E. Moneta, D.P. Smith, S. Owens, J.A. Gilbert and D. Ercolini (2014). “Saliva from Obese Individuals Suppresses the Release of Aroma Compounds from Wine.” *PLoS ONE* **9**(1): e85611.

Rideout, J.R., Y. He, J.A. Navas-Molina, W.A. Walters, L.K. Ursell, S.M. Gibbons, J. Chase, D. McDonald, A. Gonzalez, A. Robbins-Pianka, J.C. Clemente, J.A. Gilbert, S.M. Huse, H.W. Zhou, R. Knight and J.G. Caporaso (2014). “Subsampled Open-reference Clustering Creates Consistent, Comprehensive OTU Definitions and Scales to Billions of Sequences.” *PeerJ* **2**(e545).

Rubin, B.R., J.G. Sanders, J. Hampton-Marcell, S.M. Owens, J.A. Gilbert and C.S. Moreau (2014). “DNA Extraction Protocols Cause Differences in 16S rRNA Amplicon Sequencing Efficiency but not in Community Profile Composition or Structure.” *MicrobiologyOpen* **3**(6): 910–921.

Shade, A., S.E. Jones, G. Caporasoc, J. Handelsman, R. Knight, N. Fierer and J.A. Gilbert (2014). “Conditionally Rare Taxa Disproportionately Contribute to Temporal Changes in Microbial Diversity.” *mBio* **5**(4): e01371–01314.

Shogan, B.D., D.P. Smith, S. Christley, J.A. Gilbert, O. Zaborina and J.C. Alverdy (2014). “Intestinal Anastomotic Injury Alters Spatially Defined Microbiome Composition and Function.” *Microbiome* **2**(35).

Winston, M., J. Hampton-Marcell, I. Zorraonaindia Martinez, S. Owens, C.S. Moreau, J.A. Gilbert, J. Hartsel and S.M. Gibbons (2014). “Understanding Cultivar-Specificity and Soil Determinants of the *Cannabis* Microbiome.” *PLoS ONE* **9**(6): e99641.

Xiong, J., H. Sun, F. Peng, H. Zhang, X. Xue, S.M. Gibbons, J.A. Gilbert and H. Chu (2014). “Characterizing Changes in Soil Bacterial Community Structure in Response to Short-term Warming.” *FEMS Microbiology Reviews* **89**(2): 281–292.

Zaborin, A., D. Smith, K. Garfield, J. Quensen, S. Baddr, M. Kade, M. Tirrell, J. Tiedje, J.A. Gilbert, O. Zaborina and J.C. Alverdy (2014). “Membership and Behavior of Ultra-Low-Diversity Pathogen Communities Present in the Gut of Humans During Prolonged Critical Illness.” *mBio* **5**(5): e01361–01314.

## PRESENTATIONS

Marshall, C.W. and J.A. Gilbert (2016). “Microbial Ecology of Floodplains and Electrosynthesis Systems.” US-China Biodiversity Workshop, Raleigh, NC, October 16–18, 2015.

Marshall, C., S.L. O’Brien, K.M. Kemner, E.J. O’Loughlin, P. Weisenhorn, N.R. Gottel, S. Alvarez Clare, A. Best, T.M. Flynn and J.A. Gilbert (2016). “Microbial Ecology of Restored Floodplains.” 7th Annual Argonne Soil Metagenomics Meeting, Argonne, IL, October 21–23, 2015.

Marshall, C., S.L. O’Brien, K.M. Kemner, E.J. O’Loughlin, N.R. Gottel, S. Alvarez Clare, A. Best, T.M. Flynn and J.A. Gilbert (2015). “Microbial Ecology of Floodplains.” 115th American Society for Microbiology General Meeting, New Orleans, LA, May 30–June 2, 2015.

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## 2014-157-R2

### PRESENTATION

Babnigg, G., B. Nocek, K. Michalska, R. Jedrzejczak, Y. Kim, J.L. Johnson, C. Akins, R. Haake, G. Joachimiak, H. Li, C.H. Hatzos-Skintges, M. Endres and A. Joachimiak (2016). “Microfluidics-based Crystallography.” Microfluidics 2016, Heidelberg, Germany, July 24–26, 2016.

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**2014-183-R2****REFEREED PUBLICATIONS**

Albrecht, B.A., M. Fang and V.P. Ghate (2016). “Exploring Stratocumulus Cloud-Top Entrainment Processes and Parameterizations by Using Doppler Cloud Radar Observations.” *Journal of the Atmospheric Sciences* **73**(2): 729–742.

Fang, M., B.A. Albrecht, V.P. Ghate and P. Kollias (2014). “Turbulence in Continental Stratocumulus, Part I: External Forcings and Turbulence Structures.” *Boundary-Layer Meteorology* **150**(3): 341–360.

Fang, M., B.A. Albrecht, V.P. Ghate and P. Kollias (2014). “Turbulence in Continental Stratocumulus, Part II: Eddy Dissipation Rates and Large-Eddy Coherent Structures.” *Boundary-Layer Meteorology* **150**(3): 361–380.

Ghate, V.P., M.A. Miller and P. Zhu (2016). “Differences Between Nonprecipitating Tropical and Trade Wind Marine Shallow Cumuli.” *American Meteorological Society Journal Monthly Weather Review* **144**(2): 681–701. (Also see 2014-193.)

Ghate, V.P., M.A. Miller, B.A. Albrecht and C.W. Fairall (2015). “Thermodynamic and Radiative Structure of Stratocumulus-topped Boundary Layers.” *Journal of the Atmospheric Sciences* **72**(1): 430–451.

**PRESENTATIONS**

Ghate, V.P., M.A. Miller and P. Zhu (2015). “Similarities and Differences between Tropical and Trade Wind Cumulus Topped Marine Boundary Layers.” Jet Propulsion Laboratory Earth Science Seminar, California Institute of Technology, Pasadena, CA, March 27, 2015. (Also see 2014-193.)

Schwartz, M.C. and V.P. Ghate (2015). “Stratocumulus-to-Cumulus Cloud Transition: A Case Study from the MAGIC Field Campaign.” Atmospheric System Research (ASR) Science Team Meeting, Vienna, VA, March 16–20, 2015.

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**2015-170-R1****PRESENTATIONS**

Negri, M.C. and H. Ssegane (2015). “Biomimetic Approaches for Water Smart Landscape.” University of Chicago Institute for Molecular Engineering (IME) Collaborative Water Research Conference, Chicago, IL, August 17, 2015.

Negri, M.C. and H. Ssegane (2015). “Efficient Green Roofs.” The Array of Things Workshop, Chicago, IL, September 3, 2015.

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**2015-179-R1****PRESENTATIONS**

Flynn, T.M., M.F. Sladek, Z. Jensvold, D.A. Antonopoulos, J.C. Koval, K. Kemner and E.J. O’Loughlin (2017). “Soluble Electron Shuttles Control Microbial Community Development Under Iron-reducing Conditions in Wetland Sediment.” American Geophysical Union Fall Meeting, San Francisco, CA, December 12–16, 2016.

Johnson, L.S., Z. Jensvold, E.J. O’Loughlin and T.M. Flynn (2017). “Investigating the Effects of Fe(III) Inputs into Methanogenic Environments.” 2016 Midwest Geobiology Symposium, Cincinnati, OH, October 11–15, 2016.

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**HARD X-RAY SCIENCES**

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**2014-127-R2****REFEREED PUBLICATION**

Kim, J., X. Shi, D. Casa, J. Qian, X. Huang and T. Gog (2016). “Collimating Montel Mirror as Part of a Multi-Crystal Analyzer System for Resonant Inelastic X-ray Scattering.” *Journal of Synchrotron Radiation* **23**: 880–886.

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**2014-134-R2****REFEREED PUBLICATIONS**

Cha, W., A. Ulvestad, M. Allain, V. Chamard, R. Harder, S. Leake, J. Maser, P.H. Fuoss and S.O. Hruszkewycz (2017). “Three Dimensional Variable-wavelength X-ray Bragg Coherent Diffraction Imaging.” *Physical Review Letters* **117**(22): 225501.

Cha, W., W. Liu, R. Harder, R. Xu, P.H. Fuoss and S.O. Hruszkewycz (2016). “Utilizing Broadband X-rays in a Bragg Coherent X-ray Diffraction Imaging Experiment.” *Journal of Synchrotron Radiation* **23**(Pt 5): 1241–1244.

**PRESENTATIONS**

Cha, W., S. Hruszkewycz, M. Highland, R. Sichel-Tissot, P. Fuoss, R. Harder, J. Maser and W. Liu (2015). “Three-dimensional Bragg Coherent Diffractive Imaging Using Polychromatic X-rays.” 144th TMS Annual Meeting and Exhibition, Orlando, FL, March 15–19, 2015.

Cha, W., S. Hruszkewycz, R. Sichel-Tissot, M.J. Highland, R. Harder, W. Liu, J. Maser and P. Fuoss (2014). “Three-dimensional Bragg Coherent Diffraction Imaging Using Polychromatic X-rays.” International Workshop of Phase Retrieval and Coherent Scattering, Evanston, IL, September 2–5, 2014.

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**2014-137-R2****REFEREED PUBLICATIONS**

Kesgin, I., M. Kasa, Y. Ivanyushenkov and U. Welp. “High-Temperature Superconducting Undulator Magnets.” *Superconductor Science & Technology*. **30**(4): 04LT01.

Kesgin, I., Q. Hasse, Y. Ivanyushenkov and U. Welp (2017). “Performance of 2G–HTS REBCO Undulator Coils Impregnated Epoxies Mixed with Different Fillers.” *IEEE Transactions on Applied Superconductivity* **27**(4): 1-4.

Kesgin, I., C.L. Doose, M.T. Kasa, Y. Ivanyushenkov and U. Welp (2016). “Design of a REBCO Thin Film Superconducting Undulator.” *Proceedings of the International Cryogenic Materials Conference Series: Advances in Cryogenic Engineering Materials*, Tucson, AZ, June 28–July 2, 2015, **101**: 912953.

Kesgin, I., M. Kasa, C. Doose, Y. Ivanyushenkov, Y. Zhang, P. Brownsey, D. Hazelton and U. Welp (2016). “Feasibility and Electromagnetic Analysis of a REBCO Superconducting Undulator.” *Superconductor Science & Technology* **29**(5): 055001.

**NON-REFEREED PUBLICATIONS**

Kesgin, I., C. Doose, M. Kasa, Y. Ivanyushenkov and U. Welp (2016). “High-temperature Superconducting REBCO Conductors for Undulators in X-ray Sources.” 2016 Materials Research Society Spring Meeting and Exhibit, Phoenix, AZ, March 28–April 1, 2016.

Kesgin, I., Q. Hasse, Y. Ivanyushenkov and U. Welp (2016). “Performance of 2G-HTS Undulator Coils Secured with Epoxy and Various Nanofillers.” 2016 Applied Superconductivity Conference, Denver, CO, September 4–9, 2016.

**PRESENTATIONS**

Kesgin, I., C.L. Doose, M.T. Kasa, Y. Ivanyushenkov and U. Welp (2015). “Design of a REBCO HTS Superconducting Undulator.” 2015 Cryogenic Engineering Conference and International Cryogenic Materials Conference, June 28–July 2, 2015.

Kesgin, I., Y. Ivanyushenkov, U. Welp, C.L. Doose and M. Kasa (2015). “Design of a Short Period 2G-HTS Base Undulator.” 6th International Particle Accelerator Conference (IPAC 2015), Richmond, VA, May 3–8, 2015.

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**2014-175-R2****REFEREED PUBLICATIONS**

Becker, M., D.J. Kissick and C.M. Ogata. “Locating and Visualizing Crystals for X-ray Diffraction Experiments.” *Methods in Molecular Biology*. (To be published.)

Broecker, J., V. Klingel, W. Ou, A.R. Balo, D.J. Kissick, C.M. Ogata, A. Kuo and O.P. Ernst (2017). “A Versatile System for High-throughput *in situ* X-ray Screening and Data Collection of Soluble and Membrane-protein Crystals.” *Crystal Growth & Design* **16**(11): 6318–6326.

Murray, T.D., A. Lyubimov, C.M. Ogata, H. Vo, M. Uervirojinangkoorn, A. Brunger and J. Berger (2015). “A High-transparency, Micro-patternable Chip for X-ray Diffraction Analysis of Microcrystals Under Native Growth Conditions.” *Acta Crystallogr D Biol Crystallogr* **71**(Pt 10): 1987–1997.

Scarborough, N.M., G.M.D.P. Godaliyadda, D.H. Ye, D.J. Kissick, S. Zhang, J.A. Newman, M.J. Sheedlo, A.U. Chowdhury, R.F. Fischetti and C. Das (2017-inpress). “Dynamic X-ray Diffraction Sampling for Protein Crystal Positioning.” *Journal of Synchrotron Radiation* **24**: 188–195.

## PRESENTATION

Kissick, D.J. (2016). “Development of Tools for *in situ* Data Collection at GM/CA.” 2016 APS/CNM Users Meeting APS Workshop 3: Advances in *in situ* and Serial Biological Crystallography, Argonne National Laboratory, May 8–11, 2016.

## 2015-147-R1

### PRESENTATIONS

Horan, D. (2016). “Solid State RF Amplifier Development at the Advanced Photon Source.” 9th International Workshop on CW and High Average Power, ESRF, Grenoble, France, June 21–24, 2016.

Nassiri, A. (2016). “Growth of MgB<sub>2</sub> Films on Large Area Cu Discs and RF Characterization.” 7th International Workshop on Thin Films and New Ideas for Pushing the Limits of RF Superconductivity, Newport News, VA, July 27–29, 2016.

Nassiri, A. (2016). “Some Thoughts on the Advanced Photon Source Upgrade (APS-U) 352 MHz RF System.” 9th International Workshop on CW and High Average Power, ESRF, Grenoble, France, June 21–24, 2016.

Nassiri, A. (2015). “Large Area Superconducting Magnesium Diboride on Copper Substrates for SRF Applications Using HPCVD.” 17th International Conference on RF Superconductivity, British Columbia, Canada, September 13–18, 2015.

## 2015-150-R1

### REFEREED PUBLICATIONS

Dufresne, E.M., S. Narayanan, A.R. Sandy, D.M. Kline, Q.T. Zhang, E.C. Landahl and S. Ross (2016). “Pushing X-ray Photon Correlation Spectroscopy Beyond the Continuous Frame Rate Limit.” *Optics Express* **24**(1): 355–364.

Rumaiz, A.K., D.P. Siddons, G. Deptuch, P. Maj, A.J. Kuczewski, G.A. Carini, S. Narayanan, E.M. Dufresne, A. Sandy, R. Bradford, A. Fluerasu and M.D. Sutton (2016). “First Experimental Feasibility Study of VIPIC: A Custom-made Detector for X-ray Speckle Measurements.” *Journal of Synchrotron Radiation* **23**(2): 404–409.

Zhang, Q., E.M. Dufresne, P. Grybos, P. Kmon, P. Maj, S. Narayanan, G.W. Deptuch, R. Szczygiel and A. Sandy (2016). “Submillisecond X-ray Photon Correlation Spectroscopy from Pixel-Array-Detector with Fast Dual Gating and No Readout Deadtime.” *Journal of Synchrotron Radiation* **23**(Part 3): 679–684.

### NON-REFEREED PUBLICATION

Shu, D., S. Kearney, A. Jayson, Z. Jiang, T. Sun, J. Maser, A. Sandy and J. Wang (2017). “Mechanical Design of a Sample Manipulator for X-ray Coherent Surface Scattering Imaging with Flexure Stages for 10-nm-Scale and 10-nrad-Scale Positioning.” 31st American Society for Precision Engineering Annual Meeting, Portland, OR, October 23–28, 2016.

## 2015-153-R1

### PRESENTATIONS

Mashrafi, S.T., C. Preissner and S.M. Salapaka (2017). “Fast Scanning of X-ray Optics: An Optimal Control Approach.” 31st Annual Meeting American Society for Precision Engineering (ASPE), Portland, OR, October 23–28, 2016.

Preissner, C., S. Sullivan, C. Roehrig, S. Vogt, C. Jacobsen, J. Maser, J. Deng, D. Vine, S.M. Salapaka, S.T. Mashrafi and F. Marin (2016). “APS VelociProbe: Earth, Wind, and Fire.” Three-Way Meeting DESY, Hamburg, Germany, September 14–16, 2016.

Preissner, C., S. Sullivan, T. Mashrafi, C. Roehrig, J. Maser, B. Lai, C. Jacobsen, J. Deng, F. Marin and S. Vogt (2016). “Earth, Wind, and Fire: The New Fast Scanning VelociProbe.” (MEDSI) Mechanical Engineering Design of Synchrotron Radiation Equipment and Instrumentation 2016, Barcelona, Spain, September 11–16, 2016.

Preissner, C., S. Sullivan, C. Jacobsen, J. Maser, B. Lai and C. Roehrig (2015). “The VelociProbe Instrument Design.” NSLS-II Hard X-ray Nanoprobe Team, Upton, NY, September 9, 2015.

#### 2015-161-R1

##### REFEREED PUBLICATION

Windt, D. and R. Conley (2015). “Two-dimensional Differential Deposition: Figure Correction of Thin-shell Mirror Substrates for X-ray Astronomy.” *Proceedings of the SPIE, Optics for EUV, X-ray, and Gamma-Ray Astronomy VII*, San Diego, CA, August 9, 2015, **9603**: 96031H.

##### PRESENTATION

Conley, R., J. Qian, S.J. Izzo, E. Kasman, K. Goetze, T. Mooney, M. Erdmann, B. Shi and L. Assoufid (2016). “*In situ* Surface Figure Measurement for UHV Optics Processing Applications.” 2016 SPIE Optics and Photonics Conference, San Diego, CA, August 28–September 1, 2016.

#### 2015-182-R1

##### REFEREED PUBLICATION

Arjmand, F., S. Sharma, M. Usman, B. M. Leu, M. Y. Hu, L. Toupet, D. Gosztola and S. Tabassum (2016). “Vibrational Dynamics (IR, Raman, NRVS) and DFT Study of New Antitumor Tetranuclear Stannoxane Cluster, Sn(IV)-oxo-(di-o-vanillin) Dimethyl Dichloride.” *Physical Chemistry Chemical Physics* **18**(27): 17805–17809.

##### PRESENTATIONS

Hu, M. (2015). “Pressure Induced Amorphization in SnI<sub>4</sub>.” International Conference on the Applications of the Mössbauer Effect (ICAME), Hamburg, Germany, September 13–18, 2015.

Leu, B.M. (2015). “High-energy Resolution Inelastic X-ray Scattering at Beamline 30-ID, Advanced Photon Source.” 8th North American Mössbauer Symposium, Boston, MA, January 8–9, 2015.

Perez, D. and B.M. Leu (2015). “Vibrational and Superconducting Properties of <sup>119</sup>Sn Nanowires.” Superconductivity on the Verge, Leiden, The Netherlands, July 27–31, 2015.

#### 2015-184-R1

##### PRESENTATION

Feng, Y. (2016). “X-ray Magnetic Diffraction at High Pressure.” High Pressure, Research at Gordon Research Conference, Holderness, NH, July 17–22, 2016.

#### 2016-150-NO

##### PRESENTATIONS

Chavan, A.H., B. Hu, A.D. DiChiara, P. Den Hartog and K.J. Suthar (2016). “Characterization of the Acoustic Field Generated by the Single-Axis Acoustic Levitator.” 9th International Conference on Mechanical Engineering Design of Synchrotron Radiation Equipment and Instrumentation (MEDSI 2016), Barcelona, Spain, September 11–16, 2016.

Suthar, K., A.D. DiChiara, J.E. Lerch, B. Hu, A. Chavan and C.J. Benmore (2017). “Acoustically Levitated Liquid Droplet.” Illinois Institute of Technology Physics Colloquium, Chicago, IL, October 20, 2016.

Suthar, K., J.L. Clough, J.E. Lerch, A. Di Chiara and B. Hu (2016). "Acoustic Levitation." Western Michigan University, Kalamazoo, MI, March 31, 2016.

## MATERIALS AND MOLECULES TO MANUFACTURING

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### 2013-184-R3

#### REFEREED PUBLICATIONS

Armas-Pérez, J.C., A. Londono-Hurtado, O. Guzmán, J.P. Hernández-Ortiz and J.J. de Pablo (2015). "Theoretically Informed Monte Carlo Simulation of Liquid Crystals by Sampling of Alignment-tensor Fields." *Journal of Chemical Physics* **143**(4): 044107.

Buchanan, L.E., E.B. Dunkelberger, H.Q. Tran, P.-N. Cheng, C.C. Chiu, P. Cao, D.P. Raleigh, J.J. de Pablo, J.S. Nowick and M.T. Zanni (2014). "Mechanism of IAPP Amyloid Fibril Formation Involves an Intermediate with a Transient  $\beta$ -sheet." *Proceedings of the National Academy of Sciences of the United States of America*, November 26, 2013, **110**(48): 19285–19290.

Chiu, C.-C. and J.J. de Pablo (2015). "Fibrillar Dimer Formation of Islet Amyloid Polypeptides." *AIP Advances* **5**(9): 092501.

Chiu, C.C., S. Singh and J.J. de Pablo (2013). "Effect of Proline Mutations on the Monomer Conformations of Amylin." *Biophysical Journal* **105**(5): 1227–1235.

Cordoba, A., T. Stieger, M.G. Mazza, M. Schoen and J.J. de Pablo (2016). "Anisotropy and Probe-medium Interactions in the Microrheology of Nematic Fluids." *Journal of Rheology* **60**(1): 75–95.

Fluitt, A.M. and J.J. de Pablo (2015). "An Analysis of Biomolecular Force Fields for Simulations of Polyglutamine in Solution." *Biophysical Journal* **109**(5): 1009–1018.

Freeman, G.S., D.M. Hinckley, J.P. Lequieu, J.K. Whitmer and J.J. de Pablo (2015). "Coarse-grained Modeling of DNA Curvature." *Journal of Chemical Physics* **141**(16): 165103.

Freeman, G.S., D.M. Hinckley, J.P. Lequieu, J.K. Whitmer and J.J. De Pablo (2015). "DNA Shape Dominates Sequence Affinity in Nucleosome Formation." *Physical Review Letters* **113**(16): 168101.

Hinckley, D.M. and J.J. de Pablo (2016). "Coarse-grained Ions for Nucleic Acid Modeling." *Journal of Chemical Theory Computation* **11**(11): 5436–5446.

Hinckley, D.M., J.P. Lequieu and J.J. de Pablo (2014). "Coarse-grained Modeling of DNA Oligonucleotide Hybridization: Length, Sequence, and Salt Effects." *Journal of Chemical Physics* **141**(3): 035102.

Hinckley, D.M., G.S. Freeman, J.K. Whitmer and J.J. de Pablo (2014). "An Experimentally-Informed Coarse-Grained 3-Site-Per-Nucleotide Model of DNA: Structure, Thermodynamics, and Dynamics of Hybridization." *Journal of Chemical Physics* **139**(14): 144903.

Hoffmann, K., M. McGovern, C.C. Chiu and J.J. De Pablo (2015). "Secondary Structure of Rat and Human Amylin Across Force Fields." *PLOS One* **10**(7): e0134091.

Hur, S.M., V. Thapar, A. Ramirez-Hernandez, G. Khaira, T. Segal-Peretz, P.A. Rincon-Delgadillo, W. Li, M. Muller, P.F. Nealey and J.J. de Pablo (2016). "Molecular Pathways for Defect Annihilation in Directed Self-assembly." *Proceedings of the National Academy of Sciences (PNAS)* **112**(46): 14144–14149.

Hur, S.M., G.S. Khaira, A. Ramirez-Hernandez, M. Mueller, P.F. Nealey and J.J. De Pablo (2015). "Simulation of Defect Reduction in Block Copolymer Thin Films by Solvent Annealing." *ACS Macro Letters* **4**(1): 11–15.

- Jiang, X., J. Li, X. Zhao, J. Qin, D. Karpeev, J. Hernandez-Ortiz, J. de Pablo and O. Heinonen (2016). "An  $O(N)$  and Parallel Approach to Integral Problems By A Kernel-independent Fast Multipole Method: Application to Polarization and Magnetization of Interacting Particles." *Journal of Chemical Physics* **145**(6): 064307.
- Joshi, A.A., J.K. Whitmer, O. Guzman, N. Abbott and J.J. de Pablo (2014). "Measuring Liquid Crystal Elastic Constants with Free Energy Perturbations." *Soft Matter* **10**(6): 882–893.
- Lequieu, J., A. Cordoba, D. Hinckley and J.J. de Pablo (2016). "Mechanical Response of DNA – Nanoparticle Crystals to Controlled Deformation." *ACS Central Science* **2**(9): 614–620.
- Lequieu, J., A. Cordoba, D. Schwartz and J.J. de Pablo (2016). "Tension-dependent Free Energies of Nucleosome Unwrapping." *ACS Central Science* **2**(9): 660–666.
- Li, W., P.F. Nealey, J.J. de Pablo and M. Müller (2015). "Defect Removal in the Course of Directed Self-Assembly is Facilitated in the Vicinity of the Order-Disorder Transition." *Physical Review Letters* **113**(16): 168301.
- Liu, C.C., A. Ramirez-Hernandez, E. Han, G.S. W. Craig, Y. Tada, H. Yoshida, H.M. Kang, S.X. Ji, P. Gopalan, J.J. de Pablo and P.F. Nealey (2013). "Chemical Patterns for Directed Self-assembly of Lamellae-Forming Block Copolymers with Density Multiplication of Features." *Macromolecules* **46**(4): 1415–1424.
- Martinez-Gonzalez, J.A., Y. Zhou, M. Rahimi, E. Bukusoglu, N.L. Abbott and J.J. de Pablo (2016). "Blue-phase Liquid Crystal Droplets." *Proceedings of the National Academy of Sciences (PNAS)* **112**(43): 13195–13200.
- Miskin, M., G.S. Khaira, J.J. de Pablo and H.M. Jaeger (2016). "Turning Statistical Physics Models into Materials Design Engines." *Proceedings of the National Academy of Sciences of the United States of America* **113**(1): 34–39.
- Onses, M.S., A. Ramirez-Hernandez, S.M. Hur, E. Sutanto, L. Williamson, A.G. Alleyne, P.F. Nealey, J.J. de Pablo and J.A. Rogers (2014). "Block Copolymer Assembly on Nanoscale Patterns of Polymer Brushes Formed by Electrohydrodynamic Jet Printing." *ACS Nano* **8**(7): 6606–6613.
- Qin, J. and J.J. de Pablo (2016). "Ordering Transition in Salt-doped Diblock Copolymers." *Macromolecules* **49**(9): 3630–3638.
- Qin, J., G.S. Khaira, Y.R. Su, G.P. Garner, M. Miskin, H.M. Jaeger and J.J. de Pablo (2014). "Evolutionary Pattern Design for Copolymer Directed Self-assembly." *Soft Matter* **9**(48): 11467–11472.
- Qin, J., D. Priftis, R. Farina, S.L. Perry, L. Leon, J. Whitmer, K. Hoffmann, M. Tirrell and J.J. de Pablo (2014). "Interfacial Tension of Polyelectrolyte Complex Coacervate Phases." *ACS Macro Letters* **3**(6): 565–568.
- Rahimi, M., T.F. Roberts, J.C. Armas-Perez, X.G. Wang, E. Bukusoglu, N.L. Abbott and J.J. de Pablo (2015). "Nanoparticle Self-assembly at the Interface of Liquid Crystal Droplets." *Proceedings of the National Academy of Sciences (PNAS)* **112**(17): 5297–5302.
- Ramirez-Hernandez, A., H.S. Suh, P.F. Nealey and J.J. de Pablo (2014). "Control of Directed Self-assembly in Block Copolymers by Polymeric Top Coats." *Macromolecules* **47**(10): 3520–3527.
- Ramirez-Hernandez, A., F.A. Detcheverry, B.L. Peters, V.C. Chappa, K.S. Schweizer, M. Muller and J.J. de Pablo (2013). "Dynamical Simulations of Coarse Grain Polymeric Systems: Rouse and Entangled Dynamics." *Macromolecules* **46**(15): 6287–6299.
- Ramirez-Hernandez, A., M. Muller and J.J. de Pablo (2013). "Theoretically Informed Entangled Polymer Simulations: Linear and Non-linear Rheology of Melts." *Soft Matter* **9**(6): 2030–2036.
- Sadati, M., A.I. Apik, J.C. Armas-Perez, J. Martinez-Gonzalez, J.P. Hernandez-Ortiz, N.L. Abbott and J.J. de Pablo (2016). "Liquid Crystal Enabled Early Stage Detection of Beta Amyloid Formation on Lipid Monolayers." *Advanced Functional Materials* **25**(38): 6050–6060.

Segal-Peretz, T., J. Ren, S. Xiong, G. Khaira, A. Bowen, L.E. Ocola, R.N.S. Divan, M. Doxastakis, N. J. Ferrier, J. de Pablo and P.F. Nealey (2017). “Quantitative Three Dimensional Characterization of Block Copolymer Directed Self-assembly on Combined Chemical and Topographical Pre-patterned Templates.” *ACS Nano*(Web).

Suh, H.S., X. Chen, P.A. Rincon-Delgadillo, Z. Jiang, J. Strzalka, J. Wang, W. Chen, R. Gronheid, J.J. de Pablo, N. Ferrier, M. Doxastakis and P.F. Nealey (2016). “Characterization of the Shape and Line Edge Roughness of Polymer Gratings with Grazing Incidence Small Angle X-ray Scattering and Atomic Force Microscopy.” *Journal of Applied Crystallography* **49**(3): 823–834.

Whitmer, J.K., C.C. Chiu, A.A. Joshi and J.J. De Pablo (2015). “Basis Function Sampling: A New Paradigm for Material Property Computations.” *Physical Review Letters* **113**(19): 190602.

Whitmer, J.K., A.A. Joshi, R.J. Carlton, N.L. Abbott and J.J. de Pablo (2015). “Surface Adsorption in Nonpolarizable Atomic Models.” *Journal of Chemical Theory and Computation* **10**(12): 5616–5624. Whitmer, J.K., X.G. Wang, F. Mondiot, D.S. Miller, N.L. Abbott and J.J. de Pablo (2014). “Nematic-Field-Driven Positioning of Particles in Liquid Crystal Droplets.” *Physical Review Letters* **111**(22): 227801.

Whitmer, J.K., A.A. Joshi, T.F. Roberts and J.J. de Pablo (2013). “Liquid-Crystal Mediated Nanoparticle Interactions and Gel Formation.” *Journal of Chemical Physics* **138**(19): 194903.

### 2013-216-R3

#### REFEREED PUBLICATIONS

Doxastakis, M., H.S. Suh, X. Chen, P.A.R. Delgadillo, L. Wan, L. Williamson, Z. Jiang, J. Strzalka, J. Wang, W. Chen, N. Ferrier, A. Ramirez-Hernandez, J.J. de Pablo, R. Gronheid and P. Nealey (2015). “Grazing-incidence Small Angle X-ray Scattering Studies of Nanoscale Polymer Gratings.” *Proceedings of the SPIE Advanced Lithography: Metrology, Inspection, and Process Control for Microlithography XXIX*, San Jose, CA, March 19, 2015, **9424**(1N): 7.

Segal-Peretz, T., J. Ren and P.F. Nealey (2016). “3D Characterization of Block Copolymer Films with TEM Tomography.” *SPIE Newsroom* (14 June 2016).

Segal-Peretz, T., C. Zhou, J. Ren, T. Dazai, L.E. Ocola, R.N.S. Divan and P.F. Nealey (2016). “Three Dimensional Assembly in Directed Self-assembly of Block Copolymers.” *Journal of Photopolymer Science and Technology* **29**(5): 653–657.

Segal-Peretz, T., J. Winterstein, M. Doxastakis, A. Ramirez-Hernandez, M. Biswas, J. Ren, H.S. Suh, S.B. Darling, J.A. Liddle, J.W. Elam, J.J. de Pablo, N.J. Zaluzec and P.F. Nealey (2015). “Characterizing the Three-Dimensional Structure of Block Copolymers via Sequential Infiltration Synthesis and Scanning Transmission Electron Tomography.” *ACS Nano* **9**(5): 5333–5347.

Suh, H.S., X. Chen, P.A. Rincon-Delgadillo, Z. Jiang, J. Strzalka, J. Wang, W. Chen, R. Gronheid, J.J. de Pablo, N. Ferrier, M. Doxastakis and P.F. Nealey (2016). “Characterization of the Shape and Line Edge Roughness of Polymer Gratings with Grazing Incidence Small Angle X-ray Scattering and Atomic Force Microscopy.” *Journal of Applied Crystallography* **49**(3): 823–834.

#### PRESENTATION

Chang, C.L. (2016). “Superconducting Detectors and Cosmology.” 19 Biennial Workshop on Superconductive Electronics: Devices, Circuits, and Systems, North Conway, NH, October 26–30, 2015.

### 2013-219-R3

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Bender, A.N., P.A.R. Ade, A.J. Anderson, J. Avva, Z. Ahmed, K. Arnold, J.E. Ausermann, R. Basu Thakur, B.A. Benson, L.E. Bleem, K. Byrum, J.E. Carlstrom, F.W. Carter, C.L. Chang, G. Wang and V. Yefremenko (2016). “Integrated Performance of a Frequency Domain Multiplexing Readout in the SPT-3G Receiver.” *Proceedings of the 2016 SPIE Astronomical Telescopes and Instrumentation*, Edinburgh, Scotland, United Kingdom, July 20, 2016, **9914**.

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#### 2014-139-R1

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## 2014-151-R2

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## 2014-161-R2

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## PRESENTATIONS

- Chan, M. (2016). “Non-equilibrium Configurational Sampling and Predictive Modeling of Renewable Energy Materials.” Hong Kong University of Science and Technology, Hong Kong, China, December 3, 2015.

- Kinaci, A., B. Narayanan, M.J. Davis, S. Gray, S. Sankaranarayanan and M. Chan (2015). "Evolutionary Algorithm Search for Global Minimum Structures of Au Nano-Clusters." Materials Research Society Fall Meeting, Boston, MA, November 30–December 5, 2014.
- Kinaci, A., B. Narayanan, M. Davis, S. Gray, S. Sankaranarayanan and M. Chan (2015). "Evolutionary Algorithm Search for Global Minimum Structures of Au Nano-Clusters." CNM/APS Users Meeting, Argonne, IL, May 11–14, 2015.
- Narayanan, B., F.G. Sen, A. Kinaci, M.J. Davis, S.K. Gray, Z.-G. Mei, M.K.Y. Chan and S.K.R.S. Sankaranarayanan (2016). "Evolutionary Strategy for Developing Interatomic Potentials to Bridge the Electronic and Atomistic Length Scales." Materials Research Society Fall Meeting, Boston, MA, November 29–December 4, 2015.
- Narayanan, B., S.A. Deshmukh, G. Kamath, E.V. Shevchenko and S.K.R.S. Sankaranarayanan (2016). "Role of Ligand Dynamics in Structural Stability and Pressure Behavior of Supercrystals Self-assembled from Crystalline Nanoparticles." Materials Research Society Fall Meeting, Boston, MA, November 29–December 4, 2015.
- Narayanan, B., S.A. Deshmukh, S. Ramanathan and S.K.R.S. Sankaranarayanan (2015). "Atomistic Insights into the Interaction of Copper Oxide Surfaces with Chloride Ions in Aqueous Media." 227th Electrochemical Society Meeting, Chicago, IL, May 24–28, 2015.
- Narayanan, B., A. Kinaci, F.G. Sen, M.J. Davis, S.K. Gray, M.K.Y. Chan and S.K.R.S. Sankaranarayanan (2015). "Bond Order Potential to Capture Size-dependent Dimensionality Effects in Au Clusters." CNM/APS Users Meeting Argonne, IL, May 11–14, 2015.
- Narayanan, B., A. Kinaci, M. Davis, M. Chan, S. Sankaranarayanan and S. Gray (2015). "Development of Novel Force Field for Gold Nanoclusters." Materials Science and Technology Conference, Pittsburgh, PA, October 12–16, 2014.
- Narayanan, B., A. Kinaci, F.G. Sen, M.J. Davis, S. Gray, M. Chan and S.K.R.S. Sankaranarayanan (2015). "A Novel Empirical Force Field to Capture Size-dependent Dimensionality Effects in Au Nanoclusters." 227th Electrochemical Society Meeting, Chicago, IL, May 24–28, 2015.
- Narayanan, B., A. Kinaci, F.G. Sen, M.J. Davis, S.K. Gray, M.K.Y. Chan and S.K.R.S. Sankaranarayanan (2015). "Size-dependent Dimensionality Effects and Structures in Au Nanoclusters Using a Novel Empirical Force Field." Materials Research Society Spring Meeting, San Francisco, CA, April 6–10, 2015.
- Narayanan, B., A. Kinaci, M.J. Davis, M.K. Chan, S. Sankaranarayanan and S.K. Gray (2014). "Development of Force Field for Reactive Interfaces from First Principles." Center for Nanoscale Materials Users Meeting, Argonne National Laboratory, Argonne, IL, May 12–15, 2014.
- Sen, F.G., A. Kinaci, B. Narayanan, M.J. Davis, S.K. Gray, S.K.R.S. Sankaranarayanan and M.K.Y. Chan (2016). "Atomistic Insights into Electrocatalytic Activity and Structural Stability of IrO<sub>2</sub> Nanoparticles." Materials Research Society Spring Meeting, Phoenix, AZ, March 28–April 1, 2016.
- Sen, F.G., B. Narayanan, A. Kinaci, M.J. Davis, S.K. Gray, S.K.R.S. Sankaranarayanan and M.K.Y. Chan (2016). "A Comparative Study of Optimization Methods for Force Field Fitting." Materials Research Society Fall Meeting, Boston, MA, November 29–December 4, 2015.
- Sen, F.G., A. Kinaci, B. Narayanan, M.J. Davis, S.K. Gray, S.K.R.S. Sankaranarayanan and M.K.Y. Chan (2015). "Development of a Variable Charge Force-field to Gain Atomistic Insights into IrO<sub>2</sub> Surfaces and Nanoclusters." Materials Research Society Spring Meeting, San Francisco, CA, April 6–10, 2015.
- Sen, F., B. Narayanan, A. Kinaci, S. Gray, M. Davis, S. Sankaranarayanan and M. Chan (2015). "Force Field Development from First Principles for Materials Design." American Physical Society March Meeting, San Antonio, TX, March 2–6, 2015.
- Sen, F.G., A. Kinaci, B. Narayanan, M.J. Davis, S.K. Gray, S.K.R.S. Sankaranarayanan and M.K.Y. Chan (2015). "IrO<sub>2</sub> Surface and Nanostructure Stability from First Principles and Variable Charge Force Field Calculations." 227th Electrochemical Society Meeting, Chicago, IL, May 24–28, 2015.

Sen, F.G., B. Narayanan, A. Kinaci, M.J. Davis, S.K. Gray, S.K.R.S. Sankaranarayanan and M.K.Y. Chan (2015). “IrO<sub>2</sub> Surface and Nanostructure Stability from first Principles and Variable Charge Force Field Calculations.” CNM/APS Users Meeting Argonne, IL, May 11–14, 2015.

Zapol, P., D. Karpeyev, K.C. Maheshwari, X. Zhong, B. Narayanan, S. Sankaranarayanan, M. Wilde and O. Heinonen (2015). “Coupled Molecular-dynamics and First-principle Transport Calculations of Metal/Oxide/Metal Heterostructures.” American Physical Society March Meeting, San Antonio, TX, March 2–6, 2015. (Also see 2014-128.)

## 2014-191-R2

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Koehl, W.F., H. Seo, G. Galli and D.D. Awschalom (2016). “Designing Defect Spins for Wafer-scale Quantum Technologies.” *MRS Bulletin* **40**(12): 1146–1153.

Koehl, W.F., B. Diler, S.J. Whiteley, A. Bourassa, N.T. Son, E. Janzén and D.D. Awschalom (2017). “Resonant Optical Spectroscopy and Coherent Control of Cr<sup>4+</sup> Spin Ensembles in SiC and GaN.” *Physical Review B* **95**(3): 035207.

## 2014-192-R2

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Brawand, N., M. Vörös, M. Govoni and G. Galli (2017). “Generalization of Dielectric-Dependent Hybrid Functionals to Finite Systems.” *Physical Review X* **6**(4): 041002. (Also see 2016-185.)

Gaiduk, A.P., M. Govoni, R. Seidel, J.H. Skone, B. Winter and G. Galli (2016). “Photoelectron Spectra of Aqueous Solutions from First Principles.” *Journal of the American Chemical Society* **138**(22): 6912–6915.

Pham, T.A., D. Lee, E. Schwegler and G. Galli (2015). “Interfacial Effects on the Band Edges of Functionalized Si Surfaces in Liquid Water.” *Journal of the American Chemical Society* **136**(49): 17071–17077.

Ping, Y., W.A. Goddard and G.A. Galli (2015). “Energetics and Solvation Effects at the Photoanode/Catalyst Interface: Ohmic Contact Versus Schottky Barrier.” *Journal of American Chemical Society* **137**(16): 5264–5267.

Seo, H., M. Govoni and G. Galli (2016). “Design of Defect Spins in Piezoelectric Aluminum Nitride for Solid-state Hybrid Quantum Technologies.” *Scientific Reports* **6**: 20803.

Skone, J.H., M. Govoni and G. Galli (2016). “Nonempirical Range-separated Hybrid Functionals for Solids and Molecules.” *Physical Review B* **93**(23): 235106.

Wan, Q. and G. Galli (2015). “First-principles Framework to Compute Sum-frequency Generation Vibrational Spectra of Semiconductors and Insulators.” *Physical Review Letters* **115**(24): 246404.

### PRESENTATIONS

Galli, G. (2016). “*Ab Initio* Studies of Heterogeneous Interfaces for Water Photocatalysis.” Gordon Research Conference Renewable Energy: Solar Fuels, Lucca, Italy, February 28–March 4, 2016.

Galli, G.A. (2016). “Aqueous Interfaces: Insights From First Principles Calculations.” Materials Research Society Fall Meeting (2015 MRS), Boston, MA, November 29–December 4, 2015.

Galli, G. (2016). “Computational Characterization of Solar Interfaces: Coupling *ab initio* Molecular Dynamics and First Principles Spectroscopies.” American Chemical Society 2016, San Diego, CA, March 13–17, 2016.

Galli, G. (2016). “Earth Abundant Materials for Solar Energy Conversion.” University of Central Florida, Orlando, FL, January 20, 2016.

Galli, G. (2016). “Energetics and Solvation Effects at the Photoanode/Catalyst Interface.” American Chemical Society 2016, San Diego, CA, March 13–17, 2016.

- Galli, G. (2016). "Engineering Materials for Sustainable Energy Sources." Materials Science and Engineering (MSE) Colloquium, Stanford University, Stanford, CT, April 8, 2016.
- Galli, G. (2016). "Engineering Materials for Sustainable Energy Sources." The Frontiers of Materials Modeling, TYC 10th Anniversary Symposium, London, UK, February 17–19, 2016.
- Galli, G. (2016). "Heterogeneous Materials for Energy and Quantum Information Technologies: First Principles Predictions." Physical Science Seminar, IBM, Yorktown Heights, NY, June 3, 2016.
- Govoni, M. and G. Galli (2016). "Large Scale GW Calculations." 2016 CAMD Summer School on Electronic Structure Theory and Materials Design, Technical University of Denmark, Lyngby, Denmark, August 14–19, 2016.
- Galli, G. (2016). "Materials for Solar Energy Conversion and Storage." American Chemical Society 2016, San Diego, CA, March 13–17, 2016.
- Galli, G. (2016). "Materials Discovery and Scientific Design by Computation: What Does It Take?" University of Central Florida, Orlando, FL, January 20, 2016.
- Galli, G. (2016). "Predicting Materials for Solar Energy Conversion." American Physical Society March Meeting 2016, Baltimore, MD, March 14–18, 2016.
- Galli, G. (2016). "Predicting the Properties of Interfaces Between Electrolytes and Electrodes: Condensed Matter Physics Meets Electrochemistry." 228th Electrochemical Society Meeting, Phoenix, AZ, October 11–15, 2015.
- Galli, G. (2016). "Spectroscopic and Transport Properties of Heterogeneous Materials." Theory and Applications of Computational Chemistry (TACC) Conference, Seattle, WA, August 28–September 2, 2016.
- Galli, G. (2016). "Spectroscopic and Transport Properties of Heterogeneous Materials." International Union of Material Research Societies: International Conference on Electronic Materials (IUMRS-ICEM), Singapore, July 4–8, 2016.
- Galli, G. (2016). "Structural and Electronic Properties of Heterogeneous Interfaces from First Principles." Materials Research Society Meeting, Phoenix, AZ, March 28–April 1, 2016.
- Galli, G. (2016). "Structure-Function Relationships in Materials for Energy Applications." American Chemical Society 2016, San Diego, CA, March 13–17, 2016.
- Galli, G. (2016). "Understanding and Predicting Materials for Sustainable Energy Sources: The Key Role of First Principles Simulations." California Institute of Technology, Pasadena, CA, May 31, 2016.
- Galli, G. (2016). "Understanding and Predicting Materials for Sustainable Energy Sources: The Key Role of Density Functional Theory." University of California, San Diego, CA, March 31, 2016.
- Galli, G.A. (2015). "First Principles Spectroscopy of Heterogeneous Systems: GW and Hybrid Functionals." 250th American Chemical Society National Meeting, Boston, MA, August 16–20, 2015.
- Galli, G. (2015). "Materials Discovery and Scientific Design by Computation: What Does It Take?" Psi-K Conference, San Sebastian, Spain, September 6–10, 2015.
- Galli, G. (2015). "Predicting Complex Materials from First Principles." Gordon Research Conference: Nanomaterials for Applications in Energy Technology, Ventura, CA, February 22–27, 2015.
- Galli, G. (2014). "Electronic Properties of Aqueous Interfaces: Coupled *ab initio* Molecular Dynamics and GW Calculations." International Center for Materials Research (ICMR) Workshop on *Ab initio* Description of Charged Systems and Solid/Liquid Interfaces for Semiconductors and Electrochemistry, University of California, Santa Barbara, CA, July 7–11, 2014.
- Galli, G. (2014). "Heterogeneous Interfaces: Insights from First Principles Calculations." American Conference on Theoretical Chemistry (ACTC) 2014, Telluride, CO, July 21–24, 2014.

Galli, G. (2014). "Light Absorbers for Photo-electrochemical Energy Conversion: First Principles Calculations." 248th American Chemical Society (ACS) National Meeting, San Francisco, CA, August 10–14, 2014.

Galli, G. (2014). "Photo-excitations in Nanostructured Semiconductors." American Physical Society (APS) March Meeting, Denver, CO, March 3–7, 2014.

Galli, G. (2014). "Predicting Materials for Water Splitting: Condensed Matter Physics Meets Electrochemistry." 248th American Chemical Society (ACS) National Meeting, Presidential Symposium Photocatalytic Conversion of Water to Hydrogen and Oxygen, San Francisco, CA, August 10–14, 2014.

Galli, G. (2014). "Water at Surfaces: Insights from First Principles Calculations." Water and Aqueous Solutions Gordon Research Conference, Holderness, NH, July 27–August 1, 2014.

## 2015-144-R1

### REFEREED PUBLICATIONS

Chen, Y., K. Wang, D. Gürsoy, C.S. Hoyuelos, F. De Carlo and M.A. Anastasio (2016). "Joint Reconstruction of Absorption and Refractive Properties in Propagation-Based X-ray Phase-Contrast Tomography via a Non-Linear Image Reconstruction Algorithm." *Proceedings of the 2016 SPIE Medical Imaging Conference*, San Diego, CA, February 27–March 3, 2016, **9783**.

Ching, D.J. and D. Gürsoy. "Xdesign: An Open-source Software Package for Designing X-ray Imaging Phantoms and Experiments." *Journal of Synchrotron Radiation* **24**(Pt 2): 537-544.

Fang, Y., Q. Liu, L. Xiao, Y. Rong, Y. Liu, Z. Chen, X. Ai, Y. Cao, H. Yang, J. Xie, C. Sun, X. Zhang, B. Aoun, X. Xing, X. Xiao and Y. Ren. "Ultra-long Lifespan and High-voltage NaVOPO<sub>4</sub> Nanoplates with Two-dimensional Ionic Diffusion Routes as Cathodes for Sodium-ion Batteries." *Nature Communications*. (To be published.)

Phatak, C. and D. Gürsoy (2015). "Iterative Reconstruction of Magnetic Induction Using Lorentz Transmission Electron Tomography." *Ultramicroscopy* **150**: 54–64.

Yang, X., D. Gürsoy, C. Phatak and F. De Carlo. "Using Convolutional Neural Network to Reduce Tomographic Reconstruction Artifacts." *Journal of Synchrotron Radiation*. (To be published.)

Zhu, Y.G., Q. Liu, Y. Rong, H. Chen, J. Yang, C. Jia, L.-J. Yu, A. Karton, Y. Ren, X. Xu, S. Adams and Q. Wang. "Proton Enhanced Dynamic Battery Chemistry for Aprotic Li-O<sub>2</sub> Batteries." *Nature Communications* **8**: 14308.

### NON-REFEREED PUBLICATION

Phatak, C., D. Gürsoy, E.B. Gulsoy, L. Trahey and V. De Andrade (2016). "Integrated Multimodal Imaging of Cathodes for Lithium Ion Battery." 145th Annual TMS Meeting (TMS 2016), Nashville, TN, February 14–18, 2016.

### PRESENTATIONS

Gürsoy, D., S.Z. Sullivan and S. Vogt (2016). "Evaluation of Contemporary Data Acquisition Schemes for X-ray Fluorescence Tomography." 65th Annual Conference on Applications of X-ray Analysis, Chicago, IL, August 1–5, 2016.

Gürsoy, D. (2015). "Compressive Sensing and Its Potential in Nanoimaging." Joint NSRC Workshop 2015: Big, Deep, and Smart Data Analytics in Materials Imaging, Oak Ridge, TN, June 8–10, 2015.

Gürsoy, D. (2015). "Current and Future Data Analysis Trends for Synchrotron Imaging." 23rd International Congress on X-ray Optics and Microanalysis, Upton, NY, September 14–18, 2015.

Phatak, C., X. Yang, D. Gürsoy, L. Trahey, E.B. Gulsoy, V. De Andrade, X. Xiao, S. Hong and A.K. Petford-Long (2016). "Integrated Multimodal Imaging: From Functional Nanostructures to Lithium-Ion Battery Cathodes." 25th International Materials Research Congress, Cancun, Mexico, August 14–19, 2016.

Phatak, C., X. Yang, D. Gürsoy, E.B. Gulsoy, L. Trahey, V. De Andrade, Q. Liu and X. Xiao (2016). "MIMES: Multimodal Imaging of Materials for Energy Storage." 145th TMS Annual Meeting, Nashville, TN, February 14–18, 2016.

Yang, X., D. Gürsoy, C. Phatak, F. De Carlo and V.J. De Andrade (2016). “Enhancing Structural Resolution of Lithium-ion Battery Particles by Multimodal Analysis of TXM and STEM Datasets.” 3D Materials Science (3DMS), St. Charles, IL, July 10–13, 2016.

Yang, X., D. Gürsoy, C. Phatak, V. De Andrade, E.B. Gulsoy and F. De Carlo (2016). “Learning from Scanning Transmission Electron Microscopy to Enhance Transmission X-ray Microscopy: How we can merge STEM and TXM datasets?” Microscopy and Microanalysis Meeting (M&M 2016), Columbus, OH, July 24–28, 2016.

Yang, X., B. Gulsoy, V.J. De Andrade, F. De Carlo, C. Phatak and D. Gürsoy (2016). “Multimodal Imaging for Lithium-ion Battery Particles.” Lorentz Workshop on Quantitative 3D X-ray Imaging: From Tomographic Images to Metrics, Leiden, The Netherlands, January 11–15, 2016.

## 2015-149-R1

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Cherukara, M.J., B. Narayanan, A. Kinaci, K. Sasikumar, S.K. Gray, M.K.Y. Chan and S.K.R.S. Sankaranarayanan (2016). “*Ab initio*-Based Bond Order Potential to Investigate Low Thermal Conductivity of Stanene Nanostructures.” *Journal of Physical Chemistry Letters* **7**(19): 3752–3759.

Cherukara, M.J. (2016). “Shock Loading of Granular Ni/Al Composites.” *Journal of Physical Chemistry C* **120**(12): 6804–6813.

Deng, J., Y.S.G. Nashed, S. Chen, N.W. Phillips, T. Peterka, R. Ross, S. Vogt, C. Jacobsen and D.J. Vine (2015). “Continuous Motion Scan Ptychography: Characterization for Increased Speed in Coherent X-ray Imaging.” *Optics Express* **23**(5): 5438–5451.

Deng, J., D.J. Vine, S. Chen, Y.S.G. Nashed, Q. Jin, N.W. Phillips, T. Peterka, R. Ross, S. Vogt and C.J. Jacobsen (2015). “Simultaneous Cryo X-ray Ptychographic and Fluorescence Microscopy of Green Algae.” *Proceedings of the National Academy of Sciences of the United States of America*, February 24, 2015 **112**(8): 2314–2319.

Li, Y., Z. Jiang, X.-M. Lin, H. Wen, D.A. Walko, S.A. Deshmukh, R. Subbaraman, S.K.R.S. Sankaranarayanan, S. Gray and P. Ho (2015). “Femto-second Laser Pulse Driven Melting in Gold Nanorod Aqueous Colloidal Suspension: Identification of a Transition from Stretched to Exponential Kinetics.” *Nature Scientific Reports* **5**(8146).

Sasikumar, K. (2015). “Nanoscale Heat Transport Phenomena in Colloidal Gold Ensembles Subjected to Femtosecond Laser Heatings.” Proceedings of the Materials Research Society Spring 2015 Meeting: Nanoscale Heat Transport From Fundamentals to Devices, San Francisco, CA, April 6–10, 2015, *Cambridge University Press/Curran Associates, Inc.* **1779**.

Ulvestad, A., R. Harder, E.R. Maxey, J.N. Clark, J.W. Kim, P. Mulvaney and O.G. Shpyrko. “Nanocatalytic Activity Under Operando Conditions.” *ACS Nano*. (To be published.)

Ulvestad, A., K. Sasikumar, J.W. Kim, R. Harder, E. Maxey, J.N. Clark, B. Narayanan, S. Deshmukh, N. Ferrier, P. Mulvaney, S.K.R.S. Sankaranarayanan and O.G. Shpyrko (2016). “*In situ* 3D Imaging of Catalysis Induced Strain in Gold Nanoparticles.” *Journal of Physical Chemistry Letters* **7**(15): 3008–3013. (Also see 2016-187.)

### PRESENTATIONS

Cherukara, M.J., D. Kim, W. Cha, H. Kim, B. Narayanan, R. Harder and S.K.R.S. Sankaranarayanan (2017). “Atomistic Picture of the Catalytic Activity of Platinum Nanoparticles through Coherent Diffraction Imaging and Reactive Molecular Dynamics Simulations.” The Electrochemical Society PRiME, Honolulu, HI, October 2–7, 2016.

McNulty, I. (2015). “Argonne Integrated Imaging Initiative: the Sum is Greater Than the Parts.” 2015 Nanoscale Science Research Centers Workshops on Big, Deep, and Smart Analytics in Materials Imaging, Oak Ridge, TN, June 8–10, 2015. (Also see 2015-154.)

Peterka, T. (2016). “Workflows Combining Simulation and Experiment.” SC15 Supercomputing Conference: Birds-of-a-Feather Characterizing Extreme-Scale Computational and Data-Intensive Workflows, Austin, TX, November 15–17, 2015.

Phatak, C., Y. Nashed and T. Peterka (2015). “Towards Multi-resolution Phase Retrieval Using Electron Ptychography.” 2015 Microscopy and Microanalysis Meeting, Portland, OR, August 2–6, 2015.

Sasikumar, K. and S.K.R.S. Sankaranarayanan (2016). “Investigation of Lattice Displacement Dynamics and Nanocatalytic Activity of Gold.” 2015 Materials Research Society Fall Meeting and Exhibit, Boston, MA, November 29–December 4, 2015.

Sasikumar, K. and S. Sankaranarayanan (2016). “Investigation of Lattice Displacement Dynamics and Nanocatalytic Activity of Gold.” 2015 International Symposium on Clusters and Nanomaterials, Richmond, VA, October 16–29, 2015.

Sasikumar, K., M.J. Cherukara, J. Clark, T. Peterka, R. Harder and S.K.R.S. Sankaranarayanan (2016). “Lattice Dynamics of Core-Shell Bimetallic Nanocrystals During Ultrafast Laser Excitation.” 2016 Materials Research Society Spring Meeting and Exhibit, Phoenix, AZ, March 28–April 1, 2016.

Sasikumar, K. (2015). “Nanoscale Heat Transport in Gold Ensembles.” ASME 2015 Applied Mechanics and Materials Conference (McMat2015), Seattle, WA, June 29–July 1, 2015.

## 2015-154-R1

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Cai, Z., S. Cai, W. Yang and M. Tang (2015). “Development of Differential Analysis Techniques for Multivariate Imaging Data Analysis.” *Proceedings of the SPIE X-ray Nanoimaging II Conference*, San Diego, CA, August 9–13, 2015.

Wu, Y.A., L. Li, Z. Li, A. Kinaci, M.K. Chan, Y. Sun, J.R. Guest, I. McNulty, T. Rajh and Y. Liu (2016). “Visualizing Redox Dynamics of a Single Ag/AgCl Heterogeneous Nanocatalyst at Atomic Resolution.” *ACS Nano* **10**(3): 3738–3746.

### NON-REFEREED PUBLICATION

Li, L., Y.A. Wu, Y. Liu, J. Guest, T. Rajh, I. McNulty, Z. Cai and M. Chan (2016). “Modeling Multi-modal Images of Photocatalysis on Cu<sub>2</sub>O.” TMS 2016 145th Annual Meeting and Exhibition, Nashville, TN, February 14–18, 2016.

### PRESENTATIONS

Li, L., R. Zhang, Y. Wu, T. Rajh, I. McNulty, Y. Liu, J.R. Guest and M.K.Y. Chan (2016). “Catalytic Activation of CO<sub>2</sub> on Defective Cu<sub>2</sub>O (110) Surface: A DFT and AIMD Study.” 2016 Car-Parrinello Molecular Dynamics, Chicago, IL, May 18–20, 2016.

Li, L., Y.A. Wu, T. Rajh, I. McNulty, Z. Cai, J.R. Guest, Y. Liu and M.K. Chan (2016). “First-principles Investigation on the Stability and Catalytic Activities of Cu<sub>2</sub>O Surfaces.” 2016 American Physical Society March Meeting, Baltimore, MD, March 14–18, 2016.

Li, L., R. Zhang, I. McNulty, Z. Cai, J.R. Guest and M.K.Y. Chan (2016). “Role of Surface Defects in Catalytic Activity of Cu<sub>2</sub>O: First-Principles Simulations of STM Images and XAS Spectra.” 2016 APS/CNM Users Meeting, Argonne National Laboratory, Argonne, IL, May 9–12, 2016.

Li, L., M.K. Chan, L. Luo, J. Ciston, W. Saidi, E.A. Stach, J. Yang and G. Zhou (2015). “First-principles Study on the Epitaxial Growth of Cu<sub>2</sub>O Thin Film and Catalytic Reactivity of Cu<sub>2</sub>O Surfaces.” 27th Annual Workshop on Recent Developments in Electronic Structure Theory, Seattle, WA, June 21–24, 2015.

McNulty, I. (2015). “Argonne Integrated Imaging Initiative: the Sum is Greater Than the Parts.” Big, Deep, and Smart Data Analytics in Materials Imaging Workshop, Oak Ridge, TN, June 2015. (Also see 2015-149-R1.)

**2015-167-R1****REFEREED PUBLICATIONS**

Almer, J., P. Chupas, B. Stephenson, D. Tiede, S. Vogt, L. Young, P. Evans, J.B. Parise and B. Suter (2016). “Emerging Opportunities in High-Energy X-ray Science: The Diffraction-Limited Storage Ring Frontier.” *Synchrotron Radiation News* **29**(1): 12–13.

Ulvestad, A., A. Tripathi, S.O. Hruszkewycz, W. Cha, S.M. Wild, G.B. Stephenson and P.H. Fuoss (2016). “Coherent Diffractive Imaging of Time-Evolving Samples with Improved Temporal Resolution.” *Physical Review B: Condensed Matter* **93**(18): 184105. (Also see 2016–187.)

**NON-REFEREED PUBLICATION**

Streiffer, S., S. Vogt, P.G. Evans, R. Suter, D. Fong, P. Chupas, R.L. Leheny, A. Sandy, G. Woloschak, R. Fischetti, L. Makowski, J. Wang, D. Vine, B. Lee, A. Joachimiak, M. Becker, X. Zuo, K. Chapman, D. Tiede, R. Harder, E. Dufresne, T. Sun, M. Balasubramanian, C. Benmore, V. De Andrade, P. Fenter, D. Haeffner, S. Heald, M. Hu, K. Kemner, J. Freeland, D. Haskel, J.F. Mitchell, J. Logan, I. McNulty, G.B. Stephenson, H. Wen, J. Almer, M. Li, S. Shastri, X. Shi and E. Austin (2016). “Understanding Structure and Dynamics During Materials Synthesis.” Early Science at the Upgraded Advanced Photon Source, Argonne, IL, October 2015.

**PRESENTATIONS**

Ju, G., M.J. Highland, C. Thompson, J.A. Eastman, G.B. Stephenson and P.H. Fuoss (2015). “Diffractometer and Growth System for *in situ* Coherent X-ray Studies of Epitaxy.” 20<sup>th</sup> American Conference on Crystal Growth and Epitaxy (ACCGE-20) and 17<sup>th</sup> US Biennial Workshop on Organometallic Vapor Phase Epitaxy (OMVPE-17), Big Sky, MT, August 2–7, 2015.

Ju, G., M.J. Highland, A. Yanguas-Gil, C. Thompson, J.A. Eastman, H. Zhou, P. Zapol, G.B. Stephenson and P.H. Fuoss (2016). “Instrument for *in situ* Coherent X-ray Studies of III-nitride MOVPE.” 18<sup>th</sup> International Conference on Metal-Organic Vapor Phase Epitaxy, San Diego, CA, July 10–15, 2016. (Also see 2014-151.)

Xu, D., E. Perret, M.J. Highland, G. Ju, P.H. Fuoss, P. Zapol, G.B. Stephenson and C. Thompson (2016). “Kinetic Monte Carlo Simulations and *in situ* X-ray Studies of GaN Vapor Phase Epitaxy.” 18<sup>th</sup> International Conference on Crystal Growth and Epitaxy, Nagoya, Japan, August 7–12, 2016. (Also see 2014-151.)

Xu, D., C. Thompson, P. Zapol, G. Ju, M.J. Highland, P.H. Fuoss and G.B. Stephenson (2016). “Kinetic Monte Carlo Simulations of MOVPE of GaN on c-Plane and m-Plane Surfaces.” 18<sup>th</sup> International Conference on Metal-Organic Vapor Phase Epitaxy, San Diego, CA, July 10–15, 2016. (Also see 2014-151.)

**2015-168-R1****REFEREED PUBLICATIONS**

Goremychkin, E.A., H. Park, R. Osborn, S. Rosenkranz, J.-P. Castellan, V.R. Fanelli, A.D. Christianson, M.B. Stone, E.D. Bauer, K.J. McClellan, D.D. Byler and J.M. Lawrence. “Band Excitations in CePd<sub>3</sub>: A Comparison of Neutron Scattering and *ab initio* Theory.” *Nature Physics*. (To be published.)

Kim, C., H. Park and C.A. Marianetti (2016). “New Class of Planar Ferroelectric Mott Insulators via First Principles Design.” *Physical Review B* **92**(23): 235122.

Park, H., A.J. Millis and C.A. Marianetti (2016). “Influence of Quantum Confinement and Strain on Orbital Polarization of Strained Four-layer LaNiO<sub>3</sub> Superlattices: A DFT+DMFT Study.” *Physical Review B* **93**(23): 235109.

Nowadnick, E.A., J.P. Ruf, H. Park, P.D. C. King, D.G. Schlom, K.M. Shen and A.J. Millis (2016). “Quantifying Electronic Correlation Strength in a Complex Oxide: A Combined DMFT and ARPES Study of LaNiO<sub>3</sub>.” *Physical Review B* **92**(24): 245109.

Upton, M.H., Y. Choi, H. Park, J. Liu, D. Meyers, J. Tchakhalian, S. Middey and J.-W. Kim (2015). “Novel Electronic Behavior Facilitating the NdNiO<sub>3</sub> Metal-insulator Transition.” *Physical Review Letters* **115**(3): 036401.

**PRESENTATIONS**

Park, H. (2016). "The Dynamical Mean Field Theory Study of Rare-earth Nickelates." US-Korea Conference, Dallas, TX, August 10–13, 2016.

Park, H. (2016). "The First-principles Study of Structural, Electronic, and Magnetic Properties of Strongly Correlated Materials: DFT+DMFT Approach." Brookhaven National Laboratory Seminar, Upton, NY, August 25, 2016.

Park, H. (2016). "Influence of Quantum Confinement and Strain of Orbital Polarization of Four-layer LaNiO<sub>3</sub> Superlattices." American Physical Society March Meeting, Baltimore, MD, March 14–18, 2016.

**2015-178-R1****REFEREED PUBLICATIONS**

Gou, G., J. Young, X. Liu and J.M. Rondinelli (2016). "Interplay of Cation Ordering and Ferroelectricity in Perovskite Tin Iodides: Designing a Polar Halide Perovskite for Photovoltaic Applications." *Inorganic Chemistry* **56**(1): 26–32.

He, J., C. Franchini and J.M. Rondinelli (2017). "Ferroelectric Oxides with Strong Visible-Light Absorption from Charge Ordering." *Chemistry of Materials* (DOI: 10.1021/acs.chemmater.6b03486).

He, J., C. Franchini and J.M. Rondinelli (2016). "Lithium Niobate-Type Oxides as Visible Light Photovoltaic Materials." *Chemistry of Materials* **28**(1): 25–29.

Young, J., E.J. Moon, D. Mukherjee, G. Stone, V. Gopalan, N. Alem, S.J. May and J.M. Rondinelli (2017). "Polar Oxides Without Inversion Symmetry Through Vacancy and Chemical Order." *Journal of the American Chemical Society* **139**(7): 2833–2841.

Young, J. and J.M. Rondinelli (2016). "Crystal Structure and Electronic Properties of Bulk and Thin Film Brownmillerite Oxides." *Physical Review B* **92**(17): 174111.

**2016-131-NO****PRESENTATION**

Bunquin, J.C., M.S. Ferrandon, U. Das, C. Liu, L.A. Curtiss, J.T. Miller, A.S. Hock, S.T. Nguyen, C.L. Marshall and P.C. Stair (2016). "Supported Organometallic Sites for Olefin Hydrogenation." Gordon Research Conference (GRC) on Catalysis: From Theory to Commercialization, New London, NH, June 12–17, 2016.

**2016-133-NO****REFEREED PUBLICATIONS**

Chang A.Y., Y.-J. Cho, K.-C. Chen, C.-W. Chen, A. Kinaci, B.T. Diroll, M.J. Wagner, M.K.Y. Chan, H.-W. Lin, R.D. Schaller (2016). "Slow Organic-to-Inorganic Sub-Lattice Thermalization in Methylammonium Lead Halide Perovskites Observed by Ultrafast Photoluminescence." *Advanced Energy Materials* **6**(15): 1600422.

Cherukara, M.J., B. Narayanan, A. Kinaci, K. Sasikumar, S.K. Gray, M.K.Y. Chan and S.K.R.S. Sankaranarayanan (2016). "Ab initio-Based Bond Order Potential to Investigate Low Thermal Conductivity of Stanene Nanostructures." *Journal of Physical Chemistry Letters* **7**(19): 3752–3759.

**PRESENTATIONS**

Chan, M. (2016). "Theory Meets Reality: Combined First Principles Modeling and Characterization Studies of Renewable Energy Materials." Massachusetts Institute of Technology, Cambridge, MA, April 7, 2016. (Also see 2016-069.)

Schaller, R.D. (2016). "Investigations of Non-Equilibrium Electron-Phonon Coupling and Phonon-Phonon Coupling For Understanding Relaxation and Dissipation." 2016 International Conference on Energy, Materials & Photonics (EMP16), Troyes, France, July 10–13, 2016.

Wiederrecht, G. (2016). "Ultrafast Energy and Heat Flow in Nanoscale Materials." 2016 International Conference on Energy, Materials & Photonics (EMP16), Troyes, France, July 10–13, 2016.

## NATIONAL AND GLOBAL SECURITY

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### 2014-194-R2

#### REFEREED PUBLICATIONS

North, M.J., P. Sydelko and I. Martinez-Moyano. "Anticipatory Complex Adaptive Network Extrapolation." *Complex Adaptive Systems Modeling*. (To be published.)

North, M.J., P. Sydelko and I. Martinez-Moyano (2016). "Applying 3D Printing and Genetic Algorithm-Generated Anticipatory System Dynamics Models to a Homeland Security Challenge." *Proceedings of the 2015 Winter Simulation Conference*, Huntington Beach, CA, December 6–9, 2015.

North, M.J., P. Sydelko and I. Martinez-Moyano (2015). "Structurally Evolving System Dynamics Models Using Genetic Algorithms." *Proceedings of the 33rd International Conference of the System Dynamics Society*, Cambridge, MA, July 19–23, 2015.

#### NON-REFEREED PUBLICATION

Sydelko, P., M. North, I. Martinez-Moyano and B. Friedman (2016). "Goldilocks and the Wicked Problem." 2016 Conference on Complex Systems, Amsterdam, The Netherlands, September 19–22, 2016.

#### PRESENTATION

Sydelko, P.J. (2016). "Resiliency is a Wicked Problem." Resilience Week 2016, Lisle, IL, August 16–18, 2016.

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### 2015-169-R1

#### NON-REFEREED PUBLICATIONS

Collier, N., J. Ozik and C.M. Macal (2015). "Large-Scale Agent-based Modeling with Repast HPC: A Case Study in Parallelizing an Agent-based Model." 3rd Workshop on Parallel and Distributed Agent-Based Simulations (PADABS) at the Workshop of Euro-Par 2015, Vienna, Austria, August 24–28, 2015.

Macal, C.M. (2016). "From Compartmentalized to Agent-Based Models Of Epidemics." American Physical Society March Meeting, Baltimore, MD, March 14–18, 2016.

Ozik, J., N.T. Collier and J.M. Wozniak (2016). "Many Resident Task Computing in Support of Dynamic Ensemble Computations." 8th Workshop on Many-Task Computing on Clouds, Grids, and Supercomputers (MTAGS 2015), Austin, TX, November 15, 2015.

#### PRESENTATIONS

Collier, N.T. and J. Ozik (2015). "High Performance Computing and Computational Modeling: Repast HPC." University College London Big Data Institute, London, England, April 30, 2015.

Macal, C.M. (2015). "Agent-Based Modeling of Ebola Spread in a Large Urban Area." INFORMS Healthcare Conference, Nashville, TN, July 29–31, 2015.

Murphy, J.T., J. Ozik, N. Collier and C. Macal (2016). "Contagion Modeling with the chiSIM and ReFACE Frameworks: Agent-Based Models of Disease Transmission in Chicago, USA." Complex Systems 2016, Amsterdam, The Netherlands, September 19–22, 2016.

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### 2015-177-R1

#### REFEREED PUBLICATIONS

Chiang, N.-Y. and V.M. Zavala (2016). "Large-Scale Optimal Control of Interconnected Natural Gas and Electrical Transmission Systems." *Applied Energy* **168**: 226–235.

Clifford, M. and F. Petit (2016). "National Call to Action: The Resilient Infrastructure Initiative." *CIP Report: George Mason University Center for Infrastructure Protection & Homeland Security*.

Hummel, J.R. (2016). "Resilience - Buzz Word or Critical Analytical Issue?" *Phalanx* **49**(3): 60–63.

Jalving, J., S. Abhyankar, K. Kim, M. Hereld and V.M. Zavala. "A Graph-Based Computational Framework for Simulation and Optimization of Coupled Infrastructure Network." *IET Generation, Transmission & Distribution*. (To be published.)

Portante, E.C., J.A. Kavicky, B.A. Craig, L.E. Talaber and S.M. Folga. "Modeling Electric Power and Natural Gas Systems Interdependencies: Application to Natural Hazards." *Journal of Infrastructure Systems*. (To be published.)

Portante, E., B. Craig, J. Kavicky, L. Talaber and S. Folga (2016). "Modeling Electric Power and Natural Gas Systems Interdependencies." *CIP Report: George Mason University Center for Infrastructure Protection & Homeland Security*.

#### **NON-REFEREED PUBLICATION**

Craig, B., E. Portante, J. Kavicky, S. Folga, L. Talaber, C. Macal and M. Clifford (2016). "Integrated Infrastructure Modeling." 84 Military Operations Research Society Symposium, Quantico, VA, June 20–23, 2016.

#### **PRESENTATIONS**

Clifford, M. and C. Macal (2016). "Argonne National Laboratory's Resilient Infrastructure Initiative." 41st Annual Natural Hazards Research and Applications Workshop, Broomfield, CO, July 10–13, 2016.

Clifford, M., F. Petit and D. Brannegan (2016). "Argonne's Resilient Infrastructure Initiative." 2016 Critical Infrastructure Symposium, Society of American Military Engineers (SAME), Charleston, SC, April 3–5, 2016.

Clifford, M. and C. Macal (2016). "SimDependency: Analyzing Cascading Infrastructure Failures." 84th Military Operations Research Society Symposium, Quantico, VA, June 20–23, 2016.

Finster, M. (2016). "Climate Change and the Wastewater Sector." 3rd National Symposium on Resilient Critical Infrastructure, Resilience Week 2016, Chicago, IL, August 16–18, 2016.

Finster, M., J. Phillips and K. Wallace (2016). "Frontline Resilience Perspectives: The Electric Grid." 3rd National Symposium on Resilient Critical Infrastructure, Resilience Week 2016, Chicago, IL, August 16–18, 2016.

Graziano, D.J., J.B. Trail, J.A. Kavicky, S.M. Folga and C.M. Macal (2016). "Human Dimensions of Infrastructure Interdependency and Resilience." 3rd National Symposium on Resilient Critical Infrastructure, Resilience Week 2016, Chicago, IL, August 16–18, 2016. (Also see 2016-156.)

Macal, C.M. (2016). "Modeling & Simulation for Resilient Infrastructure." M&S Congressional Caucus Leadership Summit, Chesapeake, VA, March 9–10, 2016. (Also see 2016-156.)

Petit, F., J. Trail, D. Dickinson and J. Phillips (2016). "Multi-Asset Protection and Resilience Assessment." 3rd National Symposium on Resilient Critical Infrastructure, Resilience Week 2016, Chicago, IL, August 16–18, 2016.

Phillips, J., M. Finster, J. Pillon, J. Trail and F. Petit (2016). "A Framework for State Energy Resilience." 3rd National Symposium on Resilient Critical Infrastructure, Resilience Week 2016, Chicago, IL, August 16–18, 2016.

Thompson, M. and A. Joyce (2016). "SimDependency." 3rd National Symposium on Resilient Critical Infrastructure, Resilience Week 2016, Chicago, IL, August 16–18, 2016.

Ton, D., C. Kelly, J. Kavicky, E. Portante, S. Folga, P. Thimmapuram, A. Tompkins, J. Reilly and G. Conzelmann (2016). "Energy Infrastructure Interdependency Training to Enhance System Operator Situational Awareness and Improve Restoration Response." 3rd National Symposium on Resilient Critical Infrastructure, Resilience Week 2016, Chicago, IL, August 16–18, 2016. (Also see 2016-156.)

Wall, T.A., D.R. Verner and F. Petit (2016). "Climate Change and Infrastructure Adaptation." 3rd National Symposium on Resilient Critical Infrastructure, Resilience Week 2016, Chicago, IL, August 16–18, 2016.

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**2016-136-NO****PRESENTATION**

Liao, S. and H.-T. Chien (2017). “THz Phase Extraction Algorithms for a Novel THz Modulating Interferometric Doppler Radar.” 18th International Conference on Microwave and Terahertz Technology, New York City, NY, October 10–11, 2016.

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**2016-156-NO****PRESENTATIONS**

Graziano, D.J., J.B. Trail, J.A. Kavicky, S.M. Folga and C.M. Macal (2016). “Human Dimensions of Infrastructure Interdependency and Resilience.” 3rd National Symposium on Resilient Critical Infrastructure, Resilience Week 2016, Chicago, IL, August 16–18, 2016. (Also see 2015-177.)

Macal, C.M. (2016). “Modeling & Simulation for Resilient Infrastructure.” M&S Congressional Caucus Leadership Summit, Chesapeake, VA, March 9–10, 2016. (Also see 2015-177.)

Ton, D., C. Kelly, J. Kavicky, E. Portante, S. Folga, P. Thimmapuram, A. Tompkins, J. Reilly and G. Conzelmann (2016). “Energy Infrastructure Interdependency Training to Enhance System Operator Situational Awareness and Improve Restoration Response.” 3rd National Symposium on Resilient Critical Infrastructure, Resilience Week 2016, Chicago, IL, August 16–18, 2016. (Also see 2015-177.)

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**NEXT GENERATION COMPUTING**

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**2014-160-R2****NON-REFEREED PUBLICATION**

Beckman, P., R. Sankaran, C. Catlett, N. Ferrier, R. Jacob and M. Papka (2017). “Waggle: An Open Sensor Platform for Edge Computing.” 2016 IEEE Sensors, Orlando, Florida, October 30–November 2, 2016.

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**2014-167-R2****PRESENTATIONS**

Drewniak, B., F. Chen, R. Jacob and C. Catlett (2014). “Urban Landscapes and Climate Change: Workshop Report.” 11th Symposium on the Urban Environment, American Meteorological Society 94th Annual Meeting, Atlanta, GA, February 2–6, 2014.

Jacob, R. (2016). “Array of Things and the Waggle Platform.” International Symposium on Urban Living Labs, Newcastle University, Newcastle, United Kingdom, February 25–26, 2016.

Jacob, R. (2016). “Informing Urban Decision Making with an Array of Things.” Novel Use of New Technologies for Decision Making: American Geophysical Union Fall Meeting, San Francisco, CA, December 14–18, 2015.

Jacob, R. (2015). “Continuous Sensing of the Urban Boundary Layer.” Air & Waste Management Association: Lake Michigan State Section 2014 Air Quality Management Conference, Chicago, IL, November 12, 2014.

Jacob, R. (2015). “Standard Onboard Sensor Control and Compute for UAVs.” International Society for Atmospheric Research Using Remotely-piloted Aircraft (ISARRA 2015), Norman, OK, May 20–22, 2015.

Sankaran, R., P. Beckman, C. Catlett, R. Jacob and K. Keahey (2015). “Waggle: A Framework for Intelligent Attentive Sensing and Actuation.” American Geophysical Union (AGU) Fall Meeting, San Francisco, CA, December 17, 2014.

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**2014-174-R2****PRESENTATIONS**

Ferrier, N. (2015). “Image-based Methods for 3D Structure.” Institute for Molecular Engineering Seminar, Chicago, IL, June 2015.

Ferrier, N. (2014). “Image-based Metrology.” Imaging Workshop, Taipei, Taiwan, May 2014.

Hereld, M. and N. Ferrier (2016). “Multi-camera Head for High-throughput Digitization of Pinned Insects.” International Conference on Computational Photography, Evanston, IL, May 13–15, 2016.

**2014-181-R2****REFEREED PUBLICATIONS**

Bautista Gomez, L.A. and F. Cappelto (2014). “Detecting Silent Data Corruption through Data Dynamic Monitoring for Scientific Applications.” *Proceedings of the 19th ACM SIGPLAN Symposium on Principals and Practice of Parallel Programming (ACM PPoPP 2014)*, Orlando, FL, February 15–19, 2014, ACM, New York, NY: 381–382.

Berrocal, E., L. Bautista-Gomez, S. Di, Z. Lan and F. Cappelto (2016). “Exploring Partial Replication to Improve Lightweight Silent Data Corruption Detection for HPC Applications.” *Proceedings of the 22nd International European Conference on Parallel and Distributed Computing (EuroPar16)*, Grenoble, France, August 24–26, 2016 **9833**: 419–430.

Berrocal, E., L. Bautista-Gomez, S. Di, Z. Lan and F. Cappelto (2016). “Exploring Partial Replication to Improve Lightweight Silent Data Corruption Detection for HPC Applications.” *Proceedings of the Euro-Par 2016: Parallel Processing*, Grenoble, France, August 24–26, 2016 **9833**: 419–430.

Cappelto, F. (2016). “Lightweight and Accurate Silent Data Corruption Detection in Ordinary Differential Equation Solvers.” *Proceedings of the 22nd International Conference on Euro-Par 2016: Parallel Processing*, New York, NY, August 24–26, 2016 **9833**: 644–656.

Cappelto, F. (2016). “Towards Optimal Online Check-Point Solution under A Two-Level HPC Checkpoint Model.” *IEEE Transactions on Parallel and Distributed Systems* **28**(1): 244–259.

Cappelto, F., A. Geist, W. Gropp, S. Kale, B. Kramer and M. Snir (2014). “Toward Exascale Resilience: 2014 Update.” *Supercomputing Frontiers and Innovations* **1**(1): 5–8.

H. Childs and F. Cappelto. (2016). “Editors of A Special Issue: Visualization and Data Analytics for Scientific Discovery.” *Parallel Computing* **55**: 1.

S. Di and F. Cappelto. (2016). “Adaptive Impact-Driven Detection of Silent Data Corruption for HPC Applications.” *IEEE Transactions on Parallel and Distributed Computing* **27**(10): 2809–2823.

Snir, M., R.W. Wisniewski, J.A. Abraham, S.V. Adve, S. Bagchi, P. Balaji, J. Belak, P. Bose, F. Cappelto, B. Carlson, A.A. Chien, P. Coteus, N.A. Debardeleben, P. Diniz, C. Engelmann, M. Erez, S. Fazzari, A. Geist, R. Gupta, F. Johnson, S. Krishnamoorthy, S. Leyffer, D. Liberty, S. Mitra, T. Munson, R. Schreiber, J. Stearley and E.V. Hensbergen (2014). “Addressing Failures in Exascale Computing.” *International Journal of High Performance Computing Applications* **28**(2): 129–173.

Subasi, O., T. Martsinkevich, F. Zyulkyarov, O. Unsal, J. Labarta and F. Cappelto (2016). “Unified Fault-tolerance Framework for Hybrid Task-parallel Message-passing Applications.” *International Journal of High Performance Computing Applications*: 1–17.

**NON-REFEREED PUBLICATIONS**

Balaprakash, P., L.A. Bautista Gomez, M.S. Bouguerra, S.M. Wild, F. Cappelto and P.D. Hovland (2014). “Energy-Performance Tradeoffs in Multilevel Checkpoint Strategies.” IEEE International Conference on Cluster Computing (CLUSTER), Madrid, Spain, September 22–26, 2014.

Bautista-Gomez, L., A. Gainaru, S. Perarnau, D. Tiwari, S. Gupta, E. Engelmann, F. Cappello and M. Snir (2016). "Reducing Waste in Large Scale Systems through Introspective Analysis." 30th IEEE International Parallel and Distributed Processing Symposium (IPDPS 2016), Chicago, IL, May 23–27, 2016.

Bautista-Gomez, L. and F. Cappello (2015). "Detecting and Correcting Data Corruption in Stencil Applications through Multivariate Interpolation." 1st International Workshop on Fault Tolerant Systems (FTS 2015) at IEEE Cluster 2015, Chicago, IL, September 8–11, 2015.

Bautista-Gomez, L. and F. Cappello (2015). "Detecting Silent Data Corruption for Extreme-Scale MPI Applications." 2015 EuroMPI (Message Passing Interface) Meeting, Bordeaux, France, September 21–23, 2015.

Bautista-Gomez, L. and F. Cappello (2015). "Exploiting Spatial Smoothness in HPC Applications to Detect Silent Data Corruption." 17th IEEE International Conference on High Performance Computing and Communications, New York, NY, August 24–26, 2015.

Bautista Gomez, L.A., F. Cappello, L. Carro, N. DeBardleben, B. Fang, S. Gurumurthi, S. Keckler, K. Pattabiraman, P. Rech and M. Sonza Reorda (2014). "GPGPUs: How to Combine High Computational Power with High Reliability." Design, Automation & Test in Europe (DATE'14), Dresden, Germany, March 24–28, 2014.

Berrocal, E., L. Bautista-Gomez, S. Di, Z. Lan and F. Cappello (2014). "Lightweight Silent Data Corruption Detection Based on Runtime Data Analysis for HPC Applications." IEEE International Parallel & Distributed Processing Symposium, Phoenix, AZ, May 19–23, 2014.

Di, S. and F. Cappello. "Fast Error-bounded Lossy HPC Data Compression with SZ." 30th IEEE International Parallel and Distributed Processing Symposium (IPDPS 2016), Chicago, IL, May 23–27, 2016.

Di, S., E. Berrocal and F. Cappello (2015). "An Efficient Silent Data Corruption Detection Method with Error-Feedback Control and Even Sampling for HPC Applications." 15th IEEE/ACM International Symposium on Cluster, Cloud and Grid Computing (IEEE/ACM CCGrid 2015), Shenzhen, Guangdong, China, May 4–7, 2015.

Di, S., L. Bautista-Gomez and F. Cappello (2015). "Optimization of Multi-Level Checkpoint Model with Uncertain Execution Scales." ACM/IEEE International Conference for High Performance Computing, Networking, Storage and Analysis (SC14), New Orleans, LA, November 16–21, 2014.

Di, S., M.S. Bouguerra, L. Bautista-Gomez and F. Cappello (2014). "Optimization Multi-Level Checkpoint Model for Large Scale HPC Applications." IEEE International Parallel & Distributed Processing Symposium (IPDPS'14), Phoenix, AZ, May 19–23, 2014.

Gainaru, A., M.S. Bouguerra, F. Cappello, M. Snir and W. Kramer (2015). "Navigating the Blue Waters: Online Failure Prediction in the Petascale Era." 29th IEEE International Parallel & Distributed Processing Symposium, Hyderabad, India, May 25–29, 2015.

Gainaru, A., G. Aupy, A. Benoit, F. Cappello, Y. Robert and M. Snir (2015). "Scheduling the I/O of HPC Applications Under Congestion." 2015 IEEE International Parallel and Distributed Processing Symposium (IPDPS), Hyderabad, India, May 25–29, 2015.

Martsinkevich, T., T. Ropars and F. Cappello (2015). "Addressing the Last Roadblock for Message Logging in HPC: Alleviating the Memory Requirement Using Dedicated Resources." 21st International European Conference on Parallel and Distributed Computing (Euro-Par) 2015–8th Workshop on Resiliency in High Performance Computing in Clusters, Clouds and Grids, Vienna, Austria, August 24–28, 2015.

Martsinkevich, T., O. Subasi, O. Unsal, F. Cappello and J. Labarta (2015). "Fault-tolerant Protocol for Hybrid Task-parallel Message-passing Applications." 1st International Workshop on Fault Tolerant Systems (FTS 2015) at IEEE Cluster 2015, Chicago, IL, September 8–11, 2015.

Subasi, O., S. Di, L. Bautista-Gomez, P. Balaprakash, O. Unsal, J. Labarta, A. Cristal and F. Cappello. “Spatial Support Vector Regression to Detect Silent Errors in the Exascale Era.” 16th IEEE/ACM International Symposium on Cluster, Cloud and Grid (CCGRID 2016) Cartagena, Columbia, May 16–19, 2016.

## PRESENTATIONS

Bautista-Gomez, L. (2016). “Opportunities for Online Data Analytics in HPC.” 4th Joint-Laboratory on Extreme Scale Computing Workshop, Bonn, Germany, December 2–4, 2015.

Bautista-Gomez, L. (2015). “Analytic Based Corruption Detection.” 3rd Joint-Laboratory for Extreme-Scale Computing Workshop, Barcelona, Spain, June 29–July 1, 2015.

Bautista-Gomez, L. (2015). “Detecting Silent Data Corruption for Extreme-Scale Application through Data Mining.” 2nd Joint-Laboratory on Extreme Scale Computing Workshop, Chicago, IL, November 24–26, 2014.

Cappello, F. (2017). “Compression of Scientific Data: From Stone Age to Renaissance.” Workshop on Clusters, Clouds, and Data for Scientific Computing (CCDSC) 2016, Lyon, France, October 3–6, 2016.

Cappello, F. (2017). “Scientific Computing and Data Analytics: How to Deal with the Flood of Data.” Distinguished Lecture, Northeastern University, Boston, MA, November 8, 2016.

Cappello, F. (2016). “Lossy Compression of Scientific Datasets.” Joint-Laboratory on Extreme Scale Computing (JLESC) Workshop, Lyon, France, June 27–29, 2016.

Cappello, F. (2016). “Silent Data Corruption Detection and Lossy Compression for Scientific Datasets.” Workshop on Advancing X-cutting Ideas for Computational Climate Science (AXICCS), Rockville, MD September 12–14, 2016.

Cappello, F. (2016). “Trust in Results of Numerical Simulation: The New Challenging Scientific Problem in Reliability.” Conference on Data Analysis: CODA 2016, Santa Fe, NM, March 2–4, 2016.

Cappello, F., E. Constantinescu, P. Hovland, T. Peterka, C. Phillips, M. Snir and S. Wild (2015). “Improving the Trust in Results of Numerical Simulations and Scientific Data Analytics.” SciTech Connect, 2015.

Cappello, F. (2015). “Let’s Forget About ‘Fault Tolerance’ and ‘Resilience’ for HPC; Trusting is the New Challenging Scientific Problem in Reliability.” 1st International Workshop on Fault Tolerant Systems (FTS 2015), Chicago, IL, September 8, 2015.

Di, S., E. Berrocal, L. Bautista-Gomez, K. Heisey, R. Gupta and F. Cappello (2015). “Towards Effective Detection of Silent Data Corruptions for HPC Applications.” International Conference for High Performance Computing, Networking, Storage and Analysis (SC14), New Orleans, LA, November 16–21, 2014.

Gomez, L.B. (2016). “Opportunities for Online Data Analytics in HPC.” Workshop of the Joint-Laboratory on Extreme Scale Computing, Bonn, Germany, December 2–4, 2015.

## 2014-182-R2

### REFEREED PUBLICATIONS

Bicer, T., D. Gursoy, R. Kettimuthu, F. De Carlo and I.T. Foster (2016). “Optimization of Tomographic Reconstruction Workflows on Geographically Distributed Resources.” *Journal of Synchrotron Radiation* **23**(Pt 4): 997–1005. (Also see 2013-165.)

Blaiszik, B.J., K. Chard, J.C. Pruyne, R. Ananthakrishnan, S.J. Tuecke and I.T. Foster (2016). “The Materials Data Facility: Data Services to Advance Materials Science Research.” *JOM: The Journal of the Minerals, Metals & Materials Society* **68**(8): 2045–2052. (Also see 2013-165.)

Foster, I., R. Ananthakrishnan, B. Blaiszik, K. Chard, R. Osborn, S. Tuecke, M. Wilde and J. Wozniak (In press). “Networking Materials Data: Accelerating Discovery at Experimental Facilities.” *Big Data and High Performance Computing: Advances in Parallel Computing*, Vol. 26: L. Grandinetti, et al., eds. (IOS Press Ebooks, Amsterdam, The Netherlands, 2015) pgs.117–132.

Meyer, P.A., S. Socias, J. Key, E. Ransey, E.C. Tjon, A. Buschiazzi, M. Lei, C. Botka, J. Withrow, D. Neau, K. Rajashankar, K.S. Anderson, R.H. Baxter, S.C. Blacklow, T.J. Boggon, A.M. Bonvin, D. Borek, T.J. Brett, A. Cafilisch, C.I. Chang, W.J. Chazin, K.D. Corbett, M.S. Cosgrove, S. Crosson, S. Dhe-Paganon, E. Di Cera, C.L. Drennan, M.J. Eck, B.F. Eichman, Q.R. Fan, A.R. Ferre-D'Amare, J.C. Fromme, K.C. Garcia, R. Gaudet, P. Gong, S.C. Harrison, E.E. Heldwein, Z. Jia, R.J. Keenan, A.C. Kruse, M. Kvensakul, J.S. McLellan, Y. Modis, Y. Nam, Z. Otwinowski, E.F. Pai, P.J. Pereira, C. Petosa, C.S. Raman, T.A. Rapoport, A. Roll-Mecak, M.K. Rosen, G. Rudenko, J. Schlessinger, T.U. Schwartz, Y. Shamoo, H. Sondermann, Y.J. Tao, N.H. Tolia, O.V. Tsodikov, K.D. Westover, H. Wu, I. Foster, J.S. Fraser, F.R. Maia, T. Gonen, T. Kirchhausen, K. Diederichs, M. Crosas and P. Sliz (2016). "Data Publication with the Structural Biology Data Grid Supports Live Analysis." *Nature Communications* **7**: 10882.

Wozniak, J.M., K. Chard, B. Blaiszik, R. Osborn, M. Wilde and I. Foster (2015). "Big Data Staging with MPI-IO for Interactive X-ray Science." *Proceedings of the 2014 IEEE/ACM International Symposium on Big Data Computing (BDC 2014)*, London, United Kingdom, December 8–9, 2014, *IEEE Computer Society*: 26–34.

### NON-REFEREED PUBLICATIONS

Balaprakash, P., V. Morozov, R. Kettimuthu, K. Kumaran and I. Foster (2016). "Improving Data Transfer Throughput with Direct Search Optimization." 45th International Conference on Parallel Processing, Philadelphia, PA, August 16–19, 2016.

Foster, I., K. Chard and S.J. Tuecke (2016). "The Discovery Cloud Accelerating and Democratizing Research on a Global Scale." 2016 IEEE International Conference on Cloud Engineering, Berlin, Germany, April 4–8, 2016. (Also see 2013-165.)

### 2016-135-NO

#### NON-REFEREED PUBLICATION

Romano, P.K. and A.R. Siegel. "Limits on the Efficiency of Event-Based Algorithms for Monte Carlo Neutron Transport." International Conference Mathematics & Computational Methods Applied to Nuclear Science & Engineering, Jeju Island, South Korea, April 16–20, 2017. (To be published.)

### 2016-148-NO

#### NON-REFEREED PUBLICATIONS

Cappello, F., K. Yoshii, H. Finkel and J. Cong (2017). "Re-Form: FPGA-Powered True Codesign Flow for High-Performance Computing In The Post-Moore Era." 2016 Post-Moore's Era Supercomputing (PMES) Workshops, Salk Lake City, UT, November 14, 2016.

Fagan, M., J. Schlachter, K. Yoshii, S. Leyffer, K. Palem, M. Snir, S. M. Wild and C. Enz (2016). "Overcoming the Power Wall by Exploiting Application Inexactness and Emerging COTS Architectural Features." The 29th International IEEE System-on-Chip Conference, Seattle, WA, September 6–9, 2016.

Yoshii, K., H. Finkel and F. Cappello (2017). "Benchmarking Under the Hood of OpenCL FPGA Platforms." 2nd International Workshop on Heterogeneous High-performance Reconfigurable Computing, Salt Lake City, UT, November 14, 2016.

### PRESENTATIONS

Cappello, F. (2016). "Reconfigurable Computing: An Ingredient of Post-Moore Scientific Computing?" Argonne Training Program on Extreme-Scale Computing (ATPESC), St. Charles, IL, August 4, 2016.

Yoshii, K. (2016). "Leveraging Modern SoC FPGAs for Next-generation High-performance Computing Systems." Workshop on FPGAs for Scientific Simulation and Data Analytics, Argonne, IL, January 21–22, 2016.

Yoshii, K., F. Cappello, F. Xia and H. Finkel (2016). "Re-form: Leveraging FPGA Reconfigurability and Floating-Point Capabilities for Next-Generation Computing Systems." Greater Chicago Area Systems Research Workshop (GCASR) Chicago, IL, April 27, 2016.

## NUCLEAR ENERGY SCIENCE AND TECHNOLOGY

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### 2014-177-R2

#### REFEREED PUBLICATIONS

Tentner, A.M., P. Vegendla, A. Obabko, A. Tomboulides, P. Fischer, O. Marin and E. Merzari (2015). "Modeling of Two-Phase Flow in a BWR Fuel Assembly Using a Highly-Scalable Code." *Proceedings of the 16th International Topical Meeting on Nuclear Reactor Thermal Hydraulics (NURETH-16)* Chicago, IL, August 30–September 4, 2015.

Tentner, A., E. Merzari and P. Vagendla (2014). "Computational Fluid Dynamics Modeling of Two-Phase Boiling Flow and Critical Heat Flux." *Proceedings of the 22nd International Conference on Nuclear Engineering ICONE22*, Prague, Czech Republic, July 7–11, 2014, *ASME Proceedings* 4(ICONE22-30844): V004T010A037.

#### NON-REFEREED PUBLICATION

Tentner, A.M., P. Vegendla, A. Tomboulides, A. Obabko, E. Merzari and D.R. Shaver (2016). "Advances in the Development of NEK-2P: A Two-Phase Flow Modeling Capability for the NEK5000 CFD Code." 2016 Computational Fluid Dynamics for Nuclear Reactor Safety CFD4NRS-6, Cambridge, MA, September 14, 2016.

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### 2015-129-R1

#### PRESENTATIONS

Botterud, A. (2016). "Nuclear Energy Competitiveness and the Value of Flexibility in Low-Carbon Electricity Markets." International Atomic Energy Agency, Vienna, Austria, June 16, 2016.

Botterud, A., F. Ganda and F.J. De Sisternes (2015). "Economic and Technical Aspects of Nuclear Energy in Electricity Markets with Renewables." U.S.-Japan Workshop on Compatibility of Nuclear and Renewables with Grid Stability, Economics and Deregulation, Massachusetts Institute of Technology, Cambridge, MA, June 18, 2015. (Also see 2015-124.)

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### 2015-136-R1

#### REFEREED PUBLICATIONS

Benmore, C.J., L.B. Skinner, B. Lee, J.R. Weber, J.B. Parise and M.A. Williamson (2016). "Topological Ordering in Liquid UO<sub>2</sub>." *Journal of Physics: Condensed Matter* 28(1): 015102. (Also see 2015-096.)

Guthrie, M., C.J. Benmore, L.B. Skinner, O.L.G. Alderman, J.K.R. Weber, J.B. Parise and M. Williamson (2017). "Thermal Expansion in UO<sub>2</sub> Determined by High-Energy X-ray Diffraction." *Journal of Nuclear Materials* 479: 19–22.

Skinner, L.B., C.J. Benmore, J.R. Weber, M.A. Williamson, A.J. Tamalonis, A.S. Hebden, T. Wiencek, O.L.G. Alderman, M. Guthrie, L. Leibowitz and J.B. Parise (2015). "Molten Uranium Dioxide Structure and Dynamics." *Science* 346(6212): 984–987. (Also see 2015-096.)

Weber, J.K.R., A.J. Tamalonis, C.J. Benmore, O.L.G. Alderman, S. Sendelbach, A. Hebden and M.A. Williamson (2016). "Aerodynamic Levitator for *in situ* X-ray Structure Measurements on High Temperature and Molten Nuclear Fuel Materials." *Review of Scientific Instruments* 87(7): 073902. (Also see 2015-096.)

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### 2015-145-R1

#### REFEREED PUBLICATIONS

Chen, Y., B. Alexandreanu, W.Y. Chen, K. Natesan, Z. Li, Y. Yang and A.S. Rao (2016). "Cracking Behavior of Thermally Aged and Irradiated CF-8 Cast Austenitic Stainless Steel." *Journal of Nuclear Materials* 466: 560–568.

Chen, Y., W.-Y. Chen, A.S. Rao, Z. Li, Y. Yang, B. Alexandreanu and K. Natesan (2016). "Fracture Resistance of Cast Austenitic Stainless Steels." *Proceedings of the 24th International Conference on Nuclear Engineering (ICONE 24)*, Charlotte, NC, June 26–30, 2016.

Li, M., M.K. Miller and W.Y. Chen (2015). "Phase Stability in Thermally-aged CASS CF-8 under Heavy Ion Irradiation." *Journal of Nuclear Materials* **462**: 214–220.

Li, Z., W.-Y. Lo, Y. Chen, J. Pakarinen, Y. Wu, T. Allen and Y. Yang (2016). "Irradiation Response of Delta Ferrite in As-cast and Thermally Aged Cast Stainless Steel." *Journal of Nuclear Materials* **466**: 201–207.

#### **NON-REFEREED PUBLICATIONS**

Chen, Y., W.-Y. Chen, X. Zhang, B. Alexandreanu, K. Natesan, C. Xu, Y. Yang and A. Rao. "Fracture Toughness and Deformation Behavior of Cast Austenitic Stainless Steels After Thermal Aging." 2017 ASME Pressure Vessels & Piping Conference, Waikoloa Village, HI, July 16–20, 2017. (To be published.)

Chen, Y., W.Y. Chen, Z. Li, Y. Yang, A.S. Rao, B. Alexandreanu and K. Natesan (2016). "Cracking of Cast Austenitic Stainless Steels after Thermal Aging and Neutron Irradiation." The International Light Water Reactor Materials Reliability Conference, Chicago, IL, August 1–4, 2016.

Chen, Y., B. Alexandreanu, W. Chen, Z. Li, Y. Yang, K. Natesan and A. Rao (2015). "Crack Growth Rate and Fracture Toughness J-R Curve Tests on Irradiated Cast Austenitic Stainless Steels." 17th International Conference on Environmental Degradation of Materials in Nuclear Power Systems—Water Reactors, Ottawa, Ontario, Canada, August 9–13, 2015.

#### **PRESENTATION**

Chen, W.-Y., Y. Chen, X. Zhang, C. Xu, M.A. Kirk and M. Li (2016). "TEM Characterization of Neutron-irradiated Cast Austenitic Stainless Steel at 320°C to 0.08 dpa." TMS 2016 145th Annual Meeting and Exhibition, Nashville, TN, February 14–18, 2016.

#### **2016-140-NO**

##### **NON-REFEREED PUBLICATIONS**

Heifetz, A., S. Bakhtiari, J. Lu and A. Bentivegna. "Nondestructive Evaluation of Alkali Silica Reaction in High-Strength Concrete for Aging Structures Sustainability." American Nuclear Society Annual Meeting 2017, June 11–15, 2017. (To be published.)

Heifetz, A., S. Bakhtiari, J. Lu, I.S. Aranson, V.M. Vinokur and A.F. Bentivegna (2016). "Development of Microwave and Impedance Spectroscopy Methods for *in situ* Nondestructive Evaluation of Alkali Silica Reaction in Concrete." 43rd Annual Review of Progress in Quantitative Nondestructive Evaluation, Atlanta, GA, July 17–22, 2016.

Heifetz, A., S. Bakhtiari, I. Aronson, V. Vinokour, J. Lu and A. Bentivegna (2016). "Development of Non-destructive Methods for Detection of Alkali Silica Reaction in Concrete Structures." 43rd Annual Review of Progress in Quantitative Nondestructive Evaluation, Atlanta, GA, July 17–22, 2016.

#### **2016-158-NO**

##### **REFEREED PUBLICATIONS**

Rotsch, D.A., K. Alford, J.L. Bailey, D.L. Bowers, T. Brossard, M.A. Brown, S.D. Chemerisov, D. Ehst, J. Greene, R.G. Gromov, J.J. Grudzinski, L. Hafenrichter, A.S. Hebden, W. Henning, T.A. Heltemes, J. Jerden, C.D. Jonah, M. Kalensky, J.F. Krebs, V. Makarashvili, B. Micklich, J. Nolen, K.J. Quigley, J.F. Schneider, N.A. Smith, D.C. Stepinski, Z. Sun, P. Tkac, G.F. Vandegrift, M.J. Virgo, K.A. Wesolowski and A.J. Youker (2017). "Production of Medical Isotopes with Electron Linacs." *Proceedings of the North American Particle Accelerator Conference (NAPAC)* Chicago, IL, October 9–14, 2016.

Rotsch, D.A., M.A. Brown, J.A. Nolen, R. Gromov, S.D. Chemerisov and G.F. Vandegrift (2016). "Purification of Electron LINAC Produced Scandium-47." *Proceedings of the 16th International Workshop on Targetry and Target Chemistry (WTTTC16)*, Santa Fe, NM, August 29–September 1, 2016.

**PRESENTATIONS**

Brown, M.A. (2016). "Radiochemistry & Medical Isotope Production at Argonne." Oregon State University, Corvallis, OR, July 19, 2016.

Rotsch, D.A. (2017). "Production of Medical Isotopes with Electron Linacs." North American Particle Accelerator Conference (NAPAC) Chicago, IL, October 9–14, 2016.

Rotsch, D.A. (2016). "Purification of Electron LINAC Produced Scandium-47." 16th International Workshop on Targetry and Target Chemistry (WTTTC16), Santa Fe, NM, August 29–September 1, 2016.

**UNIVERSE AS THE LAB (ULAB)**

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**2016-143-NO****REFEREED PUBLICATIONS**

Bender, A.N., P.A.R. Ade, A.J. Anderson, J. Avva, Z. Ahmed, K. Arnold, J.E. Ausermann, R. Basu Thakur, B.A. Benson, L.E. Bleem, K. Byrum, J.E. Carlstrom, F.W. Carter, C.L. Chang, G. Wang and V. Yefremenko (2016). "Integrated Performance of a Frequency Domain Multiplexing Readout in the SPT-3G Receiver." *Proceedings of the 2016 SPIE Astronomical Telescopes and Instrumentation*, Edinburgh, Scotland, July 20, 2016 9914. (Also see 2013-219.)

Ding, J., P.A.R. Ade, A.J. Anderson, J. Avva, Z. Ahmed, K. Arnold, J.E. Ausermann, A.N. Bender, B.A. Benson, L.E. Bleem, K. Byrum, J.E. Carlstrom, F.W. Carter, C.L. Chang, D. Czaplewski, R. Divan, R. Gannon, T. Khaire, C.S. Miller, S. Padin, V. Novosad, J. Pearson, C.M. Posada, L. Stan, G. Wang and V. Yefremenko (2017). "Optimization of Transition Edge Sensor Arrays for Cosmic Microwave Background Observations with the South Pole Telescope." *IEEE Transactions on Applied Superconductivity* **27**(4): 2100204. (Also see 2013-219.)

Posada, C.M., P.A.R. Ade, A.J. Anderson, J. Avva, Z. Ahmed, K.S. Arnold, J. Ausermann, A.N. Bender, B.A. Benson, L. Bleem, K. Byrum, J.E. Carlstrom, F.W. Carter, C.L. Chang, D.A. Czaplewski, J. Ding, R.N.S. Divan, R.N. Gannon, T. Khaire, S. Lendinez Escudero, C.S. Miller, V. Novosad, J.E. Pearson, L. Stan, G. Wang and V. Yefremenko (2016). "Large Arrays of Dual-polarized Multichroic TES Detectors for CMB Measurements with the SPT-3G Receiver." *Proceedings of SPIE –The International Society for Optical Engineering* **9914**(Part 1). (Also see 2013-219.)

**PRESENTATIONS**

Carlstrom, J. and C. Chang (2016). "Superconducting CMB Detectors at Argonne." Towards A Next Space Probe for CMB Observations and Cosmic Origins Exploration Workshop, Geneva, Switzerland, May 17–20, 2016.

Chang, C.L. (2016). "Superconducting Detectors and Studies of the Cosmic Microwave Background." APS-CNM Users Meeting, Argonne National Laboratory, Argonne, IL, May 9–12, 2016 (Also see 2013-219.)

Khaire, T., F. Carter, S. Lendinez, J. Ding, C. Posada, A. Bender, G. Wang, V. Yefremenko, J. Pearson, S. Padin, C. Chang, A. Hoffmann and V. Novosad (2016). "Dependence of Superconducting Properties of NbN Thin Films on Sputtering Parameters." American Physical Society March Meeting, Baltimore, MD, March 14–18, 2016. (Also see 2013-219.)

Posada, C. (2016). "Microfabrication of Arrays of Superconducting Transition Edge Sensors for CMB Measurements." American Physical Society March Meeting 2016, Baltimore, MD, March 14–18, 2016.

**2016-170-NO****REFEREED PUBLICATIONS**

Bayliss, M.B., J. Ruel, C.W. Stubbs, S.W. Allen, D.E. Applegate, M.L.N. Ashby, M. Bautz, B.A. Benson, L.E. Bleem, S. Bocquet, J.E. Carlstrom and C.L. Chang (2017). "Spt-Gmos: A Gemini/Gmos-South Spectroscopic Survey of Galaxy Clusters in the Spt-Sz Survey." *Astrophysical Journal. Supplement Series* **227**(1): 3.

De Haan, T., B.A. Benson, L.E. Bleem, S.W. Allen, D.E. Applegate, M.L.N. Ashby, M.W. Bautz, M. Bayliss, S. Bocquet, M. Brodwin, J.E. Carlstrom and C.L. Chang (2017). "Cosmological Constraints from Galaxy Clusters in the 2500 Square-degree SPT-SZ Survey." *Astrophysical Journal* **832**(1): 95.

Gupta, N., A. Saro, J.J. Mohr, B.A. Benson, S. Bocquet, R. Capasso, J.E. Carlstrom, I. Chiu, T.M. Crawford and T. De Haan (2017). “High Frequency Cluster Radio Galaxies: Luminosity Functions and Implications for SZE Selected Cluster Samples.” *Monthly Notices of the Royal Astronomical Society* **467**(3): 3737–3750.

Li, N., M.D. Gladders, E.M. Rangel, M.K. Florian, L.E. Bleem, K. Heitmann, S. Habib and P. Fasel (2016). “PICS: Simulations of Strong Gravitational Lensing in Galaxy Clusters.” *Astrophysical Journal* **828**(1): 54.

Nurgaliev, D., M. McDonald, B.A. Benson, L. Bleem, S. Bocquet, W.R. Forman, G.P. Garmire, N. Gupta, J. Hlavacek-Larrondo, J.J. Mohr, D. Nagai, D. Rapetti, A.A. Stark, C.W. Stubbs and A. Vikhlinin. “Testing for X-ray-SZ Differences and Redshift Evolution in the X-ray Morphology of Galaxy Clusters.” *Astrophysical Journal*. (To be published.)

Saro, A., S. Bocquet, L. Bleem, V. Vikram, J. Mohr, E. Rozo, S. Dodelson, B.A. Benson, E.S. Rykoff, T.M.C. Abbott and F.B. Abdalla. “Optical-SZE Scaling Relations for DES Optically Selected Clusters within the SPT-SZ Survey.” *Monthly Notices of the Royal Astronomical Society*. (To be published.)

Zenteno, A., J.J. Mohr, S. Desai, B. Stalder, A. Saro, J.P. Dietrich, M. Bayliss, S. Bocquet, I. Chiu and A.H. Gonzalez (2017). “Galaxy Populations in the 26 Most Massive Galaxy Clusters in the South Pole Telescope SZE Survey.” *Monthly Notices of the Royal Astronomical Society* **462**(1): 830–843.

#### 2016-171-N0

##### NON-REFEREED PUBLICATION

Bleem, L.E., O. Dore, M.W. Werner, M. Ashby, P. Banerjee, N. Battaglia, J. Bauer, R.A. Benjamin, J. Bock and A. Boogert (2016). “Science Impacts of the SPHEREx All-Sky Optical to Near-Infrared Spectral Survey: Report of a Community Workshop Examining Extragalactic, Galactic, Stellar and Planetary Science.” *Astrophysics With The SphereX All Sky Spectral Survey*, Pasadena, CA, February 24–26, 2016.

#### 2016-172-N0

##### REFEREED PUBLICATION

Frontiere, N., C.D. Raskin and J.M. Owen (2017). “CRKSPH—A Conservative Reproducing Kernel Smoothed Particle Hydrodynamics Scheme.” *Journal of Computational Physics* **332**: 160–209.

## DIRECTOR’S GRAND CHALLENGE – DATA-DRIVEN SCIENCE

#### 2013-165-R3

##### REFEREED PUBLICATIONS

Bicer, T., D. Gursoy, R. Kettimuthu, F. De Carlo and I.T. Foster (2016). “Optimization of Tomographic Reconstruction Workflows on Geographically Distributed Resources.” *Journal of Synchrotron Radiation* **23**(Pt 4): 997–1005. (Also see 2014-182.)

Blaiszik, B.J., K. Chard, J.C. Pruyne, R. Ananthakrishnan, S.J. Tuecke and I.T. Foster (2016). “The Materials Data Facility: Data Services to Advance Materials Science Research.” *JOM: The Journal of the Minerals, Metals & Materials Society* **68**(8): 2045–2052. (Also see 2014-182.)

Chen, J., L. Wang and M. Anitescu. “A Parallel Tree Code for Computing Matrix-Vector Products with the Matern Kernel.” *ACM Transactions on Mathematical Software*. (To be published.)

Habib, S., A. Pope, H. Finkel, N. Frontiere, K. Heitmann, D. Daniel, P. Fasel, V. Morozov, G. Zagaris, T. Peterka, V. Vishwanath, Z. Lukic, S. Sehrish and W.-K. Liao (2016). “HACC: Simulating Sky Surveys on State-of-the-Art Supercomputing Architectures.” *New Astronomy* **42**: 49–65.

Heitmann, K., E. Lawrence, J. Kwan, S. Habib and D. Higdon (2014). “The Coyote Universe Extended: Precision Emulation of the Matter Power Spectrum.” *Astrophysical Journal* **780**(1): 111.

Heitmann, K., S. Habib, H. Finkel, N. Frontiere, A. Pope, V. Morozov, S. Rangel, E. Kovacs, J. Kwan, N. Li, S. Rizzi, J. Insley, V. Vishwanath, T. Peterka, D. Daniel, P. Fasel and G. Zagaris (2014). “Large-Scale Simulations of Sky Surveys.” *Computing in Science & Engineering* **16**(5): 14–23.

Heitmann, K., D. Bingham, E. Lawrence, S. Bergner, S. Habib, D. Higdon, A. Pope, R. Biswas, H. Finkel, N. Frontiere and S. Bhattacharya (2016). “The Mira-Titan Universe: Precision Predictions for Dark Energy Surveys.” *Astrophysical Journal* **820**(2): 108.

Kwan, J., S. Bhattacharya, K. Heitmann and S. Habib (2013). “Cosmic Emulation: The Concentration-Mass Relation for  $\Lambda$ CDM Universes.” *Astrophysical Journal* **768**(2): 123.

Sunayama, T., N. Padmanabhan, K. Heitmann, S. Habib and E. Rangel (2016). “Efficient Construction of Mock Catalogs for Baryon Acoustic Oscillation Surveys.” *Journal of Cosmology and Astroparticle Physics* **2016**(5): 051.

Upadhye, A.R., J. Kwan, A. Pope, K. Heitmann, S. Habib, H. Finkel and N. Frontiere (2016). “Redshift-Space Distortions in Massive Neutrino and Evolving Dark Energy Cosmologies.” *Physical Review D: Particles, Fields, Gravitation, and Cosmology* **93**(6): 063515.

### NON-REFEREED PUBLICATIONS

Bicer, T., D. Gürsoy, R. Kettimuthu, F. De Carlo, G. Agrawal and I.T. Foster (2015). “Rapid Tomographic Image Reconstruction via Large-Scale Parallelization.” Euro-Par 2015: Parallel Processing—*Proceedings of the 21st International Conference on Parallel and Distributed Computing*, Vienna, Austria, August 24–28, 2015.

Foster, I., K. Chard and S.J. Tuecke (2016). “The Discovery Cloud Accelerating and Democratizing Research on a Global Scale.” 2016 IEEE International Conference on Cloud Engineering, Berlin, Germany, April 4–8, 2016. (Also see 2014-182.)

Foster, I. (2014). “Networking Materials Data.” 2014 International Advanced Research Workshop on High Performance Computing: From Clouds and Big Data to Exascale and Beyond, Centraro, Italy, July 7–11, 2014.

Malik, T., K. Chard and I. Foster (2014). “Benchmarking Cloud-based Tagging Services.” 6th International Workshop on Cloud Data Management, 30th IEEE International Conference on Data Engineering, Chicago, IL, March 31–April 4, 2014.

Wozniak, J.M., K. Chard, B. Blaiszik, R. Osborn, M. Wilde and I. Foster (2016). “Big Data Remote Access Interfaces for Light Source Science.” 2nd IEEE/ACM International Symposium on Big Data Computing, Limassol, Cyprus, December 7–10, 2015.

Wozniak, J.M., T.G. Armstrong, K.C. Maheshwari, D.S. Katz, M. Wilde and I.T. Foster (2016). “Interlanguage Parallel Scripting for Distributed Memory Scientific Computing.” 10th Workshop on Workflows in Support of Large-Scale Science, Austin, TX, November 15, 2015.

Wozniak, J.M., T.G. Armstrong, S.J. Krieger, K. Maheshwari, M. Wilde and I.T. Foster (2014). “Mega Python: Scalable Interlanguage Scripting for Scientific Computing.” Super Computer Conference (SC13), Denver, CO, November 18–22, 2013.

Wozniak, J.M., T.G. Armstrong, D.S. Katz, M. Wilde and I.T. Foster (2014). “Toward Computational Experiment Management via Multi-language Applications.” 2014 ASCR Workshop on Software Productivity for Extreme-Scale Science, Rockville, MD, January 13–14, 2014.

### PRESENTATIONS

Almer, J., S. Stock and R. Suter (2014). “Studies of Complex Materials Using High-Energy X-rays.” Diamond Light Source, Oxfordshire, United Kingdom, May 29, 2014.

Blaiszik, B., K. Chard, R. Anathakrishnan, S. Tuecke and I. Foster (2015). “Globus Data Publication Services.” US-UK Workshop on Materials Theory and Simulation, Argonne National Laboratory, Argonne, IL, January 26, 2015.

Blaiszik, B., K. Chard, S. Tuecke and I. Foster (2015). “Globus: Research Data Management-as-a-Service.” Opportunities in Materials Informatics (OMI), University of Wisconsin-Madison, Madison, WI, February 9, 2015.

Blaiszik, B., K. Chard, H. Pruyne, R. Ananthakrishnan, S. Tuecke and I. Foster (2014). “Globus Scientific Data Services Current and Future.” Materials Genome Initiative Materials Data Workshop, Air Force Research Laboratory, Dayton, OH, July 15, 2014.

Foster, I. (2014). “An Architecture for a National Data Service.” 1st National Data Service Consortium Workshop, Boulder, CO, June 12–13, 2014.

Foster, I. (2014). “Networking Materials Data.” Workshop on Building an Integrated MGI Accelerator Network, Atlanta, GA, June 2014.

Foster, I. (2014). “Publication Services for Materials.” 2014 Seminar at the PRISMS Center, University of Michigan, Ann Arbor, MI, June 24, 2014.

Habib, S. (2014). “Computing the Universe: How to Stuff a Supercomputer Inside a Laptop.” Carnegie Mellon University, Pittsburgh, PA, April 2014.

Habib, S. (2014). “HACCing the Universe on the BG/Q.” 20th Annual ScicomP 2014 BG Consortium Meeting, Chicago, IL, May 27–30, 2014.

Habib, S. (2014). “Thoughts on Next-Generation Computing and LSST DESC.” LLST DESC Dark Energy Science Collaboration Meeting, Philadelphia, PA, June 2014.

Heitmann, K. (2014). “Cosmological Simulations for Large-Scale Sky Surveys.” Oak Ridge Leadership Computing Facility (OLCF) Users Meeting, Oak Ridge, TN, July 22–24, 2014.

Krogstad, M., R. Osborn, S. Rosenkranz, K. Taddei, J. Allred and O. Chmaissem (2015). “Single Crystal Diffraction X-ray Scattering Using Continuous Rotation.” American Physical Society March Meeting, San Antonio, TX, March 2–6, 2015.

Osborn, R. and S. Rosenkranz (2015). “Advances in Single Crystal Diffuse Scattering.” 21st National Synchrotron Radiation Research Center User’s Meeting, Hsinchu, Taiwan, September 9–10, 2015.

Osborn, R., P. Zapol, A. Ngo, S. Rosenkranz, J. Allred, O. Chmaissem, M. Krogstad, J. Morris, K. Taddei, D. Bugaris, G. Jennings, P. Chaupas, X. Zhang, I. Foster, M. Wilde, J. Wozniak, M. Anitescu, K. Petra, R. Ananthakrishnan, B. Blaiszik, K. Chard and B. Allen (2015). “Big Data: Beyond the Workflow.” 2015 Workshop on Grand Challenges for Neutrons and Supercomputing, Argonne, IL, March 30–31, 2015.

Osborn, R., P. Zapol, A. Ngo, S. Rosenkranz, J. Allred, O. Chmaissem, M. Krogstad, J. Morris, K. Taddei, D. Bugaris, G. Jennings, P. Chaupas, X. Zhang, I. Foster, M. Wilde, J. Wozniak, M. Anitescu, K. Petra, R. Ananthakrishnan, B. Blaiszik, K. Chard and B. Allen (2015). “Single Crystal Diffuse Scattering: Beyond the Workflow.” APS/CNM User’s Meeting, Argonne, IL, May 11–14, 2015.

Rosenkranz, S. (2014). “Quantitative Analysis of the Diffuse Scattering from a Bilayer Manganite.” American Physical Society March Meeting 2014, Denver, CO, March 3–7, 2014.

Wozniak, J.M. (2014). “Parallel Scripting for Beamline Science: Connecting Big Data and HPC.” 2014 BES Facilities Computing Working Group Technical Meeting, Berkeley, CA, February 20, 2014.

Wozniak, J.M. (2014). “Studies in Big Data and HPC from X-ray Crystallography.” 1st Workshop of the INRIA-Illinois-ANL-BSC Joint Laboratory on Extreme Scale Computing, Sophia Antipolis, France, June 9–11, 2014.

## OTHER NOVEL R&D

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### 2014-185-R2

#### REFEREED PUBLICATIONS

Gutierrez, A., S. Kim, T.T. Fister and C.S. Johnson (2017). “Microwave-assisted Synthesis of NaCoPO<sub>4</sub> Red-phase and Initial Characterization as a High Voltage Cathode for Sodium-ion Batteries.” *ACS Applied Materials & Interfaces* **9**(5): 4391–4396.

Karan, N.K., M.D. Slater, F. Dogan, D. Kim, C.S. Johnson and M. Balasubramanian (2014). "Operando Structural Characterization of the Lithium-Substituted Layered Sodium-Ion Cathode Material  $P2\text{-Na}_{0.85}\text{Li}_{0.17}\text{Ni}_{0.21}\text{Mn}_{0.64}\text{O}_2$  by X-ray Absorption Spectroscopy." *Journal of the Electrochemical Society* **161**(6): A1107–1115.

Lee, E., S. Sahgong, C.S. Johnson and Y. Kim (2015). "Comparative Electrochemical Sodium Insertion/Extraction Behavior in Layered  $\text{Na}_x\text{VS}_2$  and  $\text{Na}_x\text{TiS}_2$ ." *Electrochimica Acta* **143**: 272–277.

Lee, E., D.E. Brown, E.E. Alp, Y. Ren, J. Lu, J.-J. Woo and C.S. Johnson (2015). "New Insights into the Performance Degradation of Fe-based Layered Oxides in Sodium-Ion Batteries: Instability of  $\text{Fe}^{3+}/\text{Fe}^{4+}$  Redox in  $\alpha\text{-NaFeO}_2$ ." *Chemistry of Materials* **27**(19): 6755–6764.

Lee, E., J. Lu, Y. Ren, X.Y. Luo, X.Y. Zhang, J.G. Wen, D. Miller, A. DeWahl, S. Hackney, B. Key, D. Kim, M.D. Slater and C.S. Johnson (2014). "Layered  $\text{P}_2/\text{O}_3$  Intergrowth Cathode: Toward High Power Na-Ion Batteries." *Advanced Energy Materials* **4**(17): 1400458.

Zhou, D., M. Peer, Z. Yang, V.G. Pol, F. Dogan-Key, J. Jorne, H. Foley and C.S. Johnson (2016). "Long Cycle Life Microporous Spherical Carbon Anodes for Sodium-ion Batteries Derived from Furfuryl Alcohol." *Journal of Materials Chemistry A: Materials for Energy and Sustainability* **4**(17): 6271–6275.

Zhou, D., M. Slater, D. Kim, E. Lee, J. Jorne and C.S. Johnson (2014). "SnSb Carbon Composite Anode in a  $\text{SnSb}_x\text{C}/\text{NaNi}_{1/3}\text{Mn}_{1/3}\text{Fe}_{1/3}\text{O}_2$  Na-Ion Battery." *ECS Transactions: Battery Chemistries Beyond Lithium Ion* **58**(12): 59–64.

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Gutierrez, A., P. Senguttuvan, S. Kim, T. Fister and C.S. Johnson (2016). "Novel Polyanion Cathode Materials For Sodium-ion Batteries." 2nd International Conference on Sodium Batteries, Chandler, AZ, October 7–9, 2016.

Gutierrez, A., P. Senguttuvan, S. Lapidus, S. Kim, T. Fister and C.S. Johnson (2016). "Synthesis and Evaluation of  $\text{NaMPO}_4$  (M=Fe, Mn, Co) Framework Polyanion Cathodes for Sodium-ion Batteries." 18-IMLB International Meeting on Lithium Batteries, Chicago, IL, June 19–24, 2016.

Johnson, C.S. (2017). "SnO Carbon Composite as Superior Anode in Sodium-ion Batteries." 2016 PRIME Conference; 230th Electrochemical Society Meeting, Honolulu, HI, October 2–7, 2016.

Johnson, C.S., E. Lee, D. Zhou and M. Slater (2015). "Na-ion Battery Technologies: Present Status and Update." 226th Electrochemical Society (ECS) Meeting, Cancun, Mexico, October 4–10, 2014.

Johnson, C.S. (2014). "Emergence of Na-Ion Battery Technologies." 248th American Chemical Society Meeting, San Francisco, CA, August 10, 2014.

Johnson, C.S. (2014). "Na-ion Batteries: A New Energy Storage Focus." International Society of Electrochemistry Society (ISE) Meeting, Lausanne, Switzerland, August 30, 2014.

Lee, E., D.E. Brown, E.E. Alp, Y. Ren, J. Lu, J.-J. Woo and C.S. Johnson (2016). "Chemical and Structural Quasi-reversibility in Layered  $\text{NaFeO}_2$ ." 2nd International Conference on Sodium Batteries, Chandler, AZ, October 7–9, 2015.

Lee, E., Z. Chen, G. Xu, D. Zhou, C.S. Johnson, J. Barker, R.J. Heap, N. Roche, C. Tan, R. Sayers, J. Whitley and Y. Liu (2016). "Sodium-ion Battery Materials: Advancement to Commercialization." 47th Power Sources Symposium, Orlando, FL, June 13–16, 2016.

Lee, E., D. Zhou, M. Slater and C.S. Johnson (2015). "Energy Storage Using Sodium-ion Batteries (SIB)." Beyond Li-ion Batteries Conference III, Oak Ridge, TN, June 2–4, 2015.

Lee, E. (2014). "Layered  $\text{P}_2/\text{O}_3$  Intergrowth Cathode: Toward High Capacity and High Power Na-Ion Batteries." 17th International Meeting on Lithium Batteries (IMLB) Meeting, Como, Italy, June 10–14, 2014.

Senguttuvan, P., A. Gutierrez, S.-D. Han, S. Tepacevic, C.K. Lin, S. Lapidus, Y. Ren, A.K. Burrell and C.S. Johnson (2015). "NaCoPO<sub>4</sub> Cathodes for Sodium Batteries and Nanostructured Bi-layered V<sub>2</sub>O<sub>5</sub> for Multivalent Battery Applications." Beyond Li-ion Batteries Conference VIII, Oak Ridge, TN, June 2–4, 2015.

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#### 2015-174-R1

##### PRESENTATIONS

Marshall, C.L. (2016). "Enhancing the Stability/Performance of Catalysts via Atomic Layer Deposition." University of Kansas, Lawrence, KS, November 13, 2015.

Marshall, C.L. (2015). "Atomic Layer Deposition Overcoating: Tuning Catalyst Selectivity for Biomass Conversion." North American Catalysis, Pittsburgh, PA, June 14–19, 2015.

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#### 2015-181-R1

##### REFEREED PUBLICATION

Kasthuri, N. (2017). "High-Performance Computing in Neuroscience for Data-Driven Discovery, Integration, and Dissemination." *Neuron* **92**(3): 628–631.

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Kasthuri, N. (2016). "Exascale Computing and The Brain Mapping." House of Representatives, Washington, DC, April 11, 2016.

Kasthuri, N. (2016). "Global Brain Initiatives." Rockefeller University, New York City, NY, September 19, 2016.

Kasthuri, N. (2016). "Sci-Foo." Google Science Fest, San Francisco, CA, July 22–24, 2016.

Kasthuri, N. (2015). "Tales From The Trenches of Connectomics." University of Iowa, Iowa City, IA, September 15, 2015.

Kasthuri, N. (2016). "Towards Complete Maps of Brains with Synchrotron Source X-ray Microscopy and Automated Serial Electron Microscopy." Center for Nanoscale Materials User Meeting, Argonne National Laboratory, Argonne, IL, May 8–11, 2016.

Kasthuri, N. (2016). "Towards Complete Maps of Brains with Synchrotron Source X-ray Microscopy and Automated Serial Electron Microscopy." Fermi National Accelerator Laboratory, Batavia, IL, February 10, 2016.

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#### 2016-120-NO

##### PRESENTATIONS

Lin, J., S. Guha, C. Chen and L. Stan. "Design of the Insulator-to-Metal Transition Properties in Vanadium Oxides for the Joule-Heating Devices." Material Research Society (MRS) Spring 2017, Phoenix, AZ, April 17–21, 2017. (To be published.)

Sonde, S., M. Jerry, Y. Liu, N. Shukla, S. Sankaranarayanan, S. Datta and S. Guha (2017). "Cu:HfO<sub>2</sub> Selector Switches for 3D Crosspoint Memory." Center for Low Energy Systems Technology Annual Review University of Notre Dame, South Bend, IN, August 10–11, 2016.

Sonde, S., K. Sasikumar, Y. Liu, J. Lin, A. Annadi, S. Sankaranarayanan and S. Guha (2017). "Low Voltage Nano-Ionics Based Selector Devices Using Doped HfO<sub>2</sub> For Application In 3D Crosspoint Memories." Materials Research Society (MRS) Spring Meeting, Phoenix, AZ, April 17–21, 2017.

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#### 2016-121-NO

##### PRESENTATIONS

Guest, J.R. (2016). "Atomic-Scale Imaging of Optically-Active Nanoscale Systems." Physics Colloquium, Emory University, Atlanta, GA, September 27, 2016.

Guest, J.R. (2016). "Atomic-Scale Imaging of Optically-Active Nanoscale Systems." Institute of Materials Science and Engineering Seminar, Washington University, St. Louis, MO, September 19, 2016.

Guest, J.R. (2016). "Atomic-Scale Imaging of Optically-Active Nanoscale Systems." Nano Seminar, South Dakota School of Mines and Technology, Rapid City, SD, April 7, 2016.

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**2016-190-NO**

**REFEREED PUBLICATION**

Kang, J., S.A. Wells, J.D. Wood, J.-H. Lee, X. Liu, C.R. Ryder, J. Zhu, J.R. Guest, C.A. Husko and M.C. Hersam (2017). "Stable Aqueous Dispersions of Optically and Electronically Active Phosphorene." *Proceedings of the National Academy of Sciences of the United States of America*, October 18, 2016 **113**(42): 11688-11693.

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# PUBLICATIONS AND PRESENTATIONS II

## (Arising from LDRD Projects Completed Prior to FY 2016 but Published/Delivered During FY 2016)

[Dates following author names indicate the *fiscal year* of appearance.]

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### 2011-005

#### REFEREED PUBLICATION

Smylie, M.P., M. Leroux, V. Mishra, L. Fang, K.M. Taddei, O. Chmaissem, H. Claus, A. Kayanil, A. Snezhko, U. Welp and W.-K. Kwok (2016). "Effect of Proton Irradiation on Superconductivity in Optimally Doped  $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$  Single Crystals." *Physical Review B: Condensed Matter* **93**(11): 115–119.

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### 2011-012

#### REFEREED PUBLICATION

Weber, J.K.R., C.J. Benmore, K.J. Suthar, A.J. Tamalonis, O.L.G. Alderman, S. Sendelbach, V. Kondev, J.L. Yarger, C.A. Rey and S.R. Byrn (2016). "Using Containerless Methods to Develop Amorphous Pharmaceuticals." *Biochimica et Biophysica Acta. G, General Subjects* **1861** (1 Pt B): 3686–3692.

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### 2011-023

#### REFEREED PUBLICATIONS

Calder, S.A., J.W. Kim, G. Cao, C. Cantoni, A.F. May, H. Cao, A.A. Aczel, M. Matsuda, Y. Choi, D. Haskel, B.C. Sales, D. Mandrus, M.D. Lumsden and A.D. Christianson (2016). "Evolution of Competing Magnetic Order in the  $J_{\text{eff}}=1/2$  Insulating State of  $\text{Sr}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_4$ ." *Physical Review B: Condensed Matter* **92**: 165128.

Pascarelli, S., D. Haskel and N. Ishimatsu (2016). "Frontiers of High Pressure X-ray Absorption Spectroscopy." *High Pressure Research* **36**(3): 235–236.

Souza-Neto, N.M., D. Haskel, R.D. dos Reis and F.C.G. Gandra (2016). "Combining State of the Art experiment and Ab-initio Calculations for a Better Understanding of the Interplay Between Valence, Magnetism and Structure in Eu Compounds at High Pressure." *High Pressure Research* **36**(3): 360–370.

Sun, F., N.N. Li, B.J. Chen, Y.T. Jia, L.J. Zhang, W.M. Li, G.Q. Zhao, L.Y. Xing, G. Fabbris, W.Y. Gang, Z. Deng, Y.J. Uemura, H.K. Mao, D. Haskel, W.G. Yang and C.Q. Jin (2016). "Pressure Effect on the Magnetism of New Diluted Magnetic Semiconductor  $(\text{Ba}_{1-x}\text{K}_x)(\text{Zn}_{1-y}\text{Mn}_y)_2\text{As}_2$  with Decoupled Spin and Charge Doping." *Physical Review B: Condensed Matter* **93**(22): 224403.

Tan, X., G. Fabbris, D. Haskel, A.A. Yaroslavtsev, H. Cao, C.M. Thompson, K. Kovnir, A.P. Menushenkov, R.V. Chernikov, V.O. Garlea and M. Shatruk (2016). "A Transition from Localized to Strongly Correlated Electron Behavior and Mixed Valence Driven by Physical or Chemical Pressure in  $\text{ACo}_2\text{As}_2$  (A = Eu and Ca)." *Journal of the American Chemical Society* **138**(8): 2724–2731.

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Haskel, D., G. Fabbris, J.W. Kim, J.H. Kim, B.J. Kim, G. Cao and V. Struzhkin (2016). "Frustration in Square Lattice of Iridium  $J_{\text{eff}}=1/2$  Moments at High Pressure." 2016 March Meeting, American Physical Society, Baltimore, MD March 14–19, 2016.

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**2011-052****REFEREED PUBLICATIONS**

Cai, H., J. Wang, Y. Feng, M. Wang, Z. Qin and J.B. Dunn (2016). "Consideration of Land Use Change-Induced Surface Albedo Effects in Life-Cycle Analysis of Biofuels." *Energy & Environmental Science* **9**(9): 2855–2867.

Feng, Y., V.R. Kotamarthi, R. Coulter, C. Zhao and M.P. Cadeddu (2016). "Radiative and Thermodynamic Responses to Aerosol Extinction Profiles during the Pre-monsoon Month over South Asia." *Atmospheric Chemistry and Physics* **16**(1): 247–264.

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Cai, H., M. Wang, J. Wang, Y. Feng, Z. Qin and J. Dunn (2016). "Impacts of Black Carbon and Albedo on Biofuel Climate Effects." 2015 CRC Life Cycle Analysis of Transportation Fuels Workshop, Argonne National Laboratory, October 27, 2015.

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**2011-063****REFEREED PUBLICATION**

Zhang, X., J.S. Park, J. Almer and M.M. Li (2016). "Characterization of Neutron-irradiated HT-UPS Steel by High-energy X-ray Diffraction Microscopy." *Journal of Nuclear Materials* **471**: 280–288.

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Zhang, X., J.-S. Park, C. Xu, H. Sharma, J. Almer and M. Li (2016). "3D Study of Deformation Behavior in Neutron Irradiated Fe-9Cr Alloy." 65<sup>th</sup> Annual Conference on Applications of X-ray Analysis, Rosemont, IL, August 1–5, 2016.

Zhang, X., C. Xu, M. Li, J.-S. Park, P. Kenesei, H. Sharma and J. Almer (2016). "*In situ* and 3D X-ray Diffraction Study of Deformation Behavior in Neutron-Irradiated Fe-9%Cr Polycrystal." American Nuclear Society: Nuclear Fuels and Structural Materials Topical Meeting, New Orleans, LA, June 12–16, 2016.

Zhang, X., C. Xu, J.S. Park, J. Almer and M. Li (2016). "*In situ* Synchrotron X-ray Study of Neutron-irradiated Steels During Tensile Tests." 145th TMS Annual Meeting and Exhibition, Nashville, TN, February 14–18, 2016.

Zhang, X., C. Xu, J.S. Park, J. Almer and M. Li (2016). "*In situ* Synchrotron X-ray Study of Neutron-irradiated Steels During Tensile Tests." 2015 Materials Research Society Fall Meeting and Exhibit, Boston, MA, November 29–December 4, 2015.

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**2011-110****REFEREED PUBLICATION**

Pereira, S.A., N. Baltzell, L. Barion, F. Benmokhtar, W. Brooks, E. Cisbani, M. Contalbrigo, A. El Alaoui, K. Hafidi, M. Hoek, V. Kubarovsky, L. Lagamba, V. Lucherini, R. Malaguti, M. Mirazita, R.A. Montgomery, A. Movsisyan, P. Musico, A. Orlandi, D. Orecchini, L.L. Pappalardo, R. Perrino, J. Phillips, S. Pisano, P. Rossi, S. Squerzanti, S. Tomassini, M. Turisini and A. Viticchie (2016). "Test of the CLAS12 RICH Large-scale Prototype in the Direct Proximity Focusing Configuration." *European Physical Journal A* **52**(2).

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**2011-123****REFEREED PUBLICATION**

Kwon, S.G., S. Chattopadhyay, B. Koo, P.C. dos Santos Claro, T. Shibata, F.G. Requejo, L.J. Giovanetti, Y. Liu, C. Johnson, V.B. Prakapenka, B. Lee and E.V. Shevchenko (2016). "Oxidation Induced Doping of Nanoparticles Revealed by *in situ* X-ray Adsorption Studies." *Nano Letters* **16**(6): 3738–3747.

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**2011-126****REFEREED PUBLICATIONS**

Edirisinghe, J.N., P. Weisenhorn, N. Conrad, F. Xia, R. Overbeek, R.L. Stevens and C.S. Henry (2016). "Modeling Central Metabolism and Energy Biosynthesis Across Microbial Life." *BMC Genomics* **17**: 568.

Faria, J.P., T. Khazaei, J.N. Edirisinghe, P.B. Weisenhorn, S.M.D. Seaver, N. Conrad, N. Harris, M. DeJongh and C. Henry (2016). "Constructing and Analyzing Metabolic Flux Models of Microbial Communities." *Hydrocarbon and Lipid Microbiology Protocols*. T.J. McGenity, K.N. Timmis and B. Nogales, (Eds.), Springer-Verlag Berlin Heidelberg. 247–273.

Henry, C.S., H. Bernstein, P. Weisenhorn, R. Taylor, J.-Y. Lee, J. Zucker and H.-S. Song (2016). "Microbial Community Metabolic Modeling: A Community Data-Driven Network Reconstruction." *Journal of Cellular Physiology* **231**(11): 2339–2345.

Lopes Faria, J.P., R. Overbeek, R.C. Taylor, N. Conrad, V. Vonstein, A. Goelzer, V. Fromion, M. Rocha, I. Rocha and C.S. Henry (2016). "Reconstruction of the Regulatory Network for *Bacillus Subtilis* and Reconciliation with Gene Expression Data." *Frontiers in Microbiology* **7**: 275.

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Assoufid, L., X. Shi, S. Marathe, E. Benda, M.J. Wojcik, K. Lang, R. Xu, W. Liu, A.T. Macrander and J.Z. Tischler (2016). "Development and Implementation of a Portable Grating Interferometer System as a Standard Tool for Testing Optics at the APS Beamline 1-BM." *Review of Scientific Instruments* **87**(5): 052004.

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**2011-188****REFEREED PUBLICATION**

Lee, J.H., I.C. Tung, S.-H. Chang, A. Bhattacharya, D.D. Fong, J.W. Freeland and H. Hong (2016). "In situ Surface/Interface X-ray Diffractometer for Oxide Molecular Beam Epitaxy." *Review of Scientific Instruments* **87**(1): 013901.

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**2011-198****REFEREED PUBLICATION**

Jellinek, J. and D. Aleinikava (2016). "Anharmonic Densities of States: A General Dynamics-Based Solution." *Journal of Chemical Physics* **144**(21): 214103.

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Jellinek, J. (2016). "Computational Exploration and Analysis of Structural and Dynamical Complexities in Homogeneous and Heterogeneous Finite Systems." International Symposium on Clusters, Cluster Assemblies and Nanomaterials (ISCAN - 2016), Thiruvananthapuram, India, March 9–12, 2016.

Jellinek, J. (2016). "Computational Studies of Structural and Dynamical Complexities on the Nanoscale." 9th International Meeting on Photodynamics and Related Aspects, Mendoza, Argentina, May 9–13, 2016.

Jellinek, J. (2016). "Computational Studies of Structural and Dynamical Complexities on the Nanoscale." XII International Scientific Research Congress (XII CIC), Santo Domingo, Dominican Republic, June 8–10, 2016.

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**2011-199****REFEREED PUBLICATION**

Shirer, K.R., A.P. Dioguardi, B.T. Bush, J. Crocker, C.H. Lin, P. Klavins, J.C. Cooley, M.B. Maple, K.B. Chang, K.R. Poeppelmeier and N.J. Curro (2016). "<sup>29</sup>Si Nuclear Magnetic Resonance Study of URu<sub>2</sub>Si<sub>2</sub> Under Pressure." *Physica B: Condensed Matter* **481**: 232–235.

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**2011-210****REFEREED PUBLICATION**

Pellin, M.J., S.C. Riha, E.C. Tyo, G. Kwon, J.A. Libera, J.W. Elam, S. Seifert, S. Lee and S. Vajda (2016). "Water Oxidation By Size Selected  $\text{Co}_{27}$  Clusters Supported on  $\text{Fe}_2\text{O}_3$ ." *ChemSusChem* **9**(20): 3005–3011.

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**2011-216****REFEREED PUBLICATION**

Feng, Y., M.P. Cadeddu, V.R. Kotamarthi, R. Renju and C.S. Raju (2016). "Humidity Bias and Effect on Simulated Aerosol Optical Properties during the Ganges Valley Experiment." *Current Science* **111**(1): 93–100.

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**2012-052****REFEREED PUBLICATIONS**

Peng, Q., C. Liu, D. Hou, W. Zhou, C.-G. Ma, G. Liu, M.G. Brik, Y. Tao and H. Liang (2016). "Luminescence of  $\text{Ce}^{3+}$ -Doped  $\text{MB}_2\text{Si}_2\text{O}_8$  (M = Sr, Ba): A Deeper Insight into the Effects of Electronic Structure and Stokes Shift." *Journal of Physical Chemistry C* **120**(1): 569–580.

Shi, R., J. Xu, G. Liu, X. Zhang, W. Zhou, F. Pan, Y. Huang, Y. Tao and H. Liang (2016). "Spectroscopy and Luminescence Dynamics of  $\text{Ce}^{3+}$  and  $\text{Sm}^{3+}$  in  $\text{LiYSiO}_4$ ." *Journal of Physical Chemistry C* **120**(8): 4529–4537.

Xia, Z., G. Liu, J. Wen, Z. Mei, M. Balasubramanian, M.S. Moloakeev, L. Peng, D.J. Miller, Q. Liu and K.R. Poeppelmeier (2016). "Tuning of Photoluminescence by Cation Nanosegregation in the  $(\text{CaMg})_x(\text{NaSc})_{1-x}\text{Si}_2\text{O}_6$  Solid Solution." *Journal of the American Chemical Society* **138**(4): 1158–1161.

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**2012-074****PRESENTATIONS**

Fan, Z., R. Matamala, J. Jastrow, C. Liang, F. Calderon, G. Michaelson, C.-L. Ping, U. Mishra and S. Hofmann (2016). "Characterizing Organic Matter Lability in Alaskan Tundra Soils Using Mid-Infrared Spectroscopy." 2016 Environmental System Science (ESS) PI Meeting, Potomac, MD, April 26–27, 2016.

Fan, Z., R. Matamala, J. Jastrow, C. Liang, F. Calderon, G.J. Michaelson, C.-L. Ping, U. Mishra and S. Hofmann (2016). "Characterizing Organic Matter Lability in Alaskan Tundra Soils Using Mid-infrared Spectroscopy." 2015 American Geophysical Union Fall Meeting, San Francisco, CA, December 14–18, 2015.

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**2012-082****NON-REFEREED PUBLICATION**

Perarnau, S., J.A. Zounmevo, B. Gerofi, K. Iskra and P. Beckman (2016). "Exploring Data Migration for Future Deep-Memory Many-Core Systems." IEEE International Conference on Cluster Computing, Taipei, Taiwan, September 12–16, 2016.

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**2012-114****REFEREED PUBLICATIONS**

He, Y., M.S. Min and D.P. Nicholls (2016). "A Spectral Element Method with Transparent Boundary Condition for Periodic Layered Media Scattering." *Journal of Computational Physics* **68**(2): 772–802.

Otten, M., J. Gong, A. Mametjanov, A. Vose, J. Levesque, P. Fischer and M. Min (2016). "An MPI/OpenACC Implementation of a High Order Electromagnetics Solver with GPUDirect Communication." *International Journal of High Performance Computing Applications* **30**(3): 320–334.

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**2012-205****REFEREED PUBLICATION**

Fan, Z., J.C. Neff and W.R. Wieder (2016). "Model Based Analysis of Environmental Controls Over Ecosystem Primary Production in an Alpine Tundra Dry Meadow." *Biogeochemistry* **128**(1–2): 35–49.

**PRESENTATION**

Mishra, U., Z. Fan and B.A. Drewniak (2016). "Informing Climate Change Studies Using Soil Survey Information." 2015 Soil Science Society of America International Annual Meeting, Minneapolis, MN, November 16, 2015.

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**2012-206****REFEREED PUBLICATION**

Jiang, Y., A. Rocha, E. Rastetter, G. Shaver, U. Mishra, Q. Zhuang and B. Kwiatkowski (2016). "C-N-P Interactions Control Climate Driven Changes in Regional Patterns of C Storage on the North Slope of Alaska." *Landscape Ecology* **31**(1): 195–213.

**PRESENTATIONS**

Mishra, U., Z. Fan, J.D. Jastrow, R.M. Matamala and W. Vitharana (2016). "Capturing Spatial Heterogeneity of Soil Organic Carbon Under Changing Climate." 2015 American Geophysical Union Fall Meeting, San Francisco, CA, December 14–18, 2015.

Mishra, U., Z. Fan and B.A. Drewniak (2016). "Informing Climate Change Studies Using Soil Survey Information." 2015 Soil Science Society of America International Annual Meeting, Minneapolis, MN, November 15–18, 2015.

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**2012-209****REFEREED PUBLICATION**

Welland, M.J., K.C. Lau, P.C. Redfern, L. Liang, D. Zhai, D. Wolf and L.A. Curtiss (2016). "An Atomistically Informed Mesoscale Model for Growth and Coarsening During Discharge in Lithium-oxygen Batteries." *Journal of Chemical Physics* **143**(22): 224113.

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**2013-016****REFEREED PUBLICATIONS**

Jungfleisch, M.B., W. Zhang, J. Sklenar, W. Jiang, J.E. Pearson, J.B. Ketterson and A. Hoffmann (2016). "Interface-driven Spin-torque Ferromagnetic Resonance by Rashba Coupling at the Interface Between Non-magnetic Materials." *Physical Review B: Condensed Matter* **93**(22): 224419.

Jungfleisch, M.B., W. Zhang, W. Jiang and A. Hoffmann (2016). "New Pathways Towards Efficient Metallic Spin Hall Spintronics." *SPIN* **05**(03): 1530005.

Li, S., W. Zhang, J. Ding, J.E. Pearson, V. Novosad and A. Hoffmann (2016). "Epitaxial Patterning of Nanometer-thick  $Y_3Fe_5O_{12}$  Films with Low Magnetic Damping." *Nanoscale* **8**(1): 388–394.

Sklenar, J., W. Zhang, M.B. Jungfleisch, W. Jiang, H. Chang, J.E. Pearson, M. Wu, J.B. Ketterson and A. Hoffmann (2016). "Driving and Detecting Ferromagnetic Resonance in Insulators with the Spin Hall Effect." *Physical Review Letters* **92**(17): 174406. Sklenar, J., W. Zhang, M.B. Jungfleisch, W. Jiang, H. Saglam, J.E. Pearson, J.B. Ketterson and A. Hoffmann (2016). "Spin Hall Effects in Metallic Antiferromagnets - Perspectives for Future Spin-orbitronics." *AIP Advances* **6**(5): 055603.

Wu, S.M., W. Zhang, A. KC, P. Borisov, J.E. Pearson, J.S. Jiang, D. Lederman, A. Hoffmann and A. Bhattacharya (2016). "Antiferromagnetic Spin Seebeck Effect." *Physical Review Letters* **116**(9): 097204.

Zhang, W., M.B. Jungfleisch, F. Freimuth, W. Jiang, J. Sklenar, J.E. Pearson, J.B. Ketterson, Y. Mokrousov and A. Hoffmann (2016). "All-electrical Manipulation of Magnetization Dynamics in a Ferromagnet by Antiferromagnets with Anisotropic Spin Hall Effects." *Physical Review B: Condensed Matter* **92**(14).

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Hoffmann, A. (2016). "Magnetization Dynamics Driven by Spin Hall Effects." Workshop Magnetodynamics, Vail, CO, March 20–23, 2016.

Hoffmann, A. (2016). "New Opportunities for Spintronics: Spin Transport with Magnetic Skyrmions and Antiferromagnets." IBM Watson Research Laboratory, Yorktown Heights, NY, June 10, 2016.

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- Science & Technology Partnerships and Outreach, Communications and Public Affairs
  - Michele Nelson (Lead, Design and Layout)

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## CONTACT

**Lee C. Zachos**

Interim LDRD Program Manager  
Strategy and Innovation Office, Office of the Director  
Phone: 630-252-8842  
E-mail: [lzachos@anl.gov](mailto:lzachos@anl.gov)

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