LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM

FY2015 ANNUAL REPORT

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SLAC NATIONAL ACCELERATOR LABORATORY • 2575 SAND HILL ROAD • MENLO PARK • CALIFORNIA • 94025 • USA

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Overview

The Department of Energy (DOE) and the SLAC National Accelerator Laboratory (SLAC) encourage innovation, creativity, originality and quality to maintain the Laboratory's research activities and staff at the forefront of science and technology. To further advance its scientific research capabilities, the Laboratory allocates a portion of its funds for the Laboratory Directed Research and Development (LDRD) program. With DOE guidance, the LDRD program enables SLAC scientists to make rapid and significant contributions that seed new strategies for solving important national science and technology problems. The LDRD program is conducted using existing research facilities. Project proposals can be characterized as:

- Proposals intended to initiate and/or develop major new capabilities or research programs aligned with the SLAC strategic plan
- "Discovery" proposals with high scientific risk and potential

In addition to building new core competencies that support the DOE missions, the LDRD project proposals may also conduct scientific research and development that support the missions of other federal agencies and/or non-federal sponsors.

The LDRD program supports the SLAC mission in several ways. First, because LDRD funds can be allocated within a relatively short time frame, SLAC researchers can support the mission of DOE and serve the needs of the nation by quickly responding to forefront scientific problems and capitalizing on new opportunities. Second, LDRD enables SLAC to attract and retain highly qualified scientists and to support their efforts to carry out world leading research. Finally, the LDRD program also supports new projects that involve graduate students and postdoctoral fellows, thus contributing to the education mission of SLAC. In FY2015, SLAC continued to see some of the previously funded LDRD programs transition to follow on funding with the Office of Science, DOE-EERE and other agencies. This external validation shows that the projects selected were important towards continuing forefront science and use-inspired applications with mission relevance and towards delivering significant results.

SLAC has a formal process for allocating funds for the LDRD program. The process relies on individual scientific investigators and the scientific leadership of the laboratory to identify opportunities that will contribute to scientific and institutional goals. The process is also designed to ensure compliance with DOE Orders, in particular DOE Order 413.2C (dated October 22, 2015). From year-to-year, the distribution of funds among the scientific program areas changes. This flexibility optimizes SLAC's ability to respond to emerging opportunities. SLAC LDRD policy and program decisions are the responsibility of the Laboratory Director. The Director directs the LDRD Program Manager to initiate the program each year in January and schedule the supporting activities. Successful proposals are usually announced in September with funds available at the beginning of the fiscal year. After the call for proposals is announced, the scientists confer with the scientific program Associate Laboratory Directors (ALDs) before submitting their proposals. Each SLAC directorate is responsible for the internal selection process prior to submitting to the LDRD program review process. The Lab-

wide proposal review process consists of two stages; a) an external peer review soliciting input from experts in the proposal research areas and b) an internal review where panels comprised of distinguished researchers from inside SLAC and Stanford University meet with the investigators to hear presentations and ask questions based in part on the feedback from the external review. The outcome of the review is a ranking and determination of the top 30-40% within each panel. In the summer, the Laboratory's Science Council meets over several weeks to prioritize amongst the top-ranked proposals and then forward their recommendations to the Director who makes the final decisions. The list is sent to the SLAC DOE Site Office for concurrence, typically in September.

LDRD accounting procedures and financial management are consistent with the Laboratory's accounting principles and stipulations under contract DE-AC02-76SF00515 between the SLAC and DOE, with accounting maintained through the Laboratory's Chief Financial Officer and Budget Office.

In FY2015, SLAC was authorized by DOE to establish a funding ceiling for the LDRD program of \$7.5M, including General & Administrative (G&A) overhead. Scientists submitted 45 proposals in total (33 proposed new project starts), requesting about \$9.4M in funding. 27 projects were selected and funded at a total of \$6.5M (including continuing projects), with individual awards ranging from \$80K to \$835K. Costs for the FY2015 program were \$6.3M, which equated to 2.46% of SLAC's FY2015 total operating costs of \$256M.

Annual reports for the FY15 project activities follow.

1.0 Ultrafast Surface Chemical Transformation at the X-ray Laser LCLS

Principal Investigator: Frank Abild-Pedersen

Project Description

Most conversion processes are performed via chemical reaction on a catalyst surface. The transition kinetics is greatly influenced by the dynamic motion of the molecules and the energy exchange process when the reaction is taking place. The present proposal aims at developing a methodology that can identify important signatures in energy transfer processes during a reaction, which in turn could provide ways to control chemical reactivity and selectivity. We will utilize ultrafast soft x-ray spectroscopy at LCLS to probe evolving transient species on a metal surface to identify the energy exchange processes: phonon-mediated and/or electron-mediated. We will also develop theoretical methods to simulate the reaction dynamics of transient species using the Born-Oppenheimer approximation with and without electronic friction.

Accomplishments

In the first year of the funding period for this LDRD proposal we have focused on several processes. We have looked at the desorption process of CO from Ru(0001) with and without co-adsorbates, the oxidation of CO on Ru(0001), and the hydrogenation of CO on Ru(0001), all projects have built on the pump-probe experimental capabilities of the LCLS combined with theoretical efforts within SUNCAT.

In the first of the processes we have studied, we show that the free energy at the precursor region is dramatically influenced by entropy, where CO with co-adsorbed O on Ru(0001) is more constrained than on Ru(0001) leaving no local precursor state prior to desorption at elevated temperatures. We found that the oxygen-induced reduction of the Pauli repulsion and increased electrostatic dative interaction between the CO σ and the positively charged Ru atom on 2O-CO/Ru(0001) drives the CO desorption via the direct desorption pathway instead of the precursor-mediated pathway. AIMD simulations further support the experimental observation and provide a microscopic view of surface bond-breaking processes. The fundamental insights gained here consolidate our understanding of surface chemical bonding and underline the importance of including co-adsorbate interactions when unraveling dynamics of surface reactions.

In the second study it was demonstrated that ultrafast pump-probe x-ray spectroscopy based on the Linac Coherent Light Source (LCLS) x-ray free-electron laser can be used to probe the electronic structure of molecular species in the transition state region during CO oxidation on a Ru surface. An optical laser pump pulse to excite electrons in the substrate was used. In this process energy is immediately transferred to the adsorbate system, which leads to an increase in vibrational excitations of the system and population of the CO oxidation pathway on a picosecond timescale. To monitor the element specific time evolution of the empty valence electronic states O K-edge XAS was used during the process.

The results obtained, suggests an ultrafast energy transfer to the adsorbed O and CO from surface electrons excited by the laser pulse. Within the first picosecond new electronic states appeared, which clearly indicated the existence of new adsorbed species that did not resemble the separate systems in terms of CO molecules or O atoms adsorbed on the Ru surface. Through a comparison between experimental spectra and calculations these new resonances were identified as due to a shift in the positions of both CO and O but more importantly to the formation of a bond between CO and O that is substantially elongated in comparison to the CO₂ final product. The potential energy surface obtained for the reaction identifies these species as OC-O fragments being in the near transition state region attempting to form CO₂. A simple probability analysis based on the state distribution within the calculated potential energy surface provided an estimated ~10% population of species in the transition state region during the first few picosecond in good agreement with the experiments. These first two studies have led to two papers, one published in Phys. Rev. Lett., and the other published in Science (see below).

Currently we are writing up our experimental and theoretical findings on one of the critical reaction steps in syngas utilization and artificial photosynthesis for production of liquid fuels and other hydrocarbons, namely the catalytic reduction of carbon monoxide (CO) using hydrogen (H). We show that, on a Ru(0001) surface, the collision of H and CO in the chemisorbed state evolves CHO as an intermediate species towards the CH₂O formation. The H-CO bond formation competes with the Ru-CO chemisorption bond scission and H-H bond formation. Upon formation of CHO, there is competition between the Ru-CHO chemisorption bond scission, H₂CO formation, and CHO dissociation back to H and CO. Among other things, the transition of CO in the chemisorbed state to the desorption precursor state at longer timescales also limits any H-CO bond formation in case some transient H remains on the surface. In the coming year we will continue our work on the CO hydrogenation reaction on Ru(0001) understanding in more detail some of the observed adsorbate-specific exchange processes.

Publications

FY2015

H. Xin, J. LaRue, H. Öberg, M. Beye, M. Dell'Angela, J. J. Turner, J. Gladh, M. L. Ng, J. A. Sellberg, S. Kaya, G. Mercurio, F. Hieke, D. Nordlund, W. F. Schlotter, G. L. Dakovski, M. P. Minitti, A. Föhlisch, M. Wolf, W. Wurth, H. Ogasawara, J. K. Nørskov, H. Öström, L. G. M Pettersson, A. Nilsson, and F. Abild-Pedersen, *"Strong Influence of Coadsorbate Interaction on CO Desorption Dynamics Probed by Ultrafast X-ray Spectroscopy and Ab Initio Simulations"*, Phys. Rev. Lett. 114, 156101 (2015)

H. Öström, H. Öberg, H. Xin, J. LaRue, M. Beye, M. Dell'Angela, J. Gladh, M. L. Ng, J. A. Sellberg, S. Kaya, G. Mercurio, D. Nordlund, M. Hantschmann, F. Hieke, D. Kühn, W. F. Schlotter, G. L. Dakovski, J. J. Turner, M. P. Minitti, A. Mitra, S. P. Moeller, A. Föhlisch, M. Wolf, W. Wurth, M. Persson, J. K. Nørskov, F. Abild-Pedersen, H. Ogasawara, L. G. M Pettersson, and A. Nilsson, *"Probing the transition state region in catalytic CO oxidation on Ru"*, Science 347, 978

Workshops

FY2015

H. Ogasawara, J. LaRue, H. Öström, H. Xin, M. Beye, M. Dell'Angela, J. Gladh, M. L. Ng, J. A. Sellberg, S. Kaya, G. Mercurio, D. Nordlund, M. Hantschmann, F. Hieke, D. Kühn, W. F. Schlotter, G. L. Dakovski, J.

J. Turner, M. P. Minitti, A. Mitra, S. P. Moeller, A. Föhlisch, M. Wolf, W. Wurth, M. Persson, J. K. Nørskov, F. Abild-Pedersen, L. G. M Pettersson, and A. Nilsson, *Probing Surface Chemical Reaction by Soft X-ray Spectroscopy*, SSRL Scientific Advisory Committee Meeting, Menlo Park March 5 2015.

A. Nilsson, H. Ogasawara, J. LaRue, H. Öström, H. Xin, M. Beye, M. Dell'Angela, J. Gladh, M. L. Ng, J. A. Sellberg, S. Kaya, G. Mercurio, D. Nordlund, M. Hantschmann, F. Hieke, D. Kühn, W. F. Schlotter, G. L. Dakovski, J. J. Turner, M. P. Minitti, A. Mitra, S. P. Moeller, A. Föhlisch, M. Wolf, W. Wurth, M. Persson, J. K. Nørskov, F. Abild-Pedersen, and L. G. M Pettersson, *Spectroscopy for Catalysis with LCLS II*, SLAC, Menlo Park February 2015.

J. LaRue, H. Ogasawara, H. Öström, H. Xin, M. Beye, M. Dell'Angela, J. Gladh, M. L. Ng, J. A. Sellberg, S. Kaya, G. Mercurio, D. Nordlund, M. Hantschmann, F. Hieke, D. Kühn, W. F. Schlotter, G. L. Dakovski, J.

J. Turner, M. P. Minitti, A. Mitra, S. P. Moeller, A. Föhlisch, M. Wolf, W. Wurth, M. Persson, J. K. Nørskov, F. Abild-Pedersen, L. G. M Pettersson, and A. Nilsson, Gordon Research Seminars; Dynamics at Surfaces, Salve Regina University, August 2015

FY2014

H. Xin, J. LaRue, H. Öström, H. Ogasawara, M. Beye, L.G.M. Pettersson, A. Nilsson, J.K. Nørskov, and F. Abild-Pedersen, Role of adsorbate-adsorbate interactions in dynamics of surface bond breaking, 2014 AIChE Annual Meeting, Atlanta GA, November 16-21, 2014.

H. Ogasawara, J. LaRue, H. Öström, H. Xin, M. Beye, M. Dell'Angela, J. Gladh, M. L. Ng, J. A. Sellberg, S. Kaya, G. Mercurio, D. Nordlund, M. Hantschmann, F. Hieke, D. Kühn, W. F. Schlotter, G. L. Dakovski, J. J. Turner, M. P. Minitti, A. Mitra, S. P. Moeller, A. Föhlisch, M. Wolf, W. Wurth, M. Persson, J. K. Nørskov, F. Abild-Pedersen, L. G. M Pettersson, and A. Nilsson, Ultrafast Surface Reaction and Desorption Probed by X-ray Free-Electron Laser, The 7th International Symposium on Surface Science, Matsue, Japan, November 4 2014.

A. Nilsson, H. Ogasawara, J. LaRue, H. Öström, H. Xin, M. Beye, M. Dell'Angela, J. Gladh, M. L. Ng, J. A. Sellberg, S. Kaya, G. Mercurio, D. Nordlund, M. Hantschmann, F. Hieke, D. Kühn, W. F. Schlotter, G. L. Dakovski, J. J. Turner, M. P. Minitti, A. Mitra, S. P. Moeller, A. Föhlisch, M. Wolf, W. Wurth, M. Persson,

J. K. Nørskov, F. Abild-- - -Pedersen, and L. G. M Pettersson, Ultrafast Surface Chemistry and Catalysis, Fermi-- - - Elettra, Italy, December 2014.

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Maybe
Source of support for follow-on funding?	TBD
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	0
Number of Post Docs supported by LDRD project in FY15?	1
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

2.0 Liquid Nobles

Principal Investigator: Dan Akerib. **Collaborator:** Tom Shutt.

Project Description

In FY15 the LDRD funds for Liquid Nobles research has supported our group's work on the LUX and LZ experiments at SLAC. LUX is the current world leader in this search over much of the WIMP mass range using a 100-kg fiducial target mass. LZ will go online in 2019 to extend this search with 5.6-tons fiducial.

Significant progress has been made in this project towards establishing the liquid nobles test stand. The initial build out consists of a liquid-nitrogen thermosyphon cryogenic platform; a xenon gas circulation, storage and purification system; a computer-based slow control and data acquisition system; and most importantly, a set of connected cryogenic chambers with a purified xenon supply, high-voltage feed-through and xenon detector prototyping volume. These systems together comprise a fully-outfitted "mini LZ" that is now being commissioned (first cool down in progress with 20% of the initial xenon target condensed) and will be used to test critical LZ prototypes, and to support longer-range R&D goals aimed at work beyond LZ.

Our work on LUX contributes to an upcoming publication that presents an improved analysis of the 2013 data set, which will carve out new parameter space in the WIMP search. We continue to take and analyze data with LUX towards a result in 2016 that will extend the search by a factor of 3-5 in sensitivity. The other supported effort is R&D towards removal of trace radioactive krypton from xenon, which will lead to a demonstration of xenon purification at level required to render this source a sub-dominant background in LZ.

Accomplishments

LZ test platform: Through FY15, we've installed and started to commission the key components of the test platform in preparation for LZ development, prototyping and test. The thermosyphon cryogenic system that provides cooling to liquid xenon temperature is now fully operational including computer control. The xenon gas circulation and storage system is fully built and is in the commissioning phase. The detector vessel has been successfully cooled and liquid xenon has been condensed into the detector chamber. A high-voltage feed through to test critical fields has been deployed, along with heat exchanger elements to aid in high-circulation rates for rapid purification and system turnaround. An LED and fiber optic camera system provided by collaborators at TAMU was installed and is operational, and will aid in locating any problems with high voltage breakdown. A photomultiplier tube, pre-amp and DAQ system, along with networked virtual machines for data handling and processing has also been deployed.

Kr removal R&D: Trace radioactive krypton present in research grade xenon produces an unacceptable level of background in xenon-based dark matter experiments. We now have the goal to produce xenon that is 100 times more pure at 10 times the processing rate. The LUX system has been reconfigured to test new ideas for this purification development and to demonstrate a modest amount (few kilograms) of purified xenon at the LZ spec. We have completed the construction and initial commissioning of this system.

LUX experiment: Work on the LUX experiment has primarily been on operations and analysis. Most group members completed one or two sets of shifts on the experiment in South Dakota to support general operations, as well as maintenance and updates of systems for which we are responsible (cryogenic thermosyphon system, internal fluid system). Data acquired in 2013 are being re-analyzed with an improved reconstruction algorithm and additional calibration techniques, and expanded statistical tools to further optimize the sensitivity achievable with current and future data sets. In FY15, the SLAC RA's also provided leadership in the Detector Operations Working Group, Data Processing Management and the Profile Likelihood Limits Working Group. Data acquisition will continue into mid-2016, and group members are contributing actively to data analysis aimed at a 3-5fold improvement in sensitivity to WIMP dark matter.

Publications

FY2015

D.S. Akerib et al. "*Radiogenic and Muon-Induced Backgrounds in the LUX Dark Matter Detector*," *Astroparticle Physics* 62 , 33 (2015).

FY2014

Akerib et al., "*First results from the LUX dark matter experiment at the Sanford Underground Research Facility*," *Phys. Rev. Lett.* 112, 091303 (2014).

Workshops

FY2015

Tom Shutt, CPAD Instrumentation Frontier Meeting, Oct 2015

Dan Akerib, TAUP 2015 XIV International Conference on Topics in Astroparticle and Underground Physics, Sept 2015

Tomasz Biesiadzinski, APS DPF-Ann Arbor, Aug 2015

FY2014

n/a

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE via LBL project funds
Has follow-on funding been obtained?	Pending
Amount of follow-on funding (\$K)?	~3,000
Number of Post Docs supported by LDRD project in FY15?	3
Number of students supported by LDRD project in FY15?	3
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

3.0 Real-time Control of Subsurface Fractures and Fluid Flow

Principal Investigator: John R. Bargar. **Collaborator:** Gordon E. Brown, Jr.

Project Description

This project is addressing the fundamental geochemical and physical transport processes that control pore and fracture-scale behavior in rocks, with emphasis on mineral dissolution, precipitation, and fluid flow in fractured rock. X-ray computed tomography (CT) is a technique of choice for studying chemical reactions and fluid transport inside of rock because of the ability of X-rays to penetrate through entire lithic objects and image processes and reactions occurring at the scale of individual microfractures and pores. To improve the characterization capabilities of SLAC and SSRL in this scientific area, this project is developing a micro-computed tomography microscope (μ CT) at SSRL capable of generating 3D reconstructions of the internal structure of rocks at sub-micron resolution fast enough to observe in situ transient fluid dynamics over a large (mm scale) field of view. By the conclusion of this LDRD project, a functional rapid μ CT microscope will have been commissioned, and an environmental chamber for measuring fluids in rocks under subsurface conditions will have been designed and tested. Knowledge gained through this project is improving the scientific understanding of oil and gas recovery in shales and carbon dioxide storage in geological reservoirs and is helping to position SLAC and SSRL for future research funding in this subject area.

Accomplishments

The team has made important strides towards achieving our goals in the first year of the LDRD. Key accomplishments include:

- Demonstrating feasibility to study chemical reactions occurring within individual pores and to image transient fluid flow in sandstone.
- Development, construction, and testing of a portable μ CT microscope, including demonstration of its ability to rapidly acquire tomograms.
- Initiation of collaborations to use the new μ CT microscope that form the basis for a new user community.
- Helping position SSRL and SLAC to compete for expanded research funding.

Pore-scale iron oxidation in model systems. Pyrite, an important mineral in shales, is susceptible to oxidation by molecular oxygen in fracture fluids that are injected during hydraulic fracturing of gas and oil shales. Pyrite oxidation drives strong local decreases in pH, which can cause additional dissolution and (initially) increased permeability of the rock system. In contrast, precipitation of Fe(III) hydroxides, a product of pyrite oxidation, in fractures and pores can decrease permeability. Pyrite oxidation is therefore expected to be an important contributor to permeability changes in the rock matrix. An early experimental milestone of the project was to investigate pyrite oxidation at the pore scale in a constructed model system comprised of micron-sized pyrite grains in a quartz matrix. Hydrogen peroxide was used to initiate pyrite oxidation. The resulting products were characterized using X-ray absorption near edge spectroscopy (XANES) and transmission X-ray microscopy imaging (TXM) at beamline 6-2C, microprobe XAS

at the sulfur and iron K-absorption edges at beamlines 14-3 and 2-3 respectively, and X-ray fluorescence tomography (XRF) at beamline 2-3. These techniques were able to speciate iron among sulfides and oxides in the sample using XAS analysis and then identify their spatial distribution in 3D using XANES-tomography with the TXM. This activity demonstrated feasibility to study these reactions in natural shales. The results of these experiments were presented in San Diego, CA at the SPIE Optics +Photonics 2016 conference and are currently being expanded into a manuscript.

Reaction of whole shale samples with fracture fluid. As proposed in the LDRD grant application, more representative experiments were also conducted which used whole pieces of shale instead of constructed models. Specifically, characterizing shale porosity before and after being reacted with HCl, a common primary additive during hydraulic fracturing, was identified as another important milestone. To perform this experiment, a single 30 μm piece of shale was mounted on a pin, imaged, and reacted with HCl (introduced via vapor phase to prevent agitation and sample loss). Imaging was performed using the TXM at beamline 6-2C, which is capable of roughly 50 nm resolution. Significant changes, including smoothing of the surfaces and deposition of a thin film of iron oxide, were observed after the sample was reacted. An additional set of whole-shale reactions with fracture fluid are described in the Leveraging section, below.

Development of a rapid μCT microscope. This component of the project is proceeding on-schedule and to date has met all of the technical design targets. The design of the microscope (Figure 1) involved careful optimization of all components. For example, a high resolution, high frame rate, visible light detector and the scintillator crystal were selected such that the peak wavelength emission of the scintillator corresponded to maximum quantum efficiency of the detector. First light experiments were performed in May. Successful completion of this step required integration of different software packages, as well as the development of some custom software, to insure that the motors, detector, and data acquisition could be synchronized. The first light experiments successfully demonstrated that the instrument is performing to design specifications (Figure 1) and provides the capability to collect tomographic data at multiple beamlines (10-2a and 11-2, as well as white light at beamline 2-2). The portability of this system is an advantage that allows beam line specific advantages to be realized. Different imaging modes were developed in order to optimize the data collection of samples. Data can be acquired in a step or continuous scanning modes, where the sample is imaged while stationary or continuously rotating. It is also desirable to expand the field of view of the sample and this has been accomplished by offsetting the axis of rotation and rotating 360°, or running a mosaic and stitching together each projection during post-processing.

Leveraging. While this LDRD has focused on the development of new instrumentation and methodologies, it has benefitted greatly from a parallel research project funded by the National Energy Technology Laboratory (NETL) to study the impacts of hydraulic fracture fluid on shale permeability. Scientific insights and research activities from the NETL project have accelerated the development of the μCT - and TXM-based science programs, while the availability of these tools has advanced the NETL project. One example of this symbiosis is demonstration of a research capability that uses μCT and nano-CT (TXM) data to build pore-scale geochemical models. This

capability will form the basis for subsequent research grant proposals to NETL and other agencies to fund continued activities at the beam line.

In another example of LDRD-NETL project symbiosis, shale samples were imaged using μ CT, exposed to hydraulic fracture fluid, and then reimaged. μ CT data were acquired through a collaboration with the Pohang Light Source because the SSRL microscope was still in development at the time. The reconstructed images still need quantitative analysis but qualitatively, there are observable morphological changes to the samples after exposure to the fracturing fluid. Measuring changes to the sample can help understand what is occurring at the microstructure level to the shale undergoing the fracturing process.

Figure 1: A photograph of the μ CT setup (a) installed in BL2-2 along with a schematic of the μ CT setup (b). A projection image of Marcellus shale imaged at beamline 11-2 with the μ CT (c) can be seen along with a 3D reconstruction of the sample (d).

As the capabilities of the microscope are demonstrated, a growing interest from potential users has been observed in several fields including geoscience, catalysis, and energy materials. In addition to the shale samples, the microscope has also been used to study catalysis particles (PI: Florian Meirer, Utrecht University), and geoscience samples such as basalt, sandstone (PI: Anthony Kovscek and Sally Benson, Stanford), pumice, and retilite (PI: Tiziana Vanorio,

Stanford). Future experiments planned for next cycle will continue collaborations with Sally Benson and Anthony Kavscek as well as attempt new experiments imaging lithium-ion battery cells (PI: Mike Toney, SSRL).

Planned activities in 2016. With the developments in the first year, the second year is on track to accomplish the goals of the LDRD application. Using the developed μ CT system, the ability to see transient changes in rock samples is possible. We are planning to conduct water imbibition experiments in which fluid motion across pores in Berea sandstone will be imaged during the imbibition process. We have completed preliminary experiments, which show feasibility of this experiment. We will make further improvements to the control system of the microscope and implement new components required to be procured, which will make data acquisition easier. We are also developing a high pressure, elevated temperature environmental chamber. This environmental chamber will be specifically developed for in situ studies of fluid flow in shale during the fracturing process. By imaging the transient behavior of water in shale pores in the most realistic conditions, we will be able to understand what is occurring at the microscale in the rock with a high temporal resolution.

A second and major effort in FY2016 will be to measure the permeability of whole shale cores (cm scale) to understand fluid flow at the in situ conditions of hydraulic fracturing. These analyses, being performed in the Zoback laboratory on the Stanford Campus, will yield estimates of average pore size, which we will compare to independent measurements by nitrogen adsorption porosimetry. The samples will subsequently be exposed to hydraulic fracturing fluid to stimulate interaction with an exposed fracture surface. Comparing the permeability and pore size distributions before and after exposure will give direct insights into how the processes documented by the geochemistry experiments affect fluid flow in the shale matrix. In addition, these cm-scale experiments will inform our plans for permeability experiments on mm-scale samples, which will contribute direction to the development of the environmental chamber for the μ CT. By incorporating tomography imaging with fluid flow using a high X-ray contrast gas, we aim to understand the pathways and time-scales of fluid flow in micro- to nanoscale features that remain unconstrained by bulk analyses.

Publications

FY2015

A. M. Kiss, A. D. Jew, C. Joe-Wong, K. M. Maher, Y. Liu, G. E. Brown, and J. Bargar, "*Synchrotron-based transmission X-ray microscopy for improved extraction in shale during hydraulic fracturing*", SPIE Optical Engineering + Applications, 95920O (2015).

A. M. Kiss, A. D. Jew, C. Joe-Wong, K. M. Maher, Y. Liu, G. E. Brown, and J. Bargar, "*Synchrotron-based transmission X-ray microscopy for improved extraction in shale during hydraulic fracturing*", in preparation.

A. M. Kiss, G. E. Brown, J. Bargar, P. Pianetta, and Y. Liu, "*Development of an in situ microtomography system at the Stanford Synchrotron Radiation Lightsource*," in preparation.

A.H. Kohli, A. Harrison, A.D. Jew, J. Bargar, K. Maher, and M.D. Zoback , *“Effects of hydraulic fracturing fluid on shale matrix permeability and microstructure”*, in preparation.

Workshops

FY2015

A. M. Kiss, S. Webb, Y. Liu, G. E. Brown, and J. Bargar, 2015 LCLC/SSRL Users’ Meeting, Menlo Park, CA, October 7-10, 2015.

A. M. Kiss, X-Ray Nanoimaging: Instruments and Methods, SPIE Optics + Photonics, San Diego, CA, August 10-13, 2015

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	NETL, DOE-BES
Has follow-on funding been obtained?	Yes
Amount of follow-on funding (\$K)?	150
Number of Post Docs supported by LDRD project in FY15?	1.25
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

4.0 cPix²: Multi-gate detector for MHz Repetition Rate Pump-probe Experiments

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Principal Investigator: Gabriella Carini

Project Description

Many scientifically interesting and technologically important investigations today, from understanding the mechanisms of charge separation in photosynthetic systems to the interaction of the electronic, atomic and magnetic lattices in multiferroics, are based on monitoring the response of a material, in time domain, after it is perturbed by an external stimulus. Signals in these experiments are often small requiring high repetition rates and photon counting for the needed statistic. But even slight beam motion or other instability can dominate the signal, making them nearly impossible. If, however, the probe signal is compared shot-by-shot with pump on and off, then the dominant sources of systematic error can be suppressed if not removed completely.

To implement this technique we have proposed to build a prototype pixel area detector with a 100 x 100 pixel size, designed for high repetition rate pump-probe experiments with at least two 100 ns gates, capable of at least 1.28 MHz repetition rate, and 14-bit counting range.

This 2D detector will be used as a proof-of-concept for high repetition rate pump-probe experiments in SSRL's low alpha operation. It can also be used at the proposed megahertz crab cavity beamlines in the Advanced Photon Source (APS) upgrade and other existent and planned x-ray sources around the world. This demonstrator would enable partnership with other laboratories and facilities. It will also provide SLAC with a technology enabling the development of fast counters for LCLS-II, useful for low photon density experiments with very sparse data.

Accomplishments

This R&D project builds on existing components developed for other pixel array detectors for LCLS (ePix). Therefore during the first 12 months of the program, we have focused the attention in developing the custom Application Specific Integrated Circuit (ASIC) which will be bump bonded to a silicon pixel array detector (PAD).

Fig. 1 shows the architecture of the ASIC with the list of specifications. The ASIC is composed of three sections: an array of pixels that perform the counting operation, a row selector that addresses rows of the matrix for column parallel readout and a common section ("balcony") that is used to configure, control the phases of operation and readout the matrix. Each pixel is composed of a charge preamplifier with continuous or time variant reset, a correlated double sampling baseline adjusting filter followed by a dual threshold discriminator and two counters (Fig. 2).

	Two Gate High Rep Rate Counter
Processing time	96ns (76ns)*
Counting rate	1.28MHz (13MHz)*
Counters per pixel	2 (i.e. double gating)
Counting length	14bits
Thresholds	high (15-32keV) and low (3-20keV)
Readout dead time	< 3ms
Pixel size	~ 100um
Energy	5keV – 30keV
Readout noise	< 350e- rms
Vacuum compatible	Yes
Module	~150kpixel
Operation mode	Synchronous

*specifications allow accommodating APS time structure.

Figure 1. Left: ASIC architecture. b) Table summarizing the ASIC specifications.

Figure 2. Schematic of the pixel circuitry.

The circuit has been simulated at the maximum counting rate of 13 MHz to be compatible with the characteristics of the APS most challenging time structure. Fig. 3 shows the results of such simulation.

Figure 3. Pixel circuitry simulated at the shortest repetition period of 76 ns.

The simulations of the digital readout have demonstrated the capability of the high-speed serializers to sustain data rates up to 1Gb/s. The serializer chain is composed of a 48x16 bit digital multiplexer followed by a buffer and a SLAC custom designed encoder based on the 8b/10b protocol which has a defined idle state and automatically packet each frame adding a start and end-of-frame code to the data. The output of the encoder, named SSP (Simple Streaming Protocol) Framer, feeds into a serializer and a LVDS transmitter. Fig. 4 shows a simulation for a worst case of 6 64x1 channels (required for a full reticle ASIC that would be eventually required for a camera useful in experiments) running at a data rate of 1Gb/s. The serializer has been layout and post-verified in simulation with parasitic showing consistent behavior.

Figure 4. Simulations demonstrating the data rate capability of the high-speed serializers.

The chip has just been received (Fig. 5) and is being prepared for testing. After testing its functionality, it will be bump-bonded at SLAC to a currently available pixelated sensor (Fig. 6a). A dedicated carrier board was designed and fabricated, and it is now ready for mounting the chip and later the chip-sensor module. They will be integrated in the currently available ePix camera assembly (Fig. 6b). A dedicated firmware needs to be developed together with the synchronization with gating signals. The ePix DAQ and software interface will be modified accordingly.

Figure 5. Image of cPix2 chips.

We have experienced delays due to design complications and we will not be able to test the prototype camera before the SPEAR shutdown. We have just received a small amount of

additional funding to extend the project to FY16. This would allow us to complete the integration of the chip into the ePix system, to perform tests both functional and with x-rays, and to analyze the results.

Figure 6. a) ePix 10k sensor: designed and fabricated in house at SLAC and SNF. b) ePix-ONE camera assembly.

Publications

none

Workshops

FY2014

C. J. Kenney et al. "Photon-Counting Detectors for Pump-Probe Science", IEEE-NSS Conference Records, Seoul, Korea (2013).

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	No
Source of support for follow-on funding?	NA
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	N/A
Number of Post Docs supported by LDRD project in FY15?	0
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0

Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

5.0 Understanding Electrochemically-Active Oxide Surfaces Far From Equilibrium at Elevated Temperatures

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Principal Investigator: W. C. Chueh

Project Description

The goal of this project is to answer the most basic question on the reactivity of oxides: how charge-transfer reactions couple to surface chemistry and structure under large driving forces. We will develop the following in-situ synchrotron-based electronic and structural analysis tools to probe electrochemically-active oxides at elevated-temperature and near ambient gas pressure: X-ray photoelectron spectroscopy, absorption spectroscopy, and surface diffraction. In particular, we will investigate the reactivity of oxygen gas molecules with model perovskite oxides, which are chemically amenable to a wide range of compositions. Therefore, they are ideally suited for understanding the coupling between physical, chemical and electronic structures at electrochemical interfaces.

Accomplishments

In Year 3 of this LDRD project, we have successfully employed in-situ surface diffraction to study the surface crystallographic structures of several oxides for catalytic and electrocatalytic applications. Using the in-situ environmental cell developed at SSRL, we characterized the pressure- and temperature-dependent surface structure of SrTiO_3 , $(\text{La,Sr})\text{FeO}_3$, $(\text{Zr,Y})\text{O}_2$, and CeO_2 . These oxides are notable for their ability to lose and gain oxygen from the environment, necessitating in-situ measurements. High quality surface diffraction patterns were collected and analyzed through computer codes developed in-house. The resulting surface structure obtained on these materials provided valuable information on the growth mechanism, as well as atomic positions, both of which are crucial toward developing better catalysts and electrocatalysts.

In the case of CeO_2 , several nanometer thin films were grown on a single crystal substrate. We have obtained the first extended atomic positions for the entire film. We observed that surface roughness at the atomic level, as well as variable terrace heights across the macroscopic sample are responsible for the diffraction features which deviate from the ideal structure. In the case of SrTiO_3 , we observed that a Ti-rich reconstruction takes place on the first two atomic layer, with a strong evidence of double Ti layer. The stability of such a reconstruction was found to be very dependent on the pressure and temperature.

In summary, this LDRD-supported effort have led to the development of in-situ surface diffraction, as well as photoemission and absorption spectroscopy for studying catalytic and electrocatalytic materials under reaction conditions. This capability positions SSRL to become a world leader in the in-situ characterization of functional materials. Follow-on funding has been obtained from DOE-BES through the X-ray Scattering program in the Materials Science Division.

Publications

FY2015

D. N. Mueller, M. L. Machala, H. Bluhm, W. C. Chueh. *"Redox activity of surface oxygen anions in oxygen-deficient perovskite oxides during electrochemical reactions,"* Nature Commun. 6:6097 (2015).

Y. Shi. *"Oxide surface and bulk structure by studied by real-space and reciprocal space probes"*. Thesis, Stanford University (2015)

Y. Shi, S. C. Lee, W. D. Nix, M. F. Toney, R. Sinclair, W. C. Chueh. *"Strain-Driven Growth Mode Transition of Ceria Ultrathin Films on Zirconia"*. Under preparation.

Workshops

FY2015

American Chemical Society National Meeting. Aug. 18, 2015. Boston, USA.

Meeting of the Electrochemical Society. May 27, 2015. Chicago, USA.

Advanced Photon Source Upgrade Workshop. May 21, 2015. Argonne, USA.

University of California, Los Angeles, Department of Materials Science & Engineering. Nov. 14, 2014. Los Angeles, USA.

University of Washington, Department of Chemical Engineering. Nov. 3, 2014. Seattle, USA.

International Symposium on Electrocatalysis. Oct. 27, 2014. Whistler, Canada.

Advanced Light Source Energy Conversion & Storage Workshop. Oct. 7, 2014. Berkeley, USA.

Advanced Light Source Users Meeting. Oct. 6, 2014. Berkeley, USA.

Advanced Light Source Diffraction-Limited Workshop. Oct. 1, 2014. Berkeley, USA.

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE-BES
Has follow-on funding been obtained?	Yes
Amount of follow-on funding (\$K)?	3,500

Number of Post Docs supported by LDRD project in FY15?	1
Number of students supported by LDRD project in FY15?	1
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

6.0 Chemistry in Motion: New Approaches to Probe Enzymatic Reaction Mechanisms in Crystallo

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Principal Investigator: Aina Cohen

Project Description

This project aims to confront several experimental problems that are impeding progress in structural enzymology through the development of a toolbox of new experimental methods broadly applicable to the study of enzymatic reaction mechanisms in crystallo at both LCLS and SSRL. A main scientific goal is to apply these tools to trap several key intermediates in the mechanisms of methane monooxygenase MMO, extradiol aromatic ring-cleaving dioxygenase 2,3-HPCD, dye-decolorizing peroxidase DypB, as well as other important heme and non-heme iron oxidoreductases that have been predicted from solution studies but have yet eluded structural characterization. We will use the combination of X-ray crystallography with optical (UV-visible-NIR absorption) and X-ray absorption spectroscopy to study catalytic mechanisms of these enzymes in crystallo. A particularly innovative aspect of these approaches will be the use of pressure techniques and flow cells in injectors to initiate and monitor reactions with gaseous substrates, as well as fast reaction initiation in crystallo for diffusion-based processes. This work will result in the development of a toolbox of new sample cells, injectors and methodologies which as a whole would be generally applicable to a wide range of crystalline enzymes, with or without a chromophore, of various sizes and morphology, and would enhance experiments carried out at both LCLS and SSRL.

We will conduct this work on the bench and at the beam line to optimize the lifetimes of intermediates under varied conditions (i.e. temperature, pressure, humidity, electronic and chemical environments), and use this information to adapt experimental designs for optimal performance. It is imperative that our methodologies produce catalytically relevant rather than radiation-affected structures. To this end, in situ spectroscopic monitoring at SSRL will determine the radiation 'lifetime' of crystals. Data from acutely radiation sensitive species will be collected using short X-ray pulses at LCLS (diffraction before destruction). When macrocrystals are available, these experiments will be conducted using the goniometer-based setup developed for LCLS XPP. For diffusion-limited reactions or when larger crystals are not available, serial femtosecond nano-crystallography experiments will be conducted at LCLS CXI. Integration of the goniometer and injector-based developments into the new LCLS-MFX station when it becomes available, will pave the way to the routine structure determination of acutely radiation sensitive metalloenzymes.

The information obtained as part of the collaborative research component to structurally characterize important reaction intermediates such as sMMO, 2,3-HPCD, DypB, and CcP Cmpd I will be of significant impact to the field of structural enzymology.

Accomplishments

Highlights of the work recently achieved for this project include the following:

Structure determination of a high-valent intermediate of DypB peroxidase in two different space groups. The structure of an extremely radiation sensitive high-valent Fe(IV)=O intermediate of DypB peroxidase was determined to 1.45 Å resolution using femtosecond diffraction data collected at the LCLS XPP, representing the highest resolution structure of a reactive intermediate solved using XFEL to date. A second structure of the same intermediate state of DypB was determined to 2.1 Å resolution using crystals of a different space group and pH conditions. The availability of datasets collected in both crystal forms enable examination of the effects of crystal packing interactions, which may influence the architecture of the active site and, ultimately stability and reactivity of the Fe(IV)=O intermediate.

Single crystal optical spectroscopy analysis carried out at SSRL BL11-1 demonstrated that metal centers in both ferric (resting) and ferryl (reacted) forms of DypB suffer rapid photo-reduction upon exposure to even small dose of x-rays. Furthermore, crystals of DypB in the resting state and reacted with peroxide, prepared using conditions similar to those used for diffraction studies, were also used for XAS experiments at SSRL BL9-3 (in collaboration with Riti Sarangi, SSRL). The results confirm formation of Fe(IV) species during the *in crystallo* reaction, and calculated bond lengths compare well with those established for Cmpd I species. These correlated spectroscopic and structural studies demonstrate the utility of optical and x-ray absorption spectroscopies to confirm enzyme oxidation state and the power of the XFEL “diffraction before destruction” paradigm to visualize the molecular structures of acutely radiation sensitive active sites of metalloenzymes.

New experimental workstation for spectroscopic monitoring of samples in flow cells and liquid jets. A workstation has been developed for *in situ* UV-Vis-NIR spectroscopic monitoring of enzymatic reactions *in-crystallo* using liquid jets and flow cells. The principle components include 1) an injector/flow cell testing station, consisting of gas pressurization systems for operating the GDVN injector, mechanical supports and positioners, nutating mixer to prevent crystal settling within sample reservoirs, and switching valves for delivery of different samples / conditions (including inert atmosphere), and 2) an integrated UV-Vis-NIR microspectrophotometer with orthogonal zoom cameras for centering and alignment. Following commissioning and SLAC ES&H approval for operation, the injector/spectroscopy workstation was used for successful testing of GDVN nozzles in atmosphere using either helium or air (20% O₂) as a sample focusing gas. This station will be available to SSRL and LCLS users.

Crystallization conditions of the MMOH-MMOB complex identified. Crystallization of the octameric MMOH-MMOB active protein complex, with the aim of producing diffraction-quality macro-crystals, has been the subject of significant effort for decades. We have initiated multi-variable screens to search for and to optimize production of nano- or micro-crystals of MMOH-MMOB complex for our experiments using injector-based techniques. Multiple hits obtained show promise as evidenced by the results from the UV-Trp fluorescence microscopy, which was used to verify that the crystalline species are of protein nature. Furthermore, these same conditions used

for MMOH hexamer alone did not produce crystals. Optimization of crystallization conditions has been carried out to reduce film and precipitate formation in droplets, and maximize crystalline material to enable scaling up for batch crystallization for x-ray diffraction and spectroscopic analysis.

Highly efficient serial femtosecond crystallography: The 1.75 Å structure of homoproteocatechuate 2,3-dioxygenase. Parallel SFX and TEM experiments were carried out using fragmented nano-crystals of wild type (WT) homoproteocatechuate 2,3-dioxygenase (2,3-HPCD) and an active site H200Q variant. The structure of the H200Q variant was solved at 1.75 Å resolution using just 14000 indexable diffraction patterns collected in only ~16 minutes of beam time at LCLS CXI. This may be the most rapidly collected high-resolution structure determined using an XFEL approach. In contrast to the H200Q sample, the indexing rate of the WT crystals was an order of magnitude lower, despite similarity in size and number of microcrystals in both samples. TEM experiments revealed that sample of the WT enzyme preparation contained an abundance of protein aggregates and crystal conglomerates, and a significantly smaller population of highly ordered lattices (collaboration with the Calero group, University of Pittsburgh). These results demonstrate the utility of TEM analysis to predict diffraction quality of microcrystal samples, which is a critical parameter that can determine the success of a SFX experiment.

The plan for FY16 activity for this project will include the following:

- 1) Two publications on the results described in sections 1 and 4 (above) will be completed and submitted.
- 2) Further optimization of reaction-triggering parameters for liquid injector-based experiments using 2,3-HPCD microcrystal samples are required and, correspondingly, improvements will be made to the experimental workstation for spectroscopic monitoring of samples in flow cells and liquid jets: optical components will be optimized to maximize the signal from the jet stream and minimize background and scatter and to enable positioning of thin injector streams (~5µm OD) into the small light spot of the reflective objectives (5 x 40 µm). Work will also continue to systematically optimize the GDVN injector parameters to evaluate pressure, capillary ID, viscosity, substrate and microcrystal concentration effects on the mixing and reaction triggering time. The microcrystal handling station inside of the anaerobic glovebox may be improved for better preparation, manipulation and efficient loading of the samples into the GDVN reservoirs ensuring a high degree of anaerobicity upon transfer back to atmosphere. This workstation will not only support the experiments described in this LDRD but will serve as a resource to other crystallographers at SLAC to prepare for upcoming experiments at LCLS and SSRL.
- 3) Continue efforts in structural and spectroscopic characterization of transient and radiation-sensitive intermediates of non-heme dioxygenase (2,3-HPCD) and methane monooxygenase (MMO). This work will take advantage of various sample handling devices (mixing injectors and flow cells) and spectroscopic methods to optimize lifetimes and identify intermediates, as well as the diffraction data acquisition facilities at SSRL. For the 2,3-HPCD system, the key steps involve optimization of reaction triggering parameters and intermediates' lifetimes using micro-crystalline

samples for liquid injector experiments and using macro-crystals for flow cell experiments. For the MMO project, the most challenging part is to optimize crystallization hits that produce co-crystals of multimeric MMOH-MMOB complex for batch crystallization (reducing surface film and precipitate). This will be followed by optimization of kinetics *in crystallo* under aerobic and anaerobic conditions, including use of mixing devices for reaction triggering within liquid injector.

Publications

FY2015

A.E. Cohen, T. Doukov, S.M. Soltis, "UV-Visible Absorption Spectroscopy Enhanced X-ray Crystallography at Synchrotron and X-ray Free Electron Laser Sources". Protein Pept Lett., In Press.

G. Chreifi, E.L. Baxter, A.E. Cohen, T. Doukov, Y.T. Mehareenna, S.M. Soltis, TL. Poulos, "Crystal Structure of the Pristine Peroxidase Ferryl Center and its Relevance to Proton-Coupled Electron Transfer". In submission.

FY2014

A.E. Cohen, S.M. Soltis, A. González, L. Aguila, R. Alonso-Mori, C.O. Barnes, E.L. Baxter, W. Brehmer, A.S. Brewster, A.T. Brunger, G. Calero, J.F. Chang, M. Chollet, P. Ehrensberger, T.L. Eriksson, Y. Feng, J. Hattne, B. Hedman, M. Hollenbeck, J.M. Holton, S. Keable, B.K. Kobilka, E.G. Kovaleva, A.C. Kruse, H.T. Lemke, G. Lin, A.Y. Lyubimov, A. Manglik, I.I. Mathews, S.E. McPhillips, S. Nelson, J.W. Peters, N.K. Sauter, C.A. Smith, J. Song, H.P. Stevenson, Y. Tsai, M. Uervirojnangkoorn, V. Vinetsky, S. Wakatsuki, W.I. Weis, O.A. Zadvornyy, O.B. Zeldin, D. Zhu, K.O. Hodgson, "Goniometer-based femtosecond crystallography with X-ray free electron lasers"., Proc Natl Acad Sci U S A., 111(48), 17122-7 (2014).

In preparation

E. G. Kovaleva, C. O. Barnes, H. P. Stevenson, A.E. Cohen and G. Calero. *The 1.75 Å Structure of an Extradiol Dioxygenase by Highly Efficient Serial Femtosecond Crystallography and Assessment of Microcrystal Quality by Transmission Electron Microscopy*".

E. G. Kovaleva, R. Sarangi, R. Singh, A.E. Cohen and L.D. Eltis, "Characterization of a ferryl intermediate in DypB peroxidase using femtosecond crystallography, optical and x-ray absorption spectroscopies".

Workshops and Presentations

FY2014

Elena G. Kovaleva, Correlated Structural and Spectroscopic Analysis to Study Macromolecular Catalysis in crystallo: Single Crystal UV-Vis and X-Ray Absorption Spectroscopy of a High-Valent

Intermediate in DypB Peroxidase. Metals in Biology, Gordon Research Conference, Ventura, CA, January 2014.

Aina E. Cohen, Goniometer-based Femtosecond diffraction studies at the LCLS. The 1st Ringberg Meeting on Structural Biology with XFELs, Ringberg, Germany, Feb 2014.

Patents/Inventions Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	NIH
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	0
Number of Post Docs supported by LDRD project in FY15?	0
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	1
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0

7.0 Compact High Power Terahertz Source

Principal Investigator: Michael Fazio / Sami Tantawi

Project Description

The goal of this LDRD is to show proof of principle for a new class of RF sources that can generate power at millimeter-wave (mmw) to Terahertz (THz) frequencies. This LDRD project explored a number of theoretical concepts and demonstrated the most promising one by multiplying from X-band (11.424GHz) to V-band (57.12GHz). This LDRD provides the necessary understanding to pave the way for building new devices capable of scaling to higher frequencies in the THz regime.

What we call mm-wave/Terahertz refers to the part of the electromagnetic frequency spectrum above 40 GHz up to several Terahertz. Although there are a vast number of visionary papers on THz applications, this part of the spectrum is still unexploited, because of the lack of sources - mainly amplifiers - that are able to provide substantial amounts of power.

The principle reason that today's available THz devices fail to produce significant power, is that their critical dimensions are small compared to the wavelength of the radiation they produce (wavelength is 300 μm at 1 THz), and therefore the amount of beam current that can be transported through them is very limited. What is needed is a device/technology that is inherently larger than the wavelength of the radiation it produces.

Compact, high power mmw-THz sources are an enabling technology for basic research, high-resolution medical imaging, navigation through sandstorms, spectroscopic detection of explosives, high bandwidth, low probability of intercept communications, debris tracking for objects less than 5cm that present hazards to space assets, and even human space flight safety.

This LDRD uses the idea of circular beam deflection produced by an input cavity at a low frequency, coupled with a spherical resonator as the output cavity at a higher frequency (Figure 1). This concept yields several advantages over other approaches. In this scenario, the beam, traveling in the z direction, enters the input cavity and gets kicked in the radial direction. As the beam travels to the output cavity it sweeps out a cone at 11.424 GHz. The rotating electromagnetic field mode in the higher frequency output cavity is designed to match the conical beam rotation. This coupling generates power at the output mode frequency (frequency multiplication). Since the frequency context is not encoded as longitudinal bunching, but as a rotational wave, space charge is no longer a limitation, in contrast to devices like klystrons or TWTs. We further observed, that when multiplying from X-band (8-12GHz) to V-band (50-75GHz) or W-Band (75GHz-110GHz), the dimensions of this resonator allow for a device that is small enough that beam expansion is minimal, even without any focusing magnetic field, but big enough to allow for significant current (needed for high power) to go through. There is therefore no need for a narrow diameter beam pipe, or any magnetic focusing. In the future, this design concept can be used to multiply to even higher frequencies in the THz regime.

Accomplishments

In September of 2015 the LDRD frequency multiplication concept was demonstrated, generating approximately 18 watts of RF power at 57 GHz using an X-band 11.4 GHz RF driver. This successfully showed proof of principle of the concept and paves the way for new devices capable of generating higher powers at mmw-Terahertz frequencies.

A cutaway of the prototype is shown in Figure 1

Figure 1: (Left) Device cross section. (Top-Right) RF circuit cross section of the input deflecting cavity and output cavity. (Bottom-Right) RF circuit particle simulation of the electron beam deflected by the input deflecting cavity.

SLAC designed, manufactured, and tested the device. Figure 2 shows pictures of the prototype and selected sub-components.

Figure 2: (Left) Final mechanical assembly of the 57.12 GHz source. (Middle) Electron gun focus electrode assembly. (Right) First pass aluminum prototype of the deflecting cavity

The electron gun performed as designed, achieving 0.6 micro-perveance in the space-charge-limited regime (Figure 3). The cathode was contaminated but easily recovered to standard behavior when operated at somewhat elevated temperatures for tens of minutes.

Figure 3: (Left) Electron gun assembly. (Right) Measured gun emission agrees with simulation.

The device was hot-tested and electrically characterized in September. With a beam voltage of 30 kV the device generated approximately 18 watts of 57 GHz RF power as shown in Figure 4. At this operating point the beam power was 69 kW and required approximately 30 kW of X-band drive for an electronic efficiency < 1%. The efficiency achieved in this first test is far below the design specification of 12% due to a combination of manufacturing imperfections and an evolving understanding of the physics of the device. There is ongoing testing to improve the device performance. Using higher beam current and voltage and RF circuits that are more sophisticated should also dramatically increase the efficiency in future devices. The device is very narrow-band. The measured bandwidth is 1.8 MHz.

The frequency spectrum of the device was measured to verify proper operation. Figure 4 shows the output spectrum of the device. The output power is predominately generated in the 5th harmonic at 57 GHz as designed, however a small amount of RF power is generated in the 4th and 6th harmonics. The signal strength of the 5th harmonic is more than one thousand times stronger than the adjacent harmonics and the 7th harmonic was not detectable at all.

Figure 4: (Left) Measured device performance showing ~18W of RF output power generated at 57GHz. (Right) Output frequency spectrum showing power is predominately generated in the 5th harmonic (57GHz).

This LDRD successfully demonstrated a promising new approach to generate mmw-THz radiation. In the first experiment the newly designed and fabricated, unoptimized device generated 18 watts of output power at 57 GHz using 11.4 GHz RF drive power. Future devices should be able to build on this concept to generate higher power at higher frequencies in the mmw-THz regime. This project enabled us to begin developing the intellectual, scientific, fabrication, and measurement capabilities that will position us to develop new RF source projects in the mmw-THz frequency spectrum.

Publications

FY2015

No publications will be made until a patent is awarded.

Workshops

FY2015

No workshops presentations until a patent is awarded.

Patents/Invention Disclosures/Copyrights

FY2015

Filing expected in late October.

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DARPA
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	n/a
Number of Post Docs supported by LDRD project in FY15?	0
Number of students supported by LDRD project in FY15?	1
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total??	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

8.0 Modeling Acceleration in Laser Driven Shocks

Principal Investigator: Frederico Fiuza

Project Description

Project Description

The goal of this LDRD project is to study the physics of collisionless shocks through first principles simulations and laboratory experiments in order to understand how the plasma conditions affect the shock structure, to identify optimal conditions for particle acceleration in high energy density (HED) plasmas, and to demonstrate the controlled generation of high-energy ion beams. We will accomplish this by using detailed first principles particle-in-cell (PIC) simulations to model the plasma conditions associated with HED and astrophysical plasmas, identify the dominant physics processes, and use this understanding to design properly scaled experiments that can probe this physics in the laboratory. The accomplishment of this project will provide a fundamental understanding of the physics of shocks and cosmic-ray acceleration in astrophysical plasmas and potentially bring a World-leading compact ion source to SLAC that sets a fast pace in the development of applications with high societal impact.

Accomplishments

With this LDRD the PI started in February 2015 a small theory and simulation group in the recently established HED science division to accomplish the different goals associated with this project. A postdoc, Charles Ruyer, was hired in August 2015, and a PhD student from Stanford, Samuel Totorica, has also been working under the guidance on the PI in this project. A summary of the accomplishments of the project in FY2015 and goals for FY2016 are listed below.

Relativistic plasma instabilities and collisionless shocks at MEC

Relativistic streaming plasma instabilities play a critical role in the generation of strong magnetic fields in high-energy astrophysical plasmas and affect the formation of shocks, acceleration of particles and radiation emission. In fusion plasmas driven by high-power lasers, these instabilities affect the energy transport and their control is important for efficient coupling of the energy to the fuel. We have studied the possibility of driving these instabilities with the MEC short pulse laser and probe the corresponding density structure with LCLS. Figure 1 summarizes the results obtained. We have shown that the relativistic electrons accelerated by the MEC laser will drive a current filamentation instability (also known as Weibel instability) that leads to density filaments with a wavelength of 1-3 microns, perturbation amplitudes of up to 50% of the background plasma density, and to the generation of 100 MG magnetic fields inside the target (Figure 1a and 1b). The corresponding phase-contrast imaging (PCI) has been modeled for 8 keV LCLS x-rays and is shown in Figure 1c and 1d. We have chosen a realistic MEC geometry, where the sample is positioned 20 mm behind the focus (FOV $\sim 25 \mu\text{m}$) and the detector 4 m downstream ($M \sim 200$). The results clearly show that we can obtain high-contrast images, measuring the wavelength of the filaments and inferring its 3D structure by the comparison of different probing angles. We have submitted a proposal to LCLS to perform this experiment and were awarded beam time in

November 2015. The measurement of the spatio-temporal dependence of the filamentation instability and the merging rate of the filaments is a critical ingredient for understanding how the filaments evolve and lead to the generation of a collisionless shock.

Figure 1. (top) *Ab initio* particle-in-cell (PIC) simulation of the Weibel/current filamentation instability driven by relativistic electrons produced in the interaction of the MEC short pulse laser with a 20 μm hydrogen plasma. The laser (20 TW power, 150 fs duration, 7 μm spot diameter) irradiates the hydrogen jet from the left-hand side for parameters of the MEC station. (a) Density and (b) magnetic field profiles are clearly correlated and show the development of regular filaments with density perturbations $\delta n/n \sim 50\%$ and magnetic field amplitudes up to 100 MG. (bottom) Post-processed x-ray diagnostics from the PIC simulation data. (c) Simulated phase-contrast image (PCI) for 8 keV x-rays probing perpendicularly to the filaments (90°). Total number of photons integrated over FOV is 3×10^{10} , assuming LCLS delivers 10^{12} photons/pulse, the lens transmission is 30% and the aperture of the focusing lens captures about 10% of the full LCLS' beam intensity. (d) Reconstructed plasma density structure from the PCI data.

Magnetic field generation in laboratory pair plasmas

In connection with the study of relativistic streaming instabilities of relevance for astrophysical plasmas, we have investigated the possibility of generating high fluxes of electron-positron pair plasma jets for laboratory astrophysics applications. Such jets can be generated experimentally by irradiating a gold foil with ns lasers of kJ energy. We have shown that the number of electron-positron pairs scales with the square of the laser energy. Based on this scaling we have performed detailed PIC simulations to model the interaction of two counter-streaming pair jets driven by near-future laser facilities, like the NIF-ARC (10 kJ laser). Our results show that under such conditions it is possible to drive a relativistic pair collisionless shock in the laboratory and study the underlying physics behind internal shocks in gamma-ray bursts. We predict the generation of magnetic fields of the order of MG, allowing for its characterization using proton radiography. These results were published in Physical Review Letters and Physics of Plasmas.

Ion acceleration from laser-plasma interactions

We have started to explore the possibility of accelerating ions by an electrostatic shock driven by intense laser-matter interactions. This work is done in collaboration with different experimental teams performing experiments at Titan (LLNL), Omega EP (LLE), and Draco (Germany). We have modeled the Titan configuration, corresponding to a laser normalized vector potential $a_0 = 2$, showing the possibility of generating proton beams with 4 MeV, in good agreement with the experimental results. Data analysis for different laser and target parameters is underway.

The progress obtained in FY2015 addresses important milestones of our project. In particular, we have 1) performed first-principles PIC simulations of the short-pulse laser-plasma interactions for MEC/LCLS conditions, 2) identified conditions to probe physics of relativistic streaming instabilities in the laboratory, 3) modeled PCI and x-ray scattering diagnostics for MEC/LCLS experiment, 4) successfully applied and guaranteed experimental beam time at MEC/LCLS, 4)

identified the conditions to study relativistic electron-positron shocks in the laboratory, 5) modeled the first set of Titan and Draco experiments on ion acceleration.

Expected progress in FY16

In FY16 we will continue to study the physics of collisionless shocks and particle acceleration through first principles simulations and laboratory experiments in order to understand how the plasma conditions affect the shock structure, to identify optimal conditions for acceleration of particles, and to demonstrate the controlled generation of high-energy ion beams. These results are expected to lead to high-profile publications, as it was already the case in FY15.

Having been awarded beam time at LCLS to study relativistic filamentation we will focus large part of our effort in FY16 to modeling this experiment, performing the experiment, analyzing its data, and developing the numerical tools that allow for direct comparison between simulation and experimental diagnostics (phase-contrast imaging, Thomson scattering, etc). We will also perform detailed 3D simulations of several experiments being planned on ion acceleration at Titan, Omega EP, and Draco facilities, with the goal of optimizing the parameters for shock acceleration and identifying the conditions for generation of >100 MeV proton beams. Finally, we will continue the study of counter-streaming flows as a function of the plasma conditions, focusing on the role of an ambient magnetic field in determining the shock formation process and particle acceleration. The main deliverables for FY16 are to 1) simulate in 3D and perform the MEC experiment on the Weibel instability and analyze corresponding data (new milestone based on awarded LCLS beam time), 2) model in 3D the Titan, Omega EP, Draco experiments on ion acceleration and identify optimal conditions for generation of high energy, high quality ion beams, 3) characterize counter-streaming flow interaction in magnetized plasmas to identify conditions that lead to formation of shocks and acceleration of particles, and 4) guarantee supercomputing time for the project through INCITE and/or ALCC.

Publications

FY2015

S. Titorica, T. Abel, F. Fiuza, *Non-thermal electron energization induced by magnetic reconnection in laboratory laser-driven plasmas*, Physical Review Letters, submitted (2015)

H. Chen, F. Fiuza, A. Link, A. Hazi, M. Hill, D. Hoarty, S. James, S. Kerr, D. D. Meyerhofer, J. Myatt, J. Park, Y. Sentoku, and G. J. Williams, *Scaling the Yield of Laser-Driven Electron-Positron Jets to Laboratory Astrophysical Applications*, Physical Review Letters 114, 215005 (2015)

H. Chen, A. Link, Y. Sentoku, P. Audebert, F. Fiuza, A. Hazi, R. F. Heeter, M. Hill, D. L. Hobbs, A. J. Kemp, G. E. Kemp, S. Kerr, D. D. Meyerhofer, J. Myatt, S. R. Nagel, J. Park, R. Tommasini, G. J. Williams, *The scaling of electron and positron generation in intense laser-solid interactions*, Physics of Plasmas 22, 056705, (2015)

Workshops

FY2015

F. Fiuza, *Particle acceleration in shocks: from astrophysics to the laboratory in silico*, Plasma Science Frontiers Workshop, Sponsored by DOE, Fusion Energy Sciences, SLAC, 2015 (*poster*)

F. Fiuza, *Generation of collisionless shocks in laser-produced plasmas*, 29th IAU General Assembly Meeting, Honolulu, 2015 (*invited*)

F. Fiuza, *High Energy Density Physics Research at SLAC*, 45th Anomalous Absorption Conference, Ventura, 2015 (*plenary*)

F. Fiuza, *Particle acceleration in Weibel-mediated shocks*, Accelerating Cosmic Ray Comprehension Workshop, Princeton University, 2015 (*invited*)

F. Fiuza, *Ab initio modeling of magnetic field generation and particle acceleration in laboratory and astrophysical plasmas*, 1st Conference on Laser Energetics, Yokohama, 2015 (*invited*)

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE
Has follow-on funding been obtained?	YES
Amount of follow-on funding (\$K)?	250
Number of Post Docs supported by LDRD project in FY15?	1
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	1
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total??	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

9.0 Center for Laboratory Astrophysics

Principal Investigator: Siegfried H. Glenzer

Project Description

The goal of this LDRD is to develop laboratory astrophysics experiments delivering world-class x-ray probing capabilities to some of the most important and difficult areas of astrophysical plasmas, i.e., cosmic particle acceleration, antimatter relativistic plasmas and high-pressure planetary physics. We will design accurate and first principles based experimental techniques to measure transient states and ultrafast phenomena, thus allowing critical experimental tests of theoretical predictions and simulations. This is accomplished through preparing and designing high-power laser experiments on novel targets using particle-in-cell (PIC) simulations. In particular, the interaction of the future 200 TW laser at LCLS/SLAC with cryogenic hydrogen plasma jets is of particular interest. This new laser capability will be amended through cryogenic target development within this LDRD. At the end of the funding period the experiments at SLAC, complemented by detailed simulations, will allow us to reach the required regime to investigate relativistic interactions for particle acceleration and the early stages of collisionless shock formation.

Accomplishments

During the second year of funding we have developed a novel continuous cryogenic hydrogen jet target and succeeded in transferring the technology to LCLS to perform the first high-power laser-jet experiment at the Matter in Extreme Conditions (MEC) instrument. We utilized the 100 mJ laser at MEC for laser-jet interaction studies. The jet pointing stability and the alignment strategy was developed at S-10 and adopted for the MEC experiment, cf. Figure 1. During the experiment, we have demonstrated jet performance using hydrogen and deuterium at various cross sections and diameters ranging from 2 to 15 micrometer. In addition, full laser-energy shots have been demonstrated with 1 Hz operation resulting in novel proton and deuteron sources with energies approaching 1 MeV for pump-probe experiments with the LCLS x-rays.

We also performed LCLS x-ray scattering at 5.5 keV photon energy and at 120 Hz on cryogenic hydrogen and deuterium measuring the Debye-Scherrer rings associated with crystal structure of solid hydrogen at temperatures of the order of 10 K. Figure 1 shows two examples on the right hand side indicating the ionic lattice produced by evaporative cooling of the jet and formation of a solid. The peaks correspond to hcp and fcc structures. When heating the jet by the laser hydrogen melts and transitions into an astrophysical plasma state. We observe a decrease in Bragg intensity as function of time and the formation of a broad ion-ion correlation peak. While the Bragg intensity behavior determines the electron-ion equilibration time scales the broad ion-ion correlation feature is sensitive to the ion-ion structure factor. These well-characterized conditions allow us to compare experimental data with particle in cell simulations of the acceleration mechanism for protons and deuterons.

Figure 1: The cryostat is shown in the center of the image together with alignment diodes and an alignment fixture. The fixture is important to keep the jet stable. The collimated jet is expanding into the vacuum (center bottom). A shadowgraphy image of the jet shows that the jet is stable with an rms jitter of ± 1 μm . The collimated jet is expanding into the vacuum (center bottom). A shadowgraphy image of the jet shows that the jet is stable with an rms jitter of ± 1 μm . The data show segments of Debye-Scherrer diffraction rings from hydrogen and deuterium measuring the structure (right).

Simulations performed with the particle in cell code PICLS have demonstrated that the high-power laser interaction with the jet shows features associated with hole boring and the generation of the Weibel instability. Figure 2 shows a simulation with the laser beam coming from the left producing energetic particles by Radiation Pressure Acceleration (RPA) and a shock front. On the exit side of the jet hydrodynamic features are sticking out that are due to the Weibel instability from counter-propagating currents. The features are consistent with observations. The simulations are presently being utilized to optimize laser and target conditions for producing mono-energetic proton beams.

Figure 2: Results from high-resolved particle in cell simulations showing the laser penetrating into the jet from the left and accelerating protons to MeV energy.

For FY2016, we expect the LDRD will continue to support the development of novel targets and probing capabilities for astrophysical plasma states. These studies are expected to result in first-class publications on their own and will subsequently become available as techniques for x-ray experiments at MEC/LCLS. The main deliverables for FY2016 are continuing the development of

1) new cryogenic target deliveries in the Sector-10 laser laboratory with a goal towards demonstrating new target materials such as CO₂ or CH₄, 2) simulations to prepare and interpret high-power laser experiments using the cryogenic jet targets, and 3) novel pump-probe diagnostics that are applicable to measure the physical properties of plasmas produced from cryogenic jets.

Publications

M. Gauthier, L. B. Fletcher, A. Ravasio, et al., New experimental platform to study high density laser-compressed matter, Rev. Sci. Instrum. 85, 11E616 (2014).

P. Sperling, E. J. Gamboa, H.-J. Lee, H. K. Chung, E. Galtier, Y. Omarbakiyeva, H. Reinholz, G. Roepke, U. Zastra, J. Hastings, L. B. Fletcher, and S. H. Glenzer, Free-electron x-ray laser measurements of collisional-damped plasmons, in preparation for Phys. Rev. Lett. 115, 115001 (2015).

E. J. Gamboa, L. B. Fletcher, H. J. Lee, U. Zastra, M. Gauthier, D. Gericke, J. Vorberger, E. Granados, M. J. MacDonald, J. B. Hastings, and S. H. Glenzer, Band gap opening in strongly compressed diamond observed by x-ray energy loss spectroscopy, submitted to Nature Phys. (2015).

E. J. Gamboa, L. B. Fletcher, H. J. Lee, U. Zastra, E. Galtier, M. J. MacDonald, M. Gauthier, J. Vorberger, D. O. Gericke, E. Granados, J. B. Hastings, and S. H. Glenzer, Single-shot measurements of plasmons in compressed diamond with an x-ray laser, Phys. Plasmas 22, 056319 (2015).

Workshops

Third MEC user workshop on High-Power Lasers, HPL-III workshop, Sponsored by DOE, Fusion Energy Sciences, Stanford CA, October 5-6, 2015. C. Bolme, A. Fry, and S. H. Glenzer.

<https://conf-slac.stanford.edu/hpl-2015/content/3rd-high-power-laser-workshop>

LCLS-II Scientific Opportunities Workshop, SLAC National Accelerator Laboratory, February 9-13, 2015, S. H. Glenzer, P. Heimann, J. B. Hastings.

https://portal.slac.stanford.edu/sites/conf_public/LCLS2ScienceFeb15/Pages/mpw.aspx

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE, NIH
Has follow-on funding been obtained?	Yes

Amount of follow-on funding (\$K)?	730
Number of Post Docs supported by LDRD project in FY15?	3
Number of students supported by LDRD project in FY15?	2
Number of scientific staff/technical staff hired with LDRD funding in FY15?	2
Number of copyrights filed in FY15 and in total?	1/1
Number of invention disclosures filed in FY15 and in total?	1/1
Number of patent applications filed in FY15 and in total?	1/1

10.0 Structural Characterization of Electrolyte and Polymer Gates Electronics to Better Control Device Properties

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Principal Investigator: David Goldhaber-Gordon

Project Description

Electrical control of materials with strong electronic correlations or exotic electronic structure is key to making next-generation devices based on their rich physics.

In the past several years, both electrolyte and polymer based gating have emerged as powerful and flexible techniques for achieving the largest carrier densities in these materials. Characterizing the structure of the interface between the channel and these unconventional gate dielectrics is critical to understanding the gating effects. In this project, we are elucidating the structure of the gating medium and channel *in situ*, which will guide improvements in device properties and function.

We are using x-ray reflectivity, crystal truncation rod measurements, and absorption spectroscopy to probe the interfacial structure of ionic liquid and polymer gated strontium titanate, graphene, and lanthanum nickelate. Specifically, as a function of applied electric field (voltage on our gate electrode) we are studying: 1) organization of ions and polymer molecules near the surface, including lateral ordering and layering normal to the surface, and 2) changes in oxidation state of transition metal ions near the channel surface.

This proposal directly addresses both aspects of the third DOE grand challenge: to understand how “remarkable properties of matter emerge from complex correlations” and to explore how these properties can be controlled.

Accomplishments

We have successfully met our major first year milestone: using x-ray reflectivity to characterize the interfacial structure of SrTiO₃ gated with the ionic liquid 1-butyl-3-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate (BMPY-FAP), including the charge density and potential as a function of distance from the interface. We have prepared a manuscript detailing these results, and we have just submitted it to a journal.

As outlined in our proposal, several technical advances were required for success. First, we built an x-ray transparent, high-vacuum electrochemical cell, interfaced with the existing sample-biasing electronics and beamline data acquisition software, to enable electrolyte gating in a clean environment.

Second, we addressed the loss of signal due to attenuation of the x-rays passing through the electrolyte and concomitant increase in the background due to scattering from the liquid in two ways. 1) We developed a method to spin thin layers (1 μm) of electrolyte gel on the surface,

reducing the x-ray path length through the electrolyte. 2) We increased the collimation of the scattered beam while reducing the need for perfect alignment by putting a new pair of motorized slits in front of the Pilatus 100K area detector. Figure 1 shows the improvement that we achieved with these 2 changes: up to three orders of magnitude increase in signal to background at low angles, and access to 2.5x higher scattering vectors.

Figure 1: Improvement in signal to background ratio during FY15. Signal intensity (large circles) and background intensity (small squares) versus scattering vector for BMPY-FAP on SrTiO₃ at the beginning of the year (black) and after the 2 improvements detailed in the text (red).

Additionally, in FY15, we ordered a cryostat which can be mounted on the beamline with the required electrical feedthroughs and alignment motors so that we can investigate the temperature dependence of the interfacial structure in BMPY-FAP on SrTiO₃. We also began developing lithography and contact recipes for LaNiO₃ films.

In FY16, we plan to finish assembly of the cryostat, which will allow us to measure scattering and absorption spectra on gated SrTiO₃ and LaNiO₃ as a function of temperature. These measurements will help illuminate the mechanisms behind observed transport effects in these films during electrolyte gating, including to what extent migration of oxygen atoms is important. To further investigate this effect, we plan to investigate how placing a thin, chemically impermeable layer of hBN between the electronic material and the electrolyte influences gating – prior results under other funding (now ended) show that this change can dramatically improve electronic conduction. X-ray studies will clarify differences in surface chemistry and electrolyte charge layering when the surface is protected in this way during gating.

Publications

FY2015

T. Petach, A. Mehta, R. Marks, B. Johnson, M. Toney, and D. Goldhaber-Gordon, “Voltage controlled interfacial layering in ionic liquid on SrTiO₃”, in review.

Workshops

FY2015

T. Petach, *Structure of ionic liquid electric double layers: beyond the dilute ion approximation*, X-ray Science Gordon Research Conference, Stonehill College, MA, July 25 – 31, 2015.

T. Petach, A. Mehta, R. Marks, B. Johnson, M. Toney, and D. Goldhaber-Gordon, *Voltage controlled layering in bmpy-fap on SrTiO₃*, SSRL Users Meeting, October 7 – 9, 2015.

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	YES—in progress
Source of support for follow-on funding?	TBD
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	0
Number of Post Docs supported by LDRD project in FY15?	0
Number of students supported by LDRD project in FY15?	1
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total??	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

11.0 Interfacial Photoelectrochemistry Using Oxide Heterostructures

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Principal Investigator: Yasuyuki Hikita

Project Description

We use epitaxial complex oxide heterostructures, grown with atomic precision using pulsed laser deposition (PLD), to provide the experimental platform to develop highly efficient heterostructures for photoelectrochemical (PEC) water splitting devices. The efficiency of hydrogen generation from water and sunlight using semiconductors remains insufficient for commercial use despite its long history. One cause restricting the progress is the use of polycrystalline samples in the majority of the studies. Effects of crystalline orientation, particle size, and surface band alignments are typically not isolated, with experiments varying multiple parameters limiting fundamental understanding necessary for significant progress. The use of highly idealized yet realistic structures in thin film forms will enable to not only identify and evaluate the essential features found in polycrystalline samples, but also to develop new design strategies based on manipulating the electrostatic boundary conditions at oxide heterointerfaces. These technical approaches seed to study complex-oxide/electrolyte electrochemistry on firm grounds.

Accomplishments

Throughout this project, we have greatly expanded the application of oxide interface dipoles originally implemented at all-perovskite oxide solid-state heterojunctions. When two different phases, either solid/solid or solid/liquid, are brought into contact, an energy barrier inevitably forms, which controls the carrier transfer across these interfaces. However, these barriers are defined by the materials selection, restricting improvements in device performance. Our approach is to exploit the strong ionic bonding in oxides to generate electrostatic dipoles and hence generate a large electric field at these interfaces to modulate their energy band alignments.

In the solid-state junctions, we achieved a Schottky barrier height modulation over 0.8 V by inserting a < 1 nm thick LaAlO_3 layer at the Pt/ TiO_2 (001) Schottky junction. Here the alternate stacking of positive and negatively charged layers in LaAlO_3 naturally forms the dipole. This demonstration of the barrier height modulation even at polycrystalline metal/binary oxide interface provides a solid foundation on which to engineer highly efficient photoanode for use in PEC devices.

By applying the same technique to oxide/aqueous electrolyte interface, we successfully modulated the oxide/ electrolyte band edge alignment in aqueous solution. The limited tunability in the control of semiconductor band edges with respect to the hydrogen/oxygen evolution potential has been a major bottleneck for improving the efficiency in PEC water splitting devices. Similar to the abovementioned Schottky junction, we formed atomic scale dipole layers on top of a single crystalline *n*-type complex oxide semiconductor photoanode. By varying the dipole layer thickness, we observed a shift in the flat band potential far surpassing any previous flat band potential shift using molecular dipoles, strongly supporting the effectiveness of dipole

engineering at the electrolyte/oxide interface. Given the large number of photoelectrodes previously studied that have been classified as “unsuitable” due to the inappropriate band edge alignment, the current results present a new strategy to revisit many of them to overcome their limitations by independently controlling the interface and the bulk properties to produce viable PEC devices.

Publications

FY2015

T. Tachikawa, M. Minohara, Y. Hikita, C. Bell, and H. Y. Hwang, *Tuning band alignment using interface dipoles at the Pt/anatase TiO₂ interface*, Adv. Mater. In press.

Workshops

FY2015

Y. Hikita, T. Tachikawa, M. Minohara, C. Bell, and H. Y. Hwang, *Barrier height control at Pt/anatase TiO₂ Schottky junctions using oxide dipole layers*, 2015 Japan Society of Applied Physics Spring Meeting, Kanagawa, Japan, March 11-14, 2015.

Y. Hikita, T. Tachikawa, M. Minohara, C. Bell, and H. Y. Hwang, *Barrier Height Control at Pt/Anatase TiO₂ Schottky Junctions Using Oxide Dipole Layers*, 2015 MRS Spring Meeting, San Francisco, California, April 6-10, 2015.

FY2014

T. Tachikawa, M. Minohara, Y. Hikita, C. Bell, and H. Y. Hwang, *Band alignment control of anatase-TiO₂ heterojunctions using oxide dipole layers*, The 41st Conference on the Physics and Chemistry of Surfaces and Interfaces (PCSI), Santa Fe, New Mexico, January 12-16, 2014.

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	Not yet determined
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	N/A
Number of Post Docs supported by LDRD project in FY15?	1

Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total??	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

12.0 Designing Monolithic CMOS Sensors

Principal Investigator: Chris Kenney

Project Description

Establishing the expertise within SLAC for designing monolithic CMOS sensors is the focus of this project. This is seen as an enabling technology for photon science, high energy physics, and beyond, as these devices are directly sensitive to charged particles and photons with energies between 1.2 eV and about 20 keV. When coupled to a transducer that converts a signal to visible light, their photon energy range can be extended much higher.

A deliverable is the establishment of a thin-entrance window to enable high efficiency recording of soft x-rays and ultraviolet light, that is thermally compatible with post-processing of a deep-sub-micron CMOS wafer. Exploration of the CMOS sensor foundry space and selection of one or more to partner with serves as a foundation for further work. The simulation, design, fabrication, and testing of small, prototype CMOS sensors that can record charged particles and x-rays is the main deliverable.

Accomplishments

Our achievements so far include fabrication of exploratory soft x-ray entrance windows, extensive simulations of various device structures, and a nearly-completed design for a prototype pixel detector for the LHC. Important collaborations have been established allowing SLAC to participate in full-wafer process runs, which greatly expand the available silicon area at a lower cost than a multi-project run.

We have developed a relationship with Lincoln Laboratory of MIT (MIT-LL) to partner with them to demonstrate fabrication of ultra-thin entrance windows to obtain high quantum efficiency for soft x-ray as needed by LCLS II. This is a post-foundry step, which allows biasing the substrate and hence controlling and deepening the depletion layer from which charge is collected. This will boost the signal size for charged particles and should also improve tolerance to radiation damage. It has been done using molecular beam epitaxy (MBE). A set of silicon wafers have been processed and prepared for shipping to Lincoln Labs. In order to have SLAC wafers processed in Lincoln Lab's cleanroom, vapor-phase decomposition ICP-MS tests have been successfully performed to certify the chemical cleanliness level of our wafers. MIT-LL has recently completed growth of thin windows on a batch of SLAC wafers and preparations are underway to extensively test them.

Computer modeling of various attributes of diffusion structures within a CMOS sensor have been performed by Dr. Segal (see figure 1). These include examining signal collection from the volume located between a pair of chips on an intact wafer. This could be instrumental in constructing large-area CMOS sensors without the complication of stitching stepper exposure fields. The capacitances for pixels with various sizes and aspect ratios has been studied as this is paramount to the design of low-noise, low-power electronics given the small signals produced from single particles. The results of these simulations have been shared with the international community via meetings and workshops.

Figure 1: Simulated device structure and electric potential distribution used to calculate the input capacitance (left); test and device wafers with MBE grown, thin entrance windows (right).

In collaboration with UCSC, the design of a prototype CMOS sensor is nearing completion and will be submitted during the first quarter of FY2016. Its main goal is to establish the ability to record the passage of ionizing radiation using a high-voltage CMOS process in a design by SLAC. If successful this will be a step towards the use of CMOS sensors in experiments at the LHC. It is a custom, full-wafer run and the foundry will use high-resistivity substrates, which is ideal for charged-particle and x-ray sensors. The diagram of the chip architecture and the layout of some functional blocks are shown in figures 2 and 3, respectively.

Figure 2: Architecture of the CHES2 chip.

Figure 3: Layouts of some functional blocks of the CHES2 tracking chip.

Project Plan

The plan for fiscal year 2016 is to complete the design of the full-size CMOS sensor prototype CHESS2, and submit it to a foundry for fabrication. Once the finished CHESS2 sensors are received, testing their properties will begin. Now that we have the MBE, thin entrance windows from MIT-LL, a program of characterizing these test wafers is starting using Secondary Ion Mass Spectroscopy, Transmission Electron Microscopy, and other techniques. In parallel the sensor wafers with MBE windows will undergo the remainder of their processing on campus. If the thin-window sensors are functional, they will be bump bonded to existing ePix circuit chips and studied with x-rays and charged particles. Papers will be published.

Publications

None

Workshops

FY2015

V. Fadeyev et al., *"Studies and status of CMOS-based sensors research and development for ATLAS strip detector upgrade"*, ATLAS ITK Workshop, Geneva, Switzerland, February, 2015.

H. Grabas et al., *"CHESS2"*, ATLAS ITK Workshop, Geneva, Switzerland, February, 2015.

A. Dragone et al., *"COOL: MAPS for the ATLAS outer pixel layers"*, ATLAS HV MAPS Workshop, Heidelberg, Germany, June 8, 2015.

H. Grabas et al., *"Developments in CMOS for Strip Detectors"*, ATLAS HV MAPS Workshop, Heidelberg, Germany, June 8, 2015.

A. Affolder et al., *"Study of built-in amplifier performance on HV-CMOS sensor for ATLAS phase-II strip tracker upgrade"*, 10th International "Hiroshima" Symposium on Development and Application of Semiconductor Tracking Detectors, Xi'an, China, September 25-29, 2015.

A. Affolder et al., *"Investigation of HV/HR-CMOS technology for the ATLAS Phase-II Strip Tracker Upgrade"*, 10th International "Hiroshima" Symposium on Development and Application of Semiconductor Tracking Detectors, Xi'an, China, September 25-29, 2015.

Patents/Invention Disclosures/Copyrights

FY2015

Invention Disclosure filed with OTL, *"Hybrid architecture coupling a CMOS image sensor to a mixed-signal integrated circuit for observing low-energy x-rays"*

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE-HEP
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	NA
Number of Post Docs supported by LDRD project in FY15?	0
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total? None	0/0
Number of invention disclosures filed in FY15 and in total?	1/1
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

13.0 An Ultrafast 11eV Source for time-Resolved Photoemission

Principal Investigator: Patrick S. Kirchmann

Project Description

The rich and novel physics in strongly correlated electron materials results in complex phase diagrams due to competing length, energy and time scales. Establishing a microscopic understanding may lead to revolutionary device applications and requires momentum-resolving spectroscopy with high energy and time resolution. Femtosecond time- and angle-resolved photoemission spectroscopy (trARPES) has proven to be a powerful tool for investigating unoccupied electronic band structures, quasi-particle scattering rates, coherent phonon modes, cooperative phenomena in ordered phases and novel states far from equilibrium.

However, current UV light sources for trARPES have severe limitations. UV generation via frequency up-conversion in solid state materials is limited to photon energies $h\nu < 7\text{eV}$, which preclude studies of the full Fermi surface due to limited momentum access. High-order harmonic generation in gases produces $h\nu > 10\text{eV}$ but the low repetition rates reduce energy resolution and statistics.

This project aims at generating 11eV photons with sub-100fs pulse duration in Xe gas using near resonant optical transitions, which increases the efficiency dramatically and in turn enables high repetition rates desirable for trARPES. Additionally, our concept can provide easy tunability of time and energy resolution required for in-depth studies of correlated materials.

The basic layout of our frequency up-conversion scheme is shown in the figure below. An amplified Ti:Sa drive laser system operates at 768nm IR wavelength with a repetition rate of 0.1 - 1MHz and produces $>3\text{mJ}$ pulses with $>50\text{fs}$ pulse duration. The collinearly propagating IR and UV pulses are focused into a Xe gas cell where 11eV photons are generated via non-linear frequency mixing. Spectral separation of the 11eV photons is achieved by a LiF prism before focusing the light into the trARPES vacuum chamber.

Accomplishments

We relocated an ultrahigh vacuum chamber including an electron analyzer from Stanford to the SIMES UHV/Laser lab. We completed designing the necessary laser safety upgrades for the lab, which we are now installing. We relocated the oscillator seed laser as well as the regenerative laser amplifier and their control electronics to the lab. While class 4 laser operations are still pending we have designed an efficient 3rd harmonic generator, which involved various dispersion

calculations and according specifications of optical crystals. Importantly, in close collaboration with the laser manufacturer KMLabs, we have made significant progress in coming up with a strategy how to tune the amplifier laser to the required, yet unconventional 768nm wavelength. As tuning to 768nm was judged as the main challenge/risk in the review of our LDRD, we used a different Ti:Sa amplifier system from Coherent to verify the signal sequence of tuning the seed laser, stretching its pulses, regenerative amplification, amplified pulse recompression, and 3rd harmonic generation; exemplary data is given in the figure below. It is very encouraging that we can use standard optical components, which are readily commercially available.

The required laser safety infrastructure is becoming available now and will permit testing and optimizing the individual lasers components of the amplifier system. In a first step, we will tune the seed oscillator laser near 768nm and analyze the resulting spectrum and pulse structure. In parallel, we will tune the laser cavity of the amplifier to 768nm as well, however, without seeding it yet. Tuning of the amplifier cavity away from its intrinsic peak near 795nm is achieved by insertion of mirrors with specifically tuned reflection curves. Once we establish proper function of the individual components, we will combine them using a commercially available stretcher/compressor unit from Coherent. We are currently discussion the specifications of this unit with Coherent. The goals for completing this project in FY2016 successfully are: (i) obtaining well-defined, compressed 768nm pulses of the amplifier system with pulse energies >10 ☐ J, (ii) achieving high efficiency 3rd harmonic generation, (iii) combining the fundamental and the 3rd harmonic in a Xe gas cell for 110nm generation, and (iv) detecting and optimizing the VUV flux in an ionization chamber.

Publications

none

Workshops

FY 2015

P. S. Kirchmann, *Ultrafast Photoemission Spectroscopy for Material Science*, SUPR 2015 - Stanford University Photonics Retreat, Asilomar, Pacific Grove CA, April 10-12, 2015.

P. S. Kirchmann, *Inequivalence of Single-Particle and Population Lifetimes in a Cuprate Superconductor, Momentum and Photon Energy Dependence of Collective Modes in a Charge Density Wave, Band Structure and Switching Pathway of the Photo-Induced, Metastable State in TaS₂*, The 9th International Symposium on Ultrafast Surface Dynamics (USD9), Lake Biwa, Japan, May 25-29, 2015

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE/BES
Has follow-on funding been obtained?	Not yet
Amount of follow-on funding (\$K)?	N/A
Number of Post Docs supported by LDRD project in FY15?	1
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total??	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

14.0 KIPAC Inflation Initiative (CMB)

Principal Investigator: Chao-Lin Kuo

Project Description

The goal of this program is to strengthen the current CMB program at SLAC through developing core technologies for CMB-S4, an ambitious ground-based survey aiming to extract full cosmological information contained in the polarization of the CMB, and maintaining leadership in science programs.

In terms of core technologies for CMB-S4, we plan to expand our current effort in

1. Detector systems (multichroic polarimeters, SQUID multiplexers)
2. Cold optics (infrared blocking filters, lenses, AR coating)

In terms of science programs, we maintain leadership/participation in

1. The BICEP/Keck program (Co-PI/PI institute)
2. SPTpol and SPT-3G (cold optics, SQUIDs, cluster science)
3. ACTpol and Advanced ACTpol (detector systems)

Accomplishments

The CMB effort at SLAC has been very small before the funding of this proposal. In 2013, the program grows substantially with the arrival of Kent Irwin's group and the funding of this proposal. In summer and fall of 2013, the SLAC CMB group worked closely with the CMB community to produce two Snowmass whitepapers that outlined the science and vision of CMB-S4. These have received strong endorsements from the P5 (Particle Physics Project Prioritization Panel) in May, 2014. This significantly improves the prospect of programmatic return for this LDRD.

The main investments include:

- Cold optics (\$1M , BICEP3 and SPT-3G)
- Focal plane system (\$1M, BICEP3 detector modules, focal plane architecture)

Project status and accomplishments:

- BICEP/Keck program
  - We used BICEP2/Keck to see a significant B-mode at 150 GHz.
  - We performed a joint BICEP2/Keck and Planck analysis that shows this signal can be interpreted as high dust polarization.
  - BICEP3 (95GHz) was deployed in 14/15 to South Pole to follow up BICEP2/Keck results.

- SPT-3G
  - Three alumina lenses fabricated and metrology completed
  - Anti-reflection coating for SPT-3G developed (with Berkeley)
- ACTpol:
  - Delivered all three ACTpol polarimeter arrays (with NIST), achieving good on-sky performance.

Publications

FY2015

BICEP2 / Keck Array V: Measurements of B-mode Polarization at Degree Angular Scales and 150 GHz by the Keck Array, The BICEP2, Keck Array Collaborations, ApJ 811,126 (2015).

Antenna-coupled TES bolometers used in BICEP2, Keck array, and SPIDER, 2015ApJ...812..176A
A Joint Analysis of BICEP2/Keck Array and Planck Data, BICEP2/Keck, Planck Collaborations, Phys. Rev. Lett. 114, 101301 (2015)

BICEP2 III: Instrumental Systematics, accepted by ApJ, 2015.

FY2014

BICEP2 I: Detection of B-mode Polarization at Degree Scales using BICEP2, BICEP2 Collaboration, Ade, P. A. R. et al. Phys. Rev. Lett. 112, 241101 (2014)

BICEP2 II: Experiment and Three-Year Data Set, BICEP2 Collaboration, Ade, P. A. R. et. Al.; The Astrophysical Journal 792, 62 (2014)

A Guide to Designing Future Ground-based CMB Experiments, Wu, W.L.K.; Errard, J.; Dvorkin, C.; Kuo, C.L.; Lee, A.; McDonald, P.; Slosar, A., and Zahn, O., The Astrophysical Journal, 788, 138 (2014).

Large-area Reflective Infrared Filters for Millimeter/sub-mm Telescopes, Ahmed, Z.; Grayson, J.A.; Thompson, K.; Kuo, C. L.; Brooks, G; Pothoven, T., Journal of Low Temperature Physics, (2014).

Workshops

FY2015

BICEP3, LTD-16, Grenoble, France, 2015.

FY2014

BICEP3: a 95 GHz refracting telescope for degree-scale CMB polarization, Ahmed, Z. et al., SPIE Astronomical Telescopes and Instrumentation 2014, Proceedings of SPIE Volume 9153, (2014) [refereed].

SPT-3G: A Next-Generation Cosmic Microwave Background Polarization Experiment on the South Pole Telescope, Benson et al., SPIE Astronomical Telescopes and Instrumentation 2014, Proceedings of SPIE Volume 9153, (2014) [refereed].

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	NSF, DOE, private
Has follow-on funding been obtained?	Yes
Amount of follow-on funding (\$K)?	\$1,130
Number of Post Docs supported by LDRD project in FY15?	0
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total??	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

15.0 Exploring the Scientific Capability of Momentum-Resolved Resonant Inelastic Soft X-ray Scattering for Material Science Research

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Principal Investigator: Wei-Sheng Lee

Project Description

An important approach to study the rich phenomena in strongly correlated quantum materials is to track elementary excitations associated with the underlying degrees of freedom. Recently, experiments using state-of-the-art RIXS instruments discovered a number of surprising behaviors of lattice, magnetic, and orbital excitations in these quantum materials, creating considerable excitement in the field. These excitements have motivated the synchrotron and x-ray free electron laser community worldwide to build next generation RIXS instruments with higher resolution and efficiency, promising to make significant impacts on future materials science research. Since SLAC is the home of two premier light sources (SSRL and LCLS) and commits to be a photon science center for materials science, this is a critical timing for SLAC to plan strategically in order to establish an on-site RIXS program. SIMES, the scientific drive for the forefront x-ray science at SLAC, is obligatory to lay the groundwork.

The goal of this proposal is to initiate a scientific RIXS program, which can further develop into a full-fledged program for materials science research, as well as serve as a driving force to realize RIXS instruments at SSRL and LCLS. We will attack important outstanding problems of quantum materials using state-of-the-art RIXS instruments worldwide. The publications and collaborations generated via this proposal will raise our scientific profile and develop the intellectual leadership in RIXS community. These activities are in conjunction with the commissioning of our q-RIXS endstation, expected in 2015 at ALS. The results of these commissioning experiments would be beneficial to develop LCLS proposals for time-resolved RIXS experiments at SXR, LCLS, expected in FY16.

Accomplishments

Dr. Laura Chaix has arrived at SALC and joined the project starting from January 2015. Her joint force will move the project in full speed.

An important approach to carry out the proposed project is to gain access to state-of-the-art RIXS instruments worldwide. To date, we have successfully obtained RIXS beamtime at to access state-of-the-art RIXS instruments worldwide, including the spectrometer at the famous ADRESS beamline at the Swiss Light Source (SLS, Switzerland) and the newly-constructed AGM-AGS spectrometer at Nation Synchrotron Radiation Research Center (NSRRC, Taiwan). These RIXS instruments have presently highest energy resolution (~ 120 meV) at the Cu L-edge. Furthermore, we have also obtained beamtime at ID32 European Synchrotron Radiation Facility (ESRF), where a next generation RIXS instrument with an energy resolution of better than 30 meV (significant higher than that at SLS and NSRRC) is now under commission. In addition, we have also achieved

one milestone for the construction of the q-RIXS endstation. One spectrometer has been assembled at the Advanced Light Source. Test of the optical path and characterization of the optical elements are in progress. The chamber assembling will finish in the autumn of 2015.

Scientifically, we have investigated doping evolution of the collective excitations in a family of electron-doped superconducting cuprates, $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. While data analysis is still in progress, we found interesting abrupt changes in the magnetic and collective excitations when the system evolves from the antiferromagnetic phase to superconducting phase via electron doping. In addition, more complete incident photon polarization dependent RIXS spectra could also allow us to gain further insight into the excitations coupled in the RIXS process.

Project Plan for 2016: We will continue to investigate collective excitations in quantum materials via state-of-the-art RIXS instruments. We will particularly focus on the following scientific topics:

Investigation of the role of competing phases in unconventional superconductors: We will continue to study the behaviors of collective excitations in high temperature superconducting cuprates. Several aspects will be explored: (1) behavior of collective excitations across the AFM-SC phase boundary. (2) The momentum-dependence of electron-phonon interaction, which can be uniquely determined by ultrahigh resolution momentum-resolved RIXS. (3) The role of CDW and related excitations. In addition, as a complimentary study to cuprates, we plan to search of charge resonance mode in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ (BPBO), which can be regarded as a “charge” counterpart of the cuprates and iron-based superconductors.

Investigation of elementary excitations in quantum materials heterostructures: Rich emergent phenomena at the interfaces of quantum materials heterostructures has recently draw significant attention. These interfaces can undergo lattice reconstructions by strain engineering, electronic reconstructions by charge transfer, and even orbital reconstructions which blend the heterogeneous building blocks. Momentum-resolved RIXS can measure the elementary excitations of spin, charge, lattice and orbital degrees of freedom to characterize these associated reconstructions. In addition, element-specific information can be obtained by tuning the incident photon energy to the absorption edges of the elements of interest, providing crucial information which clarifies the role played by each these building blocks.

Publications

FY2015

L. Chaix et al., “Abrupt changes of collective excitations across AFM-SC phase boundary in electron-doped cuprates”, in preparation.

FY2014

W. S. Lee, J. J. Lee, E. A. Nowadnick, S. Gerber, W. Tabis, S. W. Huang, V. N. Strocov, E. M. Motoyama, G. Yu, B. Moritz, H. Y. Huang, R. P. Wang, Y. B. Huang, W. B. Wu, C. T. Chen, D. J.

Huang, M. Greven, T. Schmitt, Z. X. Shen, and T. P. Devereaux, “Asymmetry of collective excitations in electron and hole doped cuprate superconductors”, Nature Physics 10, 883 – 889 (2014)

Workshops

FY2015

W. S. Lee, RIXS studies of elementary excitations in cuprates, Unraveling Emergent Phenomena in Quantum System with Experimental and Theoretical Advances in RIXS, Berkeley, California, USA, Oct. 6-7, 2015

W. S. Lee, Studies of Elementary Excitations and Field-induced CDW in High-Tc Cuprates via Novel X-ray Scattering, International Conference of Electron Spectroscopy and Spectroscopy, Stony Brook University, New York, USA, September 27- October 2, 2015

W. S. Lee, RIXS Study on Doping Dependence of Elementary Excitations across the AFM-SC Phase Boundary in Electron-doped Cuprates, Sponsored by American Physical Society, March 2-6, 2015

FY2014

W. S. Lee, Lattice, magnetic, and charge excitation in Cuprates, High resolution RIXS and Nano ARPES workshop, Sponsored by National synchrotron Radiation Center, Hsinchu, Taiwan, September 10-12, 2014.

W. S. Lee, Lattice, magnetic, and charge excitations in Cuprates, APS March Meeting, Denver, CO, USA, Sponsored by American Physical Society, March 3-7, 2014.

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE/Early Career Proposal
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	N/A
Number of Post Docs supported by LDRD project in FY15?	1
Number of students supported by LDRD project in FY15?	0

Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total??	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

16.0 Low Dimensional Quantum Materials for Energy Applications

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Principal Investigator: R.G. Moore

Project Description

The goal of this project is to develop the infrastructure necessary to explore low dimensional quantum oxide and chalcogenide materials and heterostructures with potential energy applications. Understanding the fundamental scientific processes connecting atomic and electronic structures in reduced dimensions is necessary for a full understanding of emergent material properties. The past decade has seen revolutionary advances in the precise control of thin films and heterostructures on the atomic scale. Many new emergent states have been discovered but the underlying electronic structure governing these phenomena is unknown. Coupling thin film growth systems to state of the art angle resolved photoemission spectroscopy facilities will advance the understanding of emergent states and allow for rapid feedback in developing materials with tailored properties. This project is to develop a new strategic direction at SLAC for utilizing thin film growth and electron spectroscopy, both ex-situ and in-situ, to illuminate underlying material processes and foster creative material science solutions in material design..

Accomplishments

Capitalizing on recent DOE instrumentation investment in a thin film growth system, during FY14 and FY15, we installed and commissioned a Veeco GEN930 oxide MBE system and a DCA ozone distillation unit and coupled them to the new photoemission beamline at SSRL. The beamline will be fully commissioned by the end of the calendar year and the MBE infrastructure is now ready to explore the electronic structure of quantum thin films.

We will continue to capitalize on our recent success on superconducting monolayer FeSe thin films investigated by SSRL's existing angle-resolved photoemission spectroscopy (ARPES) beamline. The electronic energy gap associated with superconductivity suggests record-breaking transition temperatures (T_c) for this class of superconductors. While previous groups have established these facts, we discovered a quantum "shake-off" band indicative of strong electron-phonon coupling between the film and substrate. We have also shown theoretically how such coupling could be responsible for the enhanced T_c . Such interplay between the monolayer and substrate creates a unique platform for tuning relevant parameters that can not only enhance T_c but also further our understanding of the underlying physics for such an exotic state. There are two interface phenomena relevant to the T_c enhancement: significant charge transfer and the forward focused electron-phonon coupling. While the results in the literature suggest both are triggered by oxygen vacancies in the STO substrates, our recent results suggest there may be other factors involved. Taking advantage of the infrastructure development supported by this LDRD, we can now take the next step and explore the interfacial interactions by tuning the substrate characteristics. By systematically controlling the number of oxygen vacancies in the substrate, we can disentangle the role they have in both the charge transfer and e-p coupling. We are also in the

process of oxygen-18 isotope substitution of the STO to understand and confirm the electron-phonon mediated Tc enhancement. We have preliminary results that are promising, but O-18 substitution in STO triggers a ferroelectric transition. While this is interesting in its own right and will be explored, such a transition interferes with our ARPES spectra for the FeSe film and we are exploring ways to suppress the transition. Systematic studies of the interfacial charge transfer processes and isotope effect are now possible with the completion of the oxide MBE infrastructure supported by this LDRD and the completion of the SSRL Beamline to which it is coupled.

To fully capture the superconducting properties of our films, the postdoc supported by this LDRD has also developed an in-situ probe for measuring the transport properties. The 4-point probe construction is complete and is in the commissioning phase. Tests of the 4-point probe will continue and will be installed at the oxide MBE system once it is fully operational. The ultimate goal is to develop neighboring oxide and chalcogenide growth chambers and create heterostructures of FeSe and oxide materials. The chalcogenide growth chamber and sample transfer chamber designs are complete and are currently under construction, supported by a separate program.

The postdoc supported by this LDRD plans to start the next phase of his career at the end of FY15. In addition, the equipment projects and infrastructure development supported by this LDRD are now completed. There will be no carry forward funds.

This project was to seed a program and develop the infrastructure necessary to explore the electronic structure of quantum thin films. The oxide MBE infrastructure is now complete and awaiting final commissioning of the new photoemission beamline. The 4-point probe is in final testing and expected to be completed prior to the end of the calendar year. Thus, the LDRD is a tremendous success. There is limited data due to the beamline delays, but the preliminary data supported by this LDRD demonstrates the proof of principle and potential of this research direction. The success enabled the pursuit of follow-on funding and the results supported by this LDRD will appear in upcoming publications. We are now in a position to make a tremendous impact in understanding emergent phenomena through the investigations of the electronic structure of quantum thin films for energy applications and place SLAC at the forefront of the field.

Publications

FY2015

none.

FY2014

none

Workshops

FY2015

R. G. Moore, *Significant Tc enhancement in FeSe films on SrTiO3 due to interfacial mode coupling*, (invited talk) APS March Meeting, Conference, Sponsored by the American Physical Society, San Antonio TX, March 2-6, 2015.

R. G. Moore, *Significant Tc enhancement superconducting FeSe films due to interfacial mode coupling with oxide substrate*, (invited talk) International Workshop on Recent Progress in the Functionality of the Artificial Oxide Structures, Workshop, Sponsored by the Institute of Physics, Chinese Academy of Sciences, Beijing, China, June 10-11, 2015.

FY2014

R. G. Moore, *Interfacial Interplay Between Superconducting FeSe Films and Underlying Substrate*, American Physical Society Annual March Meeting, March 3-7, 2014, Denver, CO.

R. G. Moore, *Growth and in-situ Investigation of the Electronic Structure of Low Dimensional Transition-Metal Complexes*, Stanford Synchrotron Radiation Lightsource Annual User's Meeting, October 7-10 2014, Menlo Park, CA

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE-BES
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	N/A
Number of Post Docs supported by LDRD project in FY15?	1
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total??	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

17.0 New Initiative for Pioneering Research in Biology, Chemistry, and Materials Science with State-of-the-Art Soft X-ray Spectroscopy

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Principal Investigator: Dennis Norlund

Project Description

Superconducting transition edge sensor (TES) technology presents a unique opportunity to build novel detectors with greatly increased sensitivity in the soft x-ray regime while maintaining excellent energy resolution. We are combining the development of a new generation soft x-ray superconducting TES spectrometer with a scientific motivation to probe the local electronic structure of ultra-low concentration sites in biology, chemistry, and materials, while simultaneously providing a powerful R&D test bed for new cryogenic detector technologies with demonstrated transformative prospects in x-ray science.

Precision energy resolved investigations of the targeted scientific goals, local electronic structure probing of active sites in biology, chemistry and materials at low concentrations, is currently inaccessible in the soft x-ray regime due to the limited sensitivity of existing technology. To this end, we have designed a TES spectrometer to explore new paradigms in soft x-ray spectroscopy, achieving sensitivity of sub-mMol concentrations in aqueous/organic solvents, sub-percent sensitivity for monolayer films immersed in a solvent, solid matrix, or high-pressure gas, and sensitivity to concentrations $<10^{19}/\text{cm}^3$ for defects and dopants in condensed-phase samples. The unprecedented sensitivity of our instrument in the soft x-ray regime will be used to investigate local electronic structure of active metal centers of bio-enzymes, active sites and intermediates in chemical catalysis, interfacial transformations in energy storage applications, and ultra-low concentration defects and dopants in semiconductors.

In order to provide scientific impact it is imperative that the detector development is pursued with operational efficiency as an important goal. Seamless integration with routine synchrotron X-ray Spectroscopy experiments is a key target that will receive special attention, from alignment to calibration and data reduction. It is also our goal to advance the detector read-out technology of TES spectrometers to extend into the time-domain and explore the unprecedented opportunities enabled by the advent of free electron lasers.

Accomplishments

FY15 activity (summary) Over the past year we have made significant progress on the LDRD program. We have hit all our internal milestones and established a very productive working environment between all parties involved in the execution (co-investigators, Stanford, NIST).

FY15 Staff/Hiring: Our postdoctoral search (late 2014) received wide interest both from US and abroad. After reviewing the applications and interviewing candidates we made an offer to Sangjun Lee, Ph.D. of NASA Goddard Space Flight Center. He accepted the position with a (late)

starting date of August 20th of 2015 (see also Budget discussion). Sang-jun is without question the top candidate with a strong background in the detector technology, having worked in the x-ray TES group under Simon Bandler at NASA. His recent work has demonstrated the best seen energy resolution for a TES x-ray detector of 0.7 eV at 1 keV, in addition to recent advances in read-out speed. SLAC is fortunate to have Sang-Jun Lee as a key person in the team. His role in the scientific analysis task will be critical.

FY15 Design Phase: We are particularly pleased with our strong collaboration with the Quantum Sensors Group at NIST (Boulder) with whom we finalized the overall TES detector system design in April of 2015, and the details of the cryo system engineering design in June of 2015. A three dimensional rendering and cutaway of the cryostat can be seen in Fig 1. Regarding the synchrotron beamline integration where the commissioning work will take place (BL10-1, SSRL), after a lot of operational efficiency considerations, we settled on an integration framework with an expanded End-Station Support Structure which ensures that the detector assembly moves in unison with the rest of the experimental station, offering operational advantages for the targeted scientific measurements. The placement of the TES detector in the expanded support structure for BL 10-1 end-station can be seen in Fig 1c. The details of the integrated design was finalized in April and frozen in May of 2015.

Figure 1: (left, middle) 3D rendering of cryo system design (right) endstation integrated design w/ cryo support

FY15 Procurement Phase: The procurement phase (primarily May, June, July) has been finalized during FY15 in which all the budgeted M&S expenditures for FY 15 was committed. This involved weekly meetings with the Quantum Sensors Group at NIST. We consider this phase of the project to be successfully completed, as FY16 will only see a very limited procurement activity (a few peripheral items, some beamline integration hardware as well as planned expenditures on sample environment).

FY15 Receiving/Shipping/Quality Control/Planning: The rest of FY15 has been spent on receiving and quality control of items, preparation of items for shipping to NIST, as well as detailed planning of the system assembly and system integration efforts to take place in the fall of 2015, first at NIST, and then at SSRL. Continuous planning of the detailed deployment and many practical considerations are reviewed on a weekly basis.

FY15 Detector Development: The TES detector system is currently being built at NIST. Fig 2 left shows the actual 50 mK detector snout package that will be mounted at the 50 mK stage of the cryostat for BL 10-1. A detector chip with an array of 240 TES pixels (Fig 2. middle) will be mounted on top of the snout package, and multiplexed read-out chips around the sides of the snout package. A Au-coated Si collimator (Fig 2. right) will be placed on top of the TES to minimize X-rays hitting the frame between TESs, which can potentially degrade the detector energy resolution.

Figure 2: (left) Detector snout package. (middle left, middle right) 240-pixel TES. (right) Au-coated Si Collimator.

FY16 Activity (planned): In FY16 we will be completing the following milestones in accordance with the LDRD project timeline and as visualized in the Gantt chart below (Fig 3):

- 1) Completion of NIST assembly and test of Detector System (->Dec 2015)
- 2) Completion of Detector Integration w/ Support Structure & BL10-1 Station (->Jan 2016)
- 3) Completion of System Integration w/ BL 10-1 and X-ray Commissioning (->Mar 2016)
- 4) Beamtime(s) on “Real” Sample Set (dilute dopants semiconductors) (Apr-Jun 2016)
- 5) Continuous Commissioning, Development, and Beamtimes through FY16 & FY17
- 6) Preparation of Conference Presentations and Manuscripts (May 2016->)
- 7) Planning, Initiating Collaborations and Drafting of White Letters for Follow-up Funding.

Figure 3: Project Management Gantt Chart showing the projected time for deliverables and sub-tasks.

Publications

FY2015

n/a

FY2014

n/a

Workshops

FY2015

Nordlund, “*Opportunities with Ultrasensitive Soft X-ray Spectroscopy*”, Advances in High-Resolution X-ray Spectroscopy Workshop, SSRL/LCLS Users Meeting, Menlo Park, CA, October 9, 2015.

FY2014

Nordlund, Irwin, “*Development of Transition Edge Sensor (TES) based Soft X-ray Spectrometer and Scientific Opportunities*”, SSRL Scientific Advisory Committee review, Workshop, SSRL/SLAC, Menlo Park, CA, September 11, 2014.

Patents/Invention Disclosures/Copyrights

None

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE, NSF, NIH
Has follow-on funding been obtained?	N/A
Amount of follow-on funding (\$K)?	N/A
Number of Post Docs supported by LDRD project in FY15?	1
Number of students supported by LDRD project in FY15?	1
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total??	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

18.0 Spatial and Time Resolving Pixel Detector - TIXEL

Principal Investigators: Timur Osipov

Project Description

The primary goal of this project is the design and fabrication of a module consisting of a Tixel integrated circuit mated to a thin silicon sensor array, as this will enable a new and exciting set of science experiments. Once this new tool is available, it is expected that the community will conceive of novel, innovative ways to make use of it. The closing objective of this LDRD is to construct a complete system around a Tixel array that will allow a demonstration science experiment to be performed. This would constitute a breakthrough in instrumentation, which would enable new types of scientific measurements to be carried out.

The Tixel detector will have a spatial resolution of 100 microns and a time resolution of a few hundred picoseconds. The prototype detector chip will have 48x48 pixels. The first prototype detector shall have an array of 2x2 chips resulting more than 9000 particle detection channels. The time resolution of the sensor and readout electronics will be benchmarked with an ultrafast laser setup. We will then further demonstrate the scientific potential of the new detector system with a Coulomb explosion imaging experiment. A momentum resolving spectrometer in combination with the Tixel detector will allow the reconstruction of the full kinematic information of the photo-induced fragmentation of a nanocluster akin a Coulomb complex. With the successful demonstration of the described experiment and thus the scientific potential of the detector we anticipate to secure significant additional outside funding to scale the new Tixel technology to larger detector units. Further, the Tixel will give SLAC a competitive advantage over other free-electron laser facilities.

Accomplishments

The design of the first version of the Tixel integrated circuit chip has been completed, submitted for fabrication, and the chips received back from the foundry as shown in figure 1. This is a critical milestone for the project.

Figure1: Layout of a single Tixel pixel (left) photograph of a Tixel integrated circuit chip (middle) and thin Tixel sensor from first batch (right).

Tixel integrated-circuits chips without a sensor have been mounted on dedicated printed circuit boards and wire bonded. An image of a pair is shown in figure 1. Very initial testing of the chip's behavior has begun with promising results so far.

Figure 2: Pair of Tixel chips mounted on a Tixel carrier board (left) testing underway (right).

Figure 3: Preliminary timing plot showing the jitter associated with part of the circuit chain.

While waiting for the read-out system (PCB board and firmware) to be completed so that the ASIC pixel-matrix data can be acquired and processed, a preliminary time-measurement test was performed using the START pixel located at the periphery of the ASIC. While the scope of the matrix pixels is to acquire an analog signal (charge) from the sensor and measure its time-of-arrival (ToA), the role of the START pixel is to measure the ToA of the START signal within the ASIC internal clock period. Since the START pixel receives directly a digital signal, it lacks the analog front-end of the matrix pixels, but it has the same digital time-measurement section. Since the START pixel is accessed as an ASIC register, it was possible to acquire its measurement data even without having the read-out system ready yet. The START pixel was used to measure two different time intervals. In blue is the measurement of the START signal time-of-arrival within the ASIC clock period. For the second measurement (the red plot) the START signal was maintained

always high and the pixel was put under reset using the R0 signal. As soon as the pixel is taken out of reset (by removing R0 signal), the pixel sees the high value of the START signal and records the corresponding time instant, effectively measuring the time-of-arrival of the R0 signal within the clock period. Both START and R0 ToA measurements show a timing jitter less than 100ps RMS. This is a preliminary measurement without any system optimization and without the jitter contribution of the analog front-end section. The more accurate measurements will follow after the matrix read-out system is completed

A batch of thin sensors with thicknesses of 50 and 75 microns has been completed and images of the devices shown in figure 1. Some of the devices show higher than desired leakage currents, while others with guard rings appear to perform acceptably well. Thin devices are required to obtain charge collection times compatible with a 100 picosecond system-level resolution. A second batch of sensors is being fabricated and will be completed in the second quarter of FY2016. Development of a procedure to flip-chip bond the thin sensors is underway and some prototype parts bonded.

Project Plan for FY2016

After bonding the sensor with the read-out electronics, we will perform benchmark experiments to demonstrate the time resolution of the Tixel detector. In a first iteration we will use picosecond laser pulses to create charges in the sensor and calibrate the read-out electronics of each pixel. As the sensor response will be different for photons than for electrons, we will also set up a picosecond electron source for demonstrating the performance of the detector. This idea has been discussed in detail with Axel Brachmann from the Accelerator Division. We will use a test cathode from the LCLS injector program that can be mounted onto our experimental system and which will allow us to produce few ten picosecond electron pulses with our laser system.

The planned science demonstration experiment will be performed with a momentum-resolving spectrometer akin a reaction microscope or Coltrims. In these spectrometers the reaction products travel along parallel E and B fields towards a time and position sensitive detector. For each fragment the arrival time and position will be measured and from that information the full kinematic information of each fragment can be calculated. So far delay-line detectors based on a microchannel plate (MCP) and a long wire anode have been used in these spectrometers which are severely limited in their multi-hit capability and therefore not suitable for experiments with free-electron lasers. These limitations will be overcome with the proposed silicon based Tixel detector. With the envisioned system it will be possible to perform for the first time massive coincidence experiments. This will be of special importance for experiments at free-electron lasers such as LCLS and electron spectroscopy.

We will demonstrate the functionality and scientific relevance of the new system with a Coulomb imaging experiment of a nanocluster. The scientific background of this experiment is to address the fragmentation dynamics of Coulomb complexes which is a good representative of common experimental challenges for gas phase experiments at LCLS. These experiments are a good representation of a whole new class of experimental studies made possible by the introduction of the high multi-hit (100+) reconstruction capable detectors. Proposed Coulomb imaging experiment will demonstrate the new capabilities and scientific potential of this novel detector technology.

Publications

none

Workshops

FY2015

C. Kenney et al., “*Detector Developments in Photon Science*”, 24th International Workshop on Vertex Detectors, Santa Fe, NM, June 1-5, 2015.

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE-HEP/BES
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	N/A
Number of Post Docs supported by LDRD project in FY15?	0
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

19.0 Non Fermi Liquids

Principal Investigator: Srinivas Raghu

Project Description

The goal of this project is to foster collaborations among theorists in Photon Science and PPA to investigate quantum field theories of strongly correlated systems. The theorists involved will use powerful methods of effective field theory to obtain new solvable limits and qualitative insight into the nature of strongly correlated materials, especially non-Fermi liquid metals

Is superconductivity enhanced in a metal near a quantum critical point? Can higher T_c superconductivity be realized in a metal with ill-defined quasiparticles? These questions are inspired by some of the materials of greatest interest in condensed matter physics, which continue to defy theoretical understanding. These include, for instance, the high temperature superconductors and heavy fermion systems. While the ground states of these materials are conventional, the higher temperature phases are strongly coupled phases of matter. For instance, high temperature superconductivity in cuprate and iron pnictide materials develops out of a metallic phase that bears little resemblance to a free electron model with small attractive interactions. This is visible from basic properties of this phase, such as its resistance to the flow of electrical currents. Controlled theoretical models, which reproduce all the behaviors of this phase are still lacking.

Our goal over a three-year period is to design a wider class of controlled models exhibiting non-Fermi liquid phases, to understand their instabilities to conventional ground states such as superconductivity, and to work toward more realistic models without losing our control of the calculations. Specifically, in the first year, we will initiate work on developing field-theoretic models of controlled fixed points that could emerge from interactions of fermions at a Fermi surface with additional bosonic fields (surprisingly, still a problem that remains largely open in 2 spatial dimensions, the dimension of relevance to the cuprate superconductors); and we will improve some of the most unrealistic features of the holographic models of non-Fermi liquids (by, for instance, relaxing the large N approximation, perhaps by using large density as a parameter instead).

In the longer term, our goal is really to improve understanding of the materials that exhibit non-Fermi liquid behaviors. A wide variety of experiments give hints of power law behaviors in e.g. specific heat and resistivity measurements in various metals, which differ from those of the conventional Fermi liquid. The "non-Fermi liquids" presumably comprise a wide class of rather different possible behaviors of interacting electrons, none of which are well understood at present. We are especially interested in predicting spectral properties of non-Fermi liquid materials, which are routinely studied by experimentalists at SIMES. Development of even quasi-realistic, controlled models of such phases would justify our effort. But a more optimistic, long term outcome of this effort, in a scenario where the project were extended beyond an era of

LDRD seed funding by continued BES and/or HEP support, would be a theory which is sufficiently well-developed to explain specific behaviors in certain classes of materials, and to guide investigation of new promising materials.

In the future, this project will involve collaboration with computational scientists. We will investigate the entanglement properties of non-Fermi liquids using Density Matrix Renormalization Group (DMRG) simulations, and will collaborate with Hong-Chen Jiang, an exceptional staff scientist in Photon Science working on computational aspects of condensed matter physics.

Accomplishments

The LDRD project led to the following publications:

Publications

A.L. Fitzpatrick, S. Kachru, J. Kaplan, S. Raghu, G. Torroba, H. Wang, “*Enhanced Pairing of Quantum Critical Metals near $d=3+1$* ”, arXiv:1410.6814.

A. L. Fitzpatrick, S. Kachru, J. Kaplan, S. Raghu, “*Non-Fermi Liquid Behavior of large NB Quantum Critical Metals*”, Phys. Rev. B 89, 165114 (2014).

H. Watanabe, S. Parameswaran, S. Raghu, A. Vishwanath, “*Anomalous Fermi Liquid Phase in Metallic Skyrmion Crystals*”, Phys. Rev. B 90, 045145 (2014).

Workshops

None

Patents/Invention Disclosures/Copyrights

None

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE
Has follow-on funding been obtained?	NO
Amount of follow-on funding (\$K)?	n/a

Number of Post Docs supported by LDRD project in FY15?	1
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0

20.0 Development of nano-Ultrafast Electron Diffraction at SLAC

Principal Investigator: Alexander Reid

Project Description

This LDRD project aims to develop and use focused electron MeV beams at the SLAC MeV Electron Diffraction Source for the study of lattice dynamics in solid-state materials.

The ultimate goal of this LDRD is to develop the nano-UED as a tool for performing time-resolved microscopy measurements of atomic dynamics in solid-state systems (and potentially more widely applicable to liquid and gas phase systems as well). Scientifically, it focuses on achieving experimental demonstrations of this capability in one or more landmark experiments.

The project has four primary tasks:

1. Development of systems and diagnostics for small, ultrafast MeV electron beams.
2. Development of the sample environment in the SLAC UED system.
3. Achieving a focused electron beam for experiments.
4. Experimental demonstration of focus capability.

The primary deliverable from this project is a working focused MeV electron beam capacity at SLAC together with the knowledge and experience of how it can be applied to materials science problems.

Accomplishments

The beginning of this LDRD coincided with the start of commissioning of the SLAC UED in October 2014. From that point, substantial progress has been made on all primary task in this project. The following details accomplishments so far:

Sample System Development: The first step towards routine ultrafast electron diffraction experiments is understanding the sample requirements for measurement. Several type of sample were prepared and trialed in the SLAC UED system. It was determined that there are two viable sample support options for transmission samples: freestanding samples on transmission electron microscopy grids and sample with ultra-thin amorphous supports (<100 nm).

The ability of UED to measure diffuse phonon excitations highlighted importance of single-crystal samples for UED measurements. As for many materials large-area single crystals are not available, this provided another important motivation for the additional of a small focused electron beam – the ability to zoom into a single material grain or crystal.

Development of systems and diagnostics: A necessary step to achieving the focused beam is developing methods to understand and operate the UED machine. A five-axis

sample/diagnostic manipulation stage which allows both nanometer scale motion, and long-range motion was constructed. The stage holds not only samples to be measured, but also diagnostics, such as spot size characterization, laser – electron overlap and time-of-arrival measurement, as well as reference films for beam emittance characterization.

Ultra-thin Bismuth films were used to characterize the temporal resolution of the electron beam by observed the well characterized ultrafast phonon softening effect. It was determined that at 20 fC a <60 fs rms bunch length was achieved [Weathersby 2015].

Machine Characterization: The emittance electron beam is the most important parameter for determining the achievable focal size. Several steps are taken to minimize the beam emittance. The UV beam is angled onto the photo cathode at 70 degrees to minimize the thermal emittance. In addition, spatial filtering is used improved the electron beam emittance after gun. A beam emittance of 2.1 nm-rad is achieved using a 100 μm spatial filter and a beam, with charge of 1.4 fC [Weathersby 2015].

Magnetic Solenoid Lens: Following the characterization of the SLAC UED gun emittance performance, the electron lens design was undertaken. It was determined that a compromise needs to be made between the ultimate spot size and the momentum resolution – an important parameter for experiments. While smaller spot sizes can be achieved by reducing the focal length, a larger focal length is need to satisfy the beam divergence and loss of momentum resolution on the detector. It was determined that a focal length of 0.35 m gave the best compromise between beam size and momentum resolution for the current source.

Several design of magnetic focusing element were considered: a permanent magnetic solenoid lens, an electromagnetic solenoid lens and a superconducting solenoid lens. It was determined that a water-cooled electromagnetic solenoid allowed the greatest flexibility for the current system. The electromagnetic solenoid allows for user adjustable compromises to be made between the beamsize at the sample and the momentum resolution at the detector. Figure 1 shows the solenoid as made to specifications by Stangenes Inc and delivered to SLAC in October 2015.

Magnetic Focus Commissioning: Commissioning of the magnetic focusing solenoid began immediately in

Figure. 1: Focus size criteria. A compromise is made between the beam divergence (blue line) after the sample and the spot size. Calculation based on 2.1 nm-rad emittance.

Figure.2: The solenoid electro magnet purchased for focusing the electron beam. Top, the bare solenoid, and bottom, the solenoid newly installed in the UED beamline.

FY2016. First result demonstrate the focusing capacity of the solenoid.

Plan for FY2016: The primary goal of this LDRD in FY2016 is the full characterization of the solenoid focusing capability and its use in demonstrational experiments. Characterization of the focusing strength and aberrations is now underway. Fig 3. shows a measurement of the beams size at the sample position as a function of the solenoid field. At a nominal charge of 30 fC a 5 μm rms spot is achieved at the sample position.

Several experimental samples have been identified for the first experiments using the focused electron beam. These include using FePt nanoparticles, nanoporous gold and single crystal biological samples.

Further development of the sample environment will also be undertaken in FY2016. It is proposed to add in-situ cooling of the UED samples to cryogenic temperatures. This is an important complement to the nano-diffraction capability for using the source for solid-state experiments.

References:

[Weathersby 2015] S. P. Weathersby, G. Brown, M. Centurion, T. F. Chase, R. Coffee, J. Corbett, J. P. Eichner, J. C. Frisch, A. R. Fry, M. Gühr, N. Hartmann, C. Hast, R. Hettel, R. K. Jobe, E. N. Jongewaard, J. R. Lewandowski, R. K. Li, A. M. Lindenberg, I. Makasyuk, J. E. May, D. McCormick, M. N. Nguyen, A. H. Reid, X. Shen, K. Sokolowski-Tinten, T. Vecchione, S. L. Vetter, J. Wu, J. Yang, H. A. Dürr and X. J. Wang, *Rev. Sci. Instrum.* **86**, 073702 (2015).

Publications

FY2015

A. H. Reid, X. Shen, R. K. Li, T. Chase, S. P. Weathersby, J. Li, T. Vecchione, N. Hartmann, R. Coffee, J. Cao, C. Hast, E.E. Fullerton, Y.K. Takahashi, J. Wu, X. Wang, & H.A. Dürr, “*Ultrafast Lattice Dynamics of Granular L10 Phase FePt Measurement by MeV Electron Diffraction*” (in preparation).

T. Chase, A.H. Reid, R.K. Li, X. Shen, S.P. Weathersby, T. Vecchione, R. Coffee, N. Hartmann, J. Wu, C. Hast, M. Trigo, D. Reis, X. Wang & H.A. Dürr, “*Non-Equilibrium Phonons in Gold*” (in preparation).

Workshops

FY2015

Figure 3: Spot size measurement as a function of solenoid field strength. For 30 fC UED operation.

A. H. Reid, *"Ultrafast Lattice Dynamics of Granular L10 Phase FePt Measurement by MeV Electron Diffraction"*, Microscopy & Microanalysis 2015 Meeting, Portland Oregon, August 2-6, 2015.

A. H. Reid, *"Ultrafast Nanoscale Spin Dynamics"*, ALS Users Meeting 2015, Berkeley California October 5-7, 2015.

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE Early Career
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	N/A
Number of Post Docs supported by LDRD project in FY15?	0
Number of students supported by LDRD project in FY15?	1
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total??	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

21.0 Prototype for a Microjoule-class Femtosecond XUV Source

Principal Investigator: David A. Reis Co-Investigator: Shambhu Ghimire

Project Description

A new scheme of generating XUV radiation from the interaction of crystalline nanoparticle with intense femtosecond infrared laser pulses is tested successfully. The interaction target is an active media of flowing nanoparticles such that the effective target density is much higher than the typical gas density in conventional high harmonic sources. Because of the use of flowing jet the interaction target is constantly replenished for the subsequent laser shot. The output radiation is characterized by using a XUV spectrometer covering the range from 20 eV to 50 eV.

Accomplishments

Figure 1: Schematics for the prototype XUV source. A liquid jet containing nanoparticles intercepts the strong near infrared laser beam. The nonlinear response of nano-particle gives rise to XUV radiation in transmission. The XUV beam is filtered out from the residual fundamental beam using a 200 nm thin aluminum foil.

This LDRD has evaluated a new approach of XUV light generation, which uses an active interacting medium containing a continuous flow of crystalline nanoparticles. The experimental setup is shown schematically in figure 1. We used MgO nano-particles suspended in a highly charged liquid buffer to make nano-droplets jet using the electro-spray method. This jet intercepts the focal spot of a millijoule-class femtosecond Ti:sapphire laser beam of wavelength 800 nm. Thus, it creates a virtually laser-damage free sample environment since as the target gets constantly replenished for consecutive laser shots with peak intensity on order of 1014 W/cm².

At high intensity intensity, the nonlinear response of nano-particles produces XUV radiation consisting of high harmonics of the fundamental frequency as well as the plasma emission lines. Figure 2 shows a measured XUV spectrum where the red arrows represent the expected location for various harmonic orders and additional lines represent plasma emission.

Figure 2: Measured spectrum of the prototype XUV light source. Red arrows are expected locations of harmonics of the fundamental laser. Additional lines correspond to plasma lines..

Publications

none

Workshops

none

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE
Has follow-on funding been obtained?	Yes
Amount of follow-on funding (\$K)?	2,500
Number of Post Docs supported by LDRD project in FY15?	1
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in	0

FY15?	
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

22.0 Integrating Testing and Characterization with Theory for Catalytic Hydrogenation of CO₂

Principal Investigator: Felix Studt

Project Description

This project aims at developing new capabilities within SUNCAT and SLAC to integrate synthesis, testing, and characterization with theory, aiding in the development of next generation catalysts for energy transformations. In particular, in situ and operando characterization at SSRL will provide the capability to observe changes in our catalyst at various time and length scales and elucidate how these features guide catalyst performance. CO₂ hydrogenation to methanol, catalyzed by novel Ni-Ga catalysts (developed by SUNCAT scientists), will serve as the focus for this study. Upon developing the tools for in situ and operando characterization, they will be applied to understand the Ni-Ga system and determine how it may be improved further.

Accomplishments

Operando experiments were prepared on beamline 6-2C with the assistance of Dr. Yijin Liu of the Stanford Synchrotron Radiation Lightsource (SSRL). First, the existing reactor setup at the TXM-XANES hutch was improved. Utilizing a novel U-shaped capillary and a custom-built support stage, this reactor was able to avoid the heating issues which degraded seals on previous designs. We'd like to acknowledge the contributions of Dr. Doug van Campen, Wes Leonard, and Mike Swanson who aided in the design of the furnace, capillaries, and stage. With a new, functional design, we performed operando TXM-XANES on the Ni-Ga catalysts as they turned over the methanol synthesis reaction (Fig. 1).

Upon reduction in the TXM-XANES reactor, only metallic nickel (determined by fitting spectra to Ni⁰⁺ and Ni³⁺ references, Fig 2.) is found in the system. However, as the reaction progresses, the nickel becomes increasingly oxidized. This change reverses partially after cooling and purging the reactor with He; however, it does not fully return to its initial reduced state. These trends are true for both catalysts tested and may offer insights into why Ni₅Ga₃ outperforms NiGa. Without further data, it is difficult to pinpoint an exact source for these changes; however, two primary hypotheses are considered:

1. Surface-bound oxygen-containing intermediates

Figure 1. TXM-XANES at the of the Ni₅Ga₃ catalyst. Inset images depict sample with Ni oxidation fit colored (Ni⁰⁺ red, Ni³⁺ green).

	Cond.	Ni ₅ Ga ₃	NiGa
		Ni ⁰⁺ Fit	Ni ⁰⁺ Fit
Initial	He 25° C	0.998	0.86*
Reduction	He/H ₂ 350° C	0.946	0.567*
Reduction (1 hr)	He/H ₂ 350° C	0.925	0.669
Reaction	H ₂ /CO ₂ 200° C	0.842	0.495
Reaction (1 hr)	H ₂ /CO ₂ 200° C	0.616	0.460
Post	He 25° C	0.849	--

Figure 2. Average Ni oxidation from fitting of TXM-XANES spectra.

- from the reaction (CH_3O -, CO) induce an observed oxidation shift in the nickel.
2. Diffusion of Ni/Ga species within the particles (particularly near the surface) due to the CO_2 atmosphere – creating a new active site at the surface

As will be described later, additional *operando* experiments are planned at SSRL in the next year to investigate these changes further and identify the true nature of the Ni-Ga active site under reaction conditions.

Preliminary ex-situ characterization studies at beam-line 6-2 (HERFD-XAS and XES) and 10-1 (soft-XAS), in collaboration with Dr. D. Sokaras and Dr. D. Nordlund, revealed small changes in the electronic structure of the Ni/Ga nanoparticles after the reaction tests. It is well known that nanoparticles morphology and oxidation state are strongly related to the gas environment, temperature and pressure. Therefore, such promising preliminary results must be followed by a more thoughtful *operando* systematic study aimed to the obtainment of more representative data. Beam time at

Figure 3. High pressure gas delivery system for operando studies at SSRL.

beam lines 4-1, 6-2 and 13-2 has already been requested to characterize the catalytic system through XAS (X-Ray Absorption Spectroscopy), HERFD-XAS (High Energy Resolution Fluorescence Detection) and APXPS (Ambient Pressure X-Ray Photoelectron Spectroscopy) in operando conditions. In particular, a portable gas delivery systems able to work up to 50 bar (Fig.3) was designed and built to be used at beam-lines 4-1 and 6-2. Two different plug flow tubular reactors were designed for high pressure catalytic tests. The reactors body material and wall thickness were chosen such as to have more than 50% of X-Ray transmission at 8 keV (Ni K-edge 8333 eV) and to withstand a pressure of at least 100 bar. Beryllium and glassy carbon were the two

Figure 4. ETEM of $\text{Ni}_5\text{Ga}_3/\text{SiO}_2$ under H_2 (1 mbar).

materials selected for the *operando* tubular reactors for the beamline tests. An external diameter of 5 mm and 6 mm and a wall thickness of 0.6 and 0.8 mm for the Be and glassy carbon tube, respectively, satisfy the above requirements. Moreover, such reactors allow us to use the optimal amount of catalyst for the tests, both from a catalytic and spectroscopic point of view. The gas delivery system and *operando* reactors will allow us to accurately reproduce the testing conditions (contact time, pressure and temperature) used on the micropilot catalytic test plant at SLAC/SUNCAT and collect X-ray data in transmission and fluorescence mode.

An in-situ preliminary ETEM (Environmental Transmission Electron Microscopy) study was conducted at PNNL in collaboration with Dr. L. Kovarik. The results show how the morphology of the bimetallic nanoparticles changes upon hydrogen treatment at different temperature (Fig. 4). At RT an oxide shell of 2 nm persists up to 400 °C in H₂ (1 mbar). The particles are well faceted and homogeneously dispersed on the support with an average diameter of 6 nm. Further reduction at 700 °C leads to a change in morphology and to the disappearance of the oxide shell. Interestingly, previous XRD data showed how the Ni₅Ga₃ intermetallic phase was stable under catalytic conditions. Future ETEM studies on the effect of the reaction mixture on the nanoparticles composition and morphology have already been planned.

The micropilot catalytic plant at SLAC/SUNCAT was recently upgraded to be able to perform catalytic test at high CO₂ pressure. High pressure is thermodynamically beneficial and increases the methanol yield. Industrially, methanol synthesis is performed at pressure between 50 and 100 bar. The influence of the reaction pressure was evaluated, as well as the addition of third component to the Ni/Ga catalyst (Fig. 5). Generally, a higher pressure leads to an increase in the methanol to carbon monoxide ratio at 200 °C for Ni₅Ga₃, while an increase in

Figure 5: Methanol/carbon monoxide ratio for different catalyst at different temperature and pressure.

temperature to 250 °C favors CO production. However, at 250 °C the commercial catalyst promotes RWGS (Reverse Water Gas Shift) to the largest extent leading to a drastic drop in methanol to carbon monoxide ratio. Differently, the increase in RWGS is negligible for the Ni₅Ga₃ catalyst. Interestingly, Ni₅Ga₃/SiO₂ shows scarce activity for carbon monoxide reduction to methanol at 40 bar, while the commercial catalyst shows excellent performances. The addition of Co and Cu (2 wt%) to the Ni₅Ga₃ systems improves the methanol/carbon monoxide ratio at 200 °C. In particular, Cu shows the best performances with the highest methanol to carbon monoxide ratio at 200 °C. At 250 °C the promotion effect seems negligible. Preliminary EDS-STEM (Energy Dispersive Spectroscopy- Scanning Transmission Electron Microscopy) data for Ni/Ga/Cu/SiO₂ showed the presence of bimetallic Ni₅Ga₃ nanoparticles homogeneously dispersed onto the support with Cu stochastically included in some of them. Further characterization is in progress to better understand the role of the promoters. The effect of Cerium oxide was also evaluated. Cerium oxide was found to be effective in promoting the catalytic performances of Ni₅Ga₃/C for

methanol synthesis, whereas it was detrimental for Ni₅Ga₃/SiO₂, leading to a higher CO and CH₄ amount.

FY16 activity:

- ***Operando* experiments at SSRL.**

As described above, *operando* characterization studies of the Ni/Ga/SiO₂ catalytic systems for methanol synthesis will be conducted at SSRL BL 4-1, BL 6-2, BL 13-2, using the *operando* reactors and gas delivery system already developed.

- **ETEM on Ni/Ga/SiO₂ model system.**

Ni₅Ga₃ nanoparticles will be deposited on SiO₂-covered Au TEM grids for ETEM studies under CO₂/H₂ mixture at methanol synthesis conditions that will be conducted at PNNL. This way we aim to acquire high-resolution images that will be helpful to understand the morphology changes of the bimetallic nanoparticles, avoiding stability problem of the silica support under the electronic beam revealed during the preliminary study.

- **Investigating the promotion effect of a third metal: Cu, Co, Au, Pd.**

Preliminary studies revealed how the presence of a third component increases the selectivity towards methanol of the Ni₅Ga₃/SiO₂ system. We will conduct a systematic study promoting the system with Cu, Co, Au and Pd. We expect the promotion effect to be different depending on the nature of the promoter (Methanol synthesis active, WGS active, inactive).

- **Investigating the influence of the catalyst synthesis methodology on the catalytic properties: mixed-oxide precursors and colloidal Ni/Ga nanoparticles.**

Different synthetic methodologies aiming to a better compositional and morphological control of the system will be evaluated for the synthesis of methanol synthesis Ni/Ga based catalysts.

The possibility to use a mixed-oxide precursor for the synthesis of the Ni/Ga catalyst will be explored and a novel methodology for colloidal synthesis of Ni/Ga nanoparticles will be established.

Publications

none

Workshops

FY2016

J. L. Snider, A. Gallo, Y. Liu, T. F. Jaramillo, “*Operando* TXM-XANES of Ni-Ga Based Methanol Synthesis Catalysts”, Presentation approved for 2015 American Institute of Chemical Engineers (AIChE) Annual Meeting, November 8-13, 2015.

FY2015

J. L. Snider, A. Gallo, Y. Liu, T. F. Jaramillo, "*Operando XAS/TXM studies of nickel-gallium catalysts for thermochemical CO₂ hydrogenation*", Poster presented at SUNCAT Summer Institute 2015: Heterogeneous Catalysis for Energy & Society, August 24-28, 2015.

J. L. Snider, A. Gallo, Y. Liu, T. F. Jaramillo, "*Operando XAS/TXM studies of nickel-gallium catalysts for thermochemical CO₂ hydrogenation*", Poster presented at 2015 Stanford Chemical Engineering Convocation, September 25, 2015.

J. L. Snider, A. Gallo, Y. Liu, T. F. Jaramillo, "*Operando XAS/TXM studies of methanol synthesis over Ni-Ga catalysts*", Presentation given at 2015 SUNCAT Industrial Affiliates Meeting, June 4, 2015.

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Maybe
Source of support for follow-on funding?	NA
Has follow-on funding been obtained?	NA
Amount of follow-on funding (\$K)?	N/A
Number of Post Docs supported by LDRD project in FY15?	0
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

23.0 Hybrid Organic/Inorganic Perovskite Films Solar Absorbers: What is the Role of Defect?

Principal Investigator: Michael F. Toney

Project Description

This LDRD will allow SLAC and NREL to jointly investigate the processing, crystallization dynamics and morphology of lead halide perovskite photovoltaic thin films using solution and thin film x-ray scattering. Lead halide perovskite thin films are of interest because of their use as the photoactive layer in high efficiency (~20%), solution-processed photovoltaic devices. Despite their high photovoltaic efficiency, there is a poor mechanistic understanding of how lead halide perovskites form from their inorganic and organic precursors. This work will further the understanding of how processing (precursor solution formulation, deposition protocol, annealing times/temps, etc.) affect perovskite crystallization dynamics and in turn how these affect final film morphology (crystallite size/shape, amorphous content, point defects, etc.). Specifically, we will uniquely produce insight into the phenomenon occurring within precursor solutions as well as how different deposition protocols affect crystallization dynamics and film morphology. This proposal meets the LDRD program criterion as a pilot, bench scale project that supports initial and exploratory work and will strategically position SLAC to apply for future funding opportunities (NSF, EERE, etc.) both independently and with NREL.

Accomplishments

Work associated with this LDRD has produced a better understanding of the amorphous vs. crystalline content in solution-processed lead halide perovskite thin films. Specifically, several x-ray diffraction techniques were used in combination to determine that a significant volume fraction (~30%) of solution-processed lead halide perovskite films is amorphous rather than crystalline. This is a novel insight for the field and helps explain some of the seemingly incongruous spectroscopic data that has been observed for these types of materials. As this work has established the methodology for quantifying amorphous content in lead halide perovskite films, moving forward this data will be combined with detailed film deposition/synthesis as well as optoelectronic and device data to determine how the amount of this amorphous content can be controlled with different fabrication processes and how this amorphous content affects optoelectronic and device properties.

In FY16 x-ray scattering of lead halide perovskite films and precursor solutions will attempt to answer the following questions:

1. Why is a stoichiometric excess of organic precursor needed in solution to form compact, uniform perovskite films free of pinholes and 1D structures?⁴
2. Why does the addition of certain solution additives lead to compact, uniform films even without a stoichiometric excess of organic precursor?

3. Does the chemical reaction between inorganic and organic precursors/nucleation and growth of the lead halide perovskite begin in solution or film?
4. What intermediates (if any) are involved in this reaction and what role do they play in determining final film morphology?
5. How does the specific lead salt affect the chemistry happening in solution?
6. What are the types and concentration of point defects present in lead halide thin films?

This is a joint proposal between NREL and SLAC, with NREL providing the film synthesis and SSRL conducting the characterization. The approach will utilize strengths from each institution and will be collaborative in nature. Perovskite films will be prepared at NREL using several different established approaches to materials synthesis that have been used to produce efficient perovskite based PV systems. We will leverage NREL's experience with inorganic and solution-processed thin film photovoltaic device fabrication and characterization with SLAC's experience with inorganic and organic thin film structural characterization.

In order to fully characterize the formation of solution-processed lead halide perovskite films, precursor solutions will be characterized with transmission small and wide angle x-ray scattering (SAXS and WAXS, respectively) while films cast from these solutions will be characterized by in-situ thermal annealing WAXS. SAXS of the precursor solutions will provide information about the size and shape of any aggregates present in solution. If the aggregates are crystalline then WAXS will be used for phase identification. Films will then be analyzed with WAXS to determine how the presence and structure of any aggregates in solution affects the formation of any intermediate or final phases. In-situ annealing of the films will then be performed to understand how any initial intermediate phases evolve into the final perovskite film. By combining solution SAXS and WAXS with in-situ thermal annealing WAXS of films we will be able to comprehensively observe the formation of lead halide perovskite from solution to as-cast film to fully formed perovskite. These measurements will be performed as a function of lead salt (PbI_2 vs. PbCl_2), solvent, solvent additives, annealing temperature, etc. to understand how these variables can be used to tune the processing of lead halide perovskite films to design processing techniques that readily produce fully converted, compact, pinhole-free lead halide perovskite films for use in high efficiency photovoltaic devices.

SLAC will additionally conduct careful crystallographic refinement of XRD data from the relevant thin films to determine the structure and defects within the films and how this depends on processing. SLAC will also use resonant elastic X-ray diffraction (REXD), when needed, to more accurately quantify specific defect concentrations. Theoretical modeling and measurement of charge carrier diffusion lengths and densities have been used to suggest that different processing methods lead to different types of electrically relevant point defects so we hope to be able to use a combination of XRD and REXD to directly experimentally probe these important point defects.

Publications

FY2015

Stone, K. H.; Yang, M.; Schelhas, L. T.; Pool, V. L.; Sanehira, E.; Ostrowski, D.; Perkins, J.; Zhu, K.; Berry, J.; Luther, J. M.; Toney, M. F.; Tassone, C. J., *"Quantification of the amorphous content in absorber layers of MAPbI₃ perovskite solar cell devices"*, In Preperation

Workshops

FY2015

C. Tassone, *"Quantitative Determination of Absolute Crystallinity and Texture in Perovskite Absorber Layers, Hyrbid and Organic Photovoltaics Conference"*, sponsored by nanoGE, Rome, Italy, May 11-13, 2015

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	yes
Source of support for follow-on funding?	EERE
Has follow-on funding been obtained?	yes
Amount of follow-on funding (\$K)?	75
Number of Post Docs supported by LDRD project in FY15?	1
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total??	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

24.0 Beyond the Current Limitations of Water Splitting Catalysts

Principal Investigator: Aleksandra Vojvodic

Project Description

The aim of this LDRD is to systematically investigate new catalytic active sites for water splitting in bulk transition metal oxides, at their surfaces, and at interfaces between the oxide and support. We expect to develop an understanding of how to design 3D active sites in a controlled way to overcome the limitations imposed by the energy scaling relations. This LDRD has the potential to give us an initial starting-point to bridge the gap between heterogeneous and homogenous catalysis.

Accomplishments

At the current stage of this LDRD we have published two articles of which one is a perspective on the need for a design paradigm within heterogeneous catalysis¹ and the other articles addresses implications of confinement in nano-channels for OER.² In the following, these published articles will be discussed followed by a description of three ongoing projects and planned research.

Finalized Projects:

In the first publication,¹ we define the boundaries and limitations on the catalytic activity that are a consequence of the energy scaling relations not only for the OER catalysis but generally within heterogeneous catalysis. Figure 1 is an attempt to systematize the different approaches that one can imagine taking in order to overcome or circumvent energy scaling relations, which are one of the main limiting factors not only in OER but in many reactions with multiple intermediates. This broad palette of general strategies shows how this might be achieved. This two-dimensional

scheme is a simplified version of a vast parameter space. The ordinate of Figure 1 represents Intrinsic versus Extrinsic Effects, while the abscissa spans over Electronic versus Structural

Figure 1. Approaches that might be used as routes to circumvent energy scaling relations. The routes are positioned in a space spanned by electronic to structural effects, and intrinsic to extrinsic effects. Adapted from Publication 1.

Figure 2. Left: Atomistic side view of the model system used to simulate confinement in a 2D nano-channel of width d_{mm} . Right: The potential needed to drive each OER step on (a) RuO₂ and (b) IrO₂ as a function of channel width. Discrete symbols represent the highest limiting potential in (a) and (b), which have been translated to overpotentials in (c). Adapted from Publication 2.

Effects. We have chosen this representation as it is inclusive and illustrates some of the major directions available in heterogeneous catalysis for tuning activity.

Attempts so far have found it challenging to circumvent scaling relations when different reaction intermediates (including transition states) adsorb on the same surface site. Hence, multi-site functionalization, that is, catalysts with several types of active sites or local binding environments for different intermediates is a promising possibility. This might be achieved in a number of ways, for example, by alloying, doping, introduction of defects, coupling between catalyst and support, nano-structuring, subsurface species, confinement, etc.

In the second publication,² we report on OER activity change because of confinement effects arising from a change of the active site due to a change in dimensionality. By introducing a 3D catalyst structure, we find that if the reaction takes place in a 2D nano-channel (see Figure 2), we are able to circumvent the energy scaling relation between the OOH and OH intermediates by changing the channel width, thereby decreasing the OER overpotential substantially (see Figure 2).

Ongoing Projects:

Only recently has it been suggested that layered active

bulk oxide s
under operat
ing OER cond

TMOs can be stabilized when interfaced with precious metal supports such as Au(111) and Pt(111) or Ir(100). Moreover, gold supported Co/Ni/Mn-based catalysts have been experimentally proven to exhibit higher OER activities than other metal supported oxide catalysts. However, the exact structure of the oxide catalysts under experimental OER conditions is not known.

1. Recently my group performed a detailed analysis of the relationship between the atomic-scale structure of Co-oxide nanoislands supported on Au in collaboration with our experimental collaborator Prof. Jeppe V. Lauritsen (Aarhus University) [ACS Nano 9, 2445 (2015). Not supported by this LDRD]. We revealed that conversion from Co²⁺ to Co³⁺ occurs by a facile

incorporation of oxygen at the interface between the nanoisland and Au, changing the islands from a Co-O-bilayer to an O-Co-O trilayer. The O-Co-O trilayer islands have the structure of a single layer of, proposed to be the active phase for the OER. Within this LDRD,³ we have set out to study the dissociation of H₂O on these nanoislands. We model the nanoislands as Co-oxide stripes on Au. These stripes have a metal and an oxygen edges exposing 3D sites that can interact with the H₂O as opposed to the 2D sites on the basal planes. Our preliminary results indicate that H₂O dissociation might only be possible on the metal edge. We have calculated the barrier for dehydrogenation and H hopping on the basal planes, which might act as hydrogen reservoirs in the form of hydroxyls. All the barriers are high. However, interestingly our preliminary results show that the barriers become surmountable if the process is mediated by water. This model has to be improved with the proper hydrogen coverage for us to gain an understanding of the edges activity of these oxide stripes.

2. We have started a study⁴ with the goal to understand a more complex and realistic active site of a high performance OER catalyst, NiCeO_x supported on Au. The reactivity of a 3D active site consisting of under-coordinated doped edge sites that are part of a hydrogenated Ni- oxide stripe supported on Au. We find that it should be possible to deconvolute the effects of coordination of the active site, of doping, and support by careful design of the studied systems. This theoretical study is performed in collaboration with our experimental collaborator Prof. Thomas F. Jaramillo (Stanford University).

3. An attractive strategy to improve the performance of OER catalysts would be to anchor a homogeneous molecular catalyst on a heterogeneous solid surface to create a hybrid catalyst. The idea of this combined system is to take advantage of the individual properties of each of the two catalyst components. In this study,⁵ we use DFT calculations to determine the stability and activity of a model hybrid water oxidation catalyst consisting of a dimeric Ir complex attached on the IrO₂(110) surface through two oxygen atoms. Interestingly, we find that the interaction between the dimeric Ir complex and the surface is rather strong due to the electron donation from both the Ir atoms in the molecular catalyst and the surface to the oxygen linkers. We also show that the reactivity/activity of the hybrid system is rather similar to the one predicted for its homogeneous constituent. These results are very encouraging as they suggest that homogeneous catalysts could be anchored to oxide surfaces without losing significant activity. Hence, designing hybrid systems that benefit from both the high tunability of activity of homogeneous catalysts and the stability of heterogeneous systems seems feasible.

Planned Projects:

In the remainder of FY16 we suggest to investigate the catalysis of complex layered oxyhydroxides and finalize the ongoing projects described above.

Several transition metal oxide (and oxyhydroxide) crystals form “layered” structures with water intercalation between cation sheets at length scales we predict to show substantial confinement effects.² Current catalytic activity models suggest that all reaction turnover happens at the outermost surface of the catalyst, though recent experimental work has shown layered transition-metal oxides behave differently. This could explain experiments suggest materials prone to these crystal structures show high OER activity. We will study the maximum

theoretical activity of bulk sites in a NiOOH crystal and elucidate the difference between surface and bulk active sites. In addition, we will study the activity for mixed-metal oxides by substituting Co, Fe, and Mn ions into the NiOOH lattice. In each case we will start by calculating the adsorption energies of reaction intermediates (HO^* , O^* , and HOO^*) at a several values of interlayer spacing to probe confinement effects. In electrochemical processes, the effect of the electrolyte or additives to the electrolyte can strongly change the surface chemistry by solvating different intermediates differently, thus providing the 3D effect discussed above. We propose determining the thermodynamic drivers for layer formation. We will calculate the optimal interlayer spacing for different intercalated cations (including Li, Na, K, Ba) to mimic the effects of electrolyte selection in experiments. We can then correlate expected changes in activity with an easily tunable experimental parameter.

When it comes to the long-term plan we suggest to investigate transition metal oxides (TMOs) and MXenes with different crystal structures, study the confinement effects, explore doping effects and study small TMO nanostructures in so called hybrid catalyst systems. In particular, we intend to explore if more efficient OER catalysts can be developed by designing 3D active sites.

Publications

FY2016

M. García-Melchor, L. Vilella, N. López, and A. Vojvodic, *“Computationally Probing the Performance of Hybrid, Heterogeneous and Homogeneous Ir-based Catalysts for Water Oxidation”*, In manuscript (2015).

J. W. Desmond Ng, M. García-Melchor, M. Bajdich, C. Kirk, P. Chakthranont, A. Vojvodic, and T. F. Jaramillo, *“Leveraging Electronic, Geometric and Support Effects in Electrocatalyst Development: Au Supported NiCeO_x for Water Oxidation”*, In manuscript (2015).

A. S. Walton, J. Fester, M. Bajdich, M. García-Melchor, A. Vojvodic, and J. V. Lauritsen, *“Edge-Mediated Water Dissociation on Cobalt Oxide Nano-Islands”*, In manuscript (2015).

FY2015

A. D. Doyle, J. H. Montoya, and A. Vojvodic, *“Improving Oxygen Electrochemistry Through Nanoscopic Confinement”*, ChemCatChem 7, 738-742 (2015).

A. Vojvodic, and J. K. Nørskov, *“New Design Paradigm for Heterogeneous Catalysts”*, National Science Review 2, 140-143 (2015).

Workshops

FY2015

A. Vojvodic, SUNCAT Summer Institute 2015: **“Heterogeneous Catalysis for Energy & Society**, Stanford, California, USA, August 26, 2015

- A. Vojvodic, **Molecular Foundry Users' Meeting**, Berkeley, California, USA, August 21, 2015.
- A. Vojvodic, **SLAC SPC meeting**, SLAC National Accelerator Laboratory, USA, April 30, 2015
- A. Vojvodic, **ACS March meeting**, Denver, Colorado, USA, March 23, 2015.

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE Early Career
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	N/A
Number of Post Docs supported by LDRD project in FY15?	1
Number of students supported by LDRD project in FY15?	0/0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	1
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total??	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

25.0 Methodology Developments for Structural Studies of Post-translational Modifications of Proteins

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Principal Investigator: Soichi Wakatsuki

Project Description

Post-translational modification of proteins, such as ubiquitination, glycosylation, phosphorylation and acetylation, play critical roles in many cellular events and functions, such as cell cycle control, quality control, and stem cell development. In this LDRD project, we aim to continue to develop new methodologies to discover novel functions of polyubiquitin chains and other post-translational modifications of proteins. We will further establish a research environment for protein production, purification, crystallization and biochemical and biophysical characterization. Using this infrastructure, we will enzymatically produce polyubiquitin chains of different linkages and lengths. The produced polyubiquitin chains will be used to screen protein complexes in various organisms to find new polyubiquitin signaling pathways. Novel protein complexes will be subjected to functional and structural studies using synchrotron protein crystallography and solution scattering and radiation-damage free XFEL nano-crystallography.

Accomplishments

Recognition of Lys48-linked polyubiquitin chains:

The Lys48-linked Ub chains act as the main targeting signals for protein degradation by the proteasome. We continued the investigation of selective binding of AIRAPL, a protein that associates with proteasome upon exposure to arsenite, to Lys48-linked tri-ubiquitin chains using x-ray crystallography, small angle x-ray scattering, surface plasmon resonance and pull down assays. AIRAPL comprises two ubiquitin-binding UIM domains in tandem (tUIM) that are linked through a flexible inter-UIM region. In the complex crystal structure UIM1 binds the proximal ubiquitin, whereas the double-sided (UIM2) binds non-symmetrically to the middle and distal ubiquitin moieties on either side of the helix. Specificity of AIRAPL for Lys48-linked ubiquitin chains is determined by UIM2, while the inter-UIM linker places the two UIMs in an orientation that facilitates binding to three ubiquitins linked through Lys48. Unlike middle and proximal ubiquitins, distal ubiquitin binds UIM2 through a novel binding surface, which leaves the canonical Ile44 hydrophobic patch accessible for binding to the proteasomal ubiquitin receptors.

A revised version of the following manuscript has been submitted to *Structure*: Simin Rahighi, Ilana Braunstein, Nicola Ternette, Benedikt Kessler⁴, Masato Kawasaki, Ryuichi Kato, Tsutomu Matsui, Thomas M. Weiss, Ariel Stanhill, Soichi Wakatsuki, "Selective binding of AIRAPL tandem UIMs to Lys48- linked tri-ubiquitin chains".

Establishing infrastructure and collaborations:

During FY15, we further expanded the infrastructure for protein expression and purification, and characterization of protein complexes involved in posttranslational modifications, in particular protein ubiquitination and ubiquitin chain recognition. After an extensive survey of state-of-the-art instruments, a surface plasmon resonance (SPR) instrument was selected and procured for characterization of protein-protein and protein-small molecule interactions. The SPR instrument has been used extensively for the structural biology projects, including the above mentioned Lys48 polyubiquitin project, during FY2015 and is expected to see further demands.

The collaboration with Prof. Daria Mochly-Rosen of Stanford School of Medicine on drug discovery project on an enzyme and a seed funding was secured from Child Health Research Institute of Stanford School of Medicine, a two-year grant, \$23,250 for FY14-15, \$23,500 for FY15-16. An R01 Grant application on the subject was submitted to NIH and received an extremely good review result and is currently pending for decision.

Another collaboration project was formed with Prof. Dave Stahl, University of Washington, a BERAC member, on ammonia oxidation, a key step in nitrogen cycle. While this collaboration continues, we started a related project on different species of ammonia oxidizing archaea with Prof. Christopher Francis of Stanford University and Dr. John Bargar, SLAC. This new project has been launched with funds from BER in September 2015 as well as a new LDRD project entitled “Molecular Basis of Ecosystem N Cycling” with Dr. Bargar as PI starting FY16.

Development of a new LCLS beamline, Macromolecular Femtosecond Crystallography:

We have continued the new XFEL instrument project of developing and constructing a dedicated atmospheric pressure Macromolecular Femtosecond Crystallography (MFX) instrument to be installed inside a new experimental hutch, referred to as Hutch 4.5, on a new hard X-ray beamline in at LCLS. Multiple crystal delivery systems and approaches will be accommodated by MFX, such as robotic fixed-target goniometer systems, on-demand liquid sample delivery systems, and LCP (lipidic cubic phase) injectors for membrane proteins. The system will also be highly flexible to allow integration of potential new sample delivery techniques to be developed. The development will be leveraged by the experiences and expertise accumulated at the CXI and XPP stations by the consortium members. Initial investments have been obtained from DOE-BER (\$2M, Wakatsuki as PI), NIGMS (\$1M, Wakatsuki as PI), and LCLS and DOE-BES. The project progressed well since its onset in April 2014. The beamline construction finished at the end of summer 2015, the endstation design project has progressed and the CDR was reviewed by a panel. Further funding from federal agencies and private foundations is being explored for completing the endstation instrument development.

Development of a two-pulse/two-color femtosecond time-resolved experiments using XFEL:

Utilization of two-color XFEL pulses for *de novo* structure determination was further developed into a two-pulse/two-color femtosecond time-resolved experiments. Following the LCLS experiment (LD91) which measured the time-evolution of radiation damage in protein crystals using x-ray pump/x-ray probe techniques based on two-color XFELs, new methods for achieving further energy separation with programmed time delay between the two LCLS pulses up to 120 fsec were identified and pursued (Marinelli et al. 2015). A 5-day experiment (LH80) was conducted on LCLS CXI station in May 2015. In the new experiment, a “pump” pulse was used to record an essentially undamaged diffraction pattern. This pulse also initiates the damage process in the sample. A second pulse (“probe”) some tens of fsec later then enabled recording of the damaged diffraction pattern. The main effect observed so far was disulfide bond breakage on 100 femtoseconds timescale. Further analysis is underway.

Publications

Wakatsuki S. “*Structural Biology Applications of Synchrotron Radiation and X-Ray Free-Electron Lasers*. In *Synchrotron Light Sources and Free-Electron Lasers Handbook*”, Editors: Eberhard Jaeschke, Shaikat Khan, Jochen R. Schneider and Jerome B. Hastings, Springer International Publishing Switzerland, *in press*.

Sakamoto H, Egashira S, Saito N, Kirisako T, Miller S, et al., “*Gliotoxin suppresses NF- κ B activation by selectively inhibiting linear ubiquitin chain assembly complex*”, (LUBAC). ACS Chem Biol. 2015 Mar 20;10(3):675-81. PubMed PMID: 25494483.

Marinelli A, Ratner D, Lutman AA, Turner J, Welch J, et al. ,“*High-intensity double-pulse X-ray free-electron laser*”. Nat Commun. 2015 Mar 6;6:6369. PubMed PMID: 25744344; PubMed Central PMCID: PMC4366525.

Takahashi T, Kojima K, Zhang W, Sasaki K, Ito M, et al., “*Structural analysis of the complex between penta-EF-hand ALG-2 protein and Sec31A peptide reveals a novel target recognition mechanism of ALG-2*”. Int J Mol Sci. 2015 Feb 6;16(2):3677-99. PubMed PMID: 25667979; PubMed Central PMCID: PMC4346919.

McEwan DG, Popovic D, Gubas A, Terawaki S, Suzuki H, et al., “*PLEKHM1 regulates autophagosome-lysosome fusion through HOPS complex and LC3/GABARAP proteins*”. Mol Cell. 2015 Jan 8;57(1):39-54. PubMed PMID: 25498145.

Lutman AA, Decker FJ, Arthur J, Chollet M, Feng Y, et al. “*Demonstration of single-crystal self-seeded two-color x-ray free-electron lasers*.” Phys Rev Lett. 2014 Dec 19;113(25):254801. PubMed PMID: 25554887.

Cohen AE, Soltis SM, González A, Aguila L, Alonso-Mori R, et al. *“Goniometer-based femtosecond crystallography with X-ray free electron lasers”*. Proc Natl Acad Sci U S A. 2014 Dec 2;111(48):17122-7. PubMed PMID: 25362050; PubMed Central PMCID: PMC42606

Workshops

FY2014

FY2015

“SLAC Bioscience Strategy and Applications of Two-Color XFEL Mode to Structural Biology”, NCI XFEL workshop, National Cancer Institute, Frederick, November 21, 2014

“LCLS applications to structural biology: the macromolecular femtosecond crystallography (MFX) project and two-color mode for de novo phasing”, 2nd International BioXFEL Meeting, Ponce, Puerto Rico, January 14, 2015

“XFEL advancements and applications to structural biology”, International Conference on Structural Genomics (ICSG) 2015 Deep Sequencing, Weizmann Institute, Israel, June 10, 2015

“Structural Biology using XFEL: Status and future accelerator based infrastructure requirements”, Future Research Infrastructure, Opportunities and Challenges, Italian Physics Society

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE BER, NIH, Stanford Children's Hospital, NSF
Has follow-on funding been obtained?	Y
Amount of follow-on funding (\$K)?	3,323.5
Number of Post Docs supported by LDRD project in FY15?	0
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in	1

FY15?	
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

26.0 Experimental Demonstrations of Gas Phase Ultrafast Electron Diffraction

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Principal Investigator: Xijie Wang

Project Description

The funding from this LDRD will support the proof-of-principle experiments of the gas phase ultrafast chemical science enabled by ASTA UED. The MeV UED@ASTA offers unique opportunity for gas phase ultrafast chemical science experiments. The higher electron beam energy leads to better temporal resolution and elimination of the velocity mis-match between the pump laser and electron beam probe. Ultrafast electron diffraction in small molecules provides a new opportunity to exclusively distinguish the nuclear rearrangements upon photo-excitation. MeV electrons show negligible interaction with valence electrons. The relativistic electrons travel through the scattering medium with about the same speed as the optical excitation pulse, which improves the time resolution compared to keV electron scattering experiments. The direct inversion of the scattering patterns for small molecules is possible, and the method could deliver highly accurate nuclear trajectories with femtoseconds temporal resolution. The cross section of elastic electrons at MeV energies is around 0.1 Mbarn and thus about 5 orders of magnitude larger than hard x-ray cross-sections. The ultrafast electron diffraction for nuclear geometry determination is thus an ideal complementary tool for soft x-ray electronic state spectroscopy at the LCLS.

Expected Results

- Demonstration the feasibility of gas phase UED: we will demonstrate the feasibility of the gas phase UED by upgrading the detector and develop a new gas chemical delivery system. The space and temporal resolution of the gas phase UED will be demonstrated by diffractive imaging of N₂ molecular rotational wavepacket .
- Observe a simple molecular dissociation in UED: Ultrashort excitation of iodine in the region around 500 nm prepares vibrational wavepackets on two different potential energy surfaces. The 3 ☐ B0u state is dissociative. The B state dominates the absorption spectrum below 500 nm while above its dissociation limit, B and 1 ☐ 0g symmetric cross sections. The polarization selection rules from the electronic ground state having 1 ☐ angular distribution of the photoexcited molecules. While the molecular ensemble of the B state is aligned parallel to the light polarization, it is aligned perpendicular for the 1 ☐ state. The dissociation in 1 ☐ and bound be most pronounced in orthogonal directions on the detector. The dissociation on the state occurs with a velocity of 0.024 Å/fs doubling the bond distance in the Frank-Condon region within 100 fs.

Accomplishments

The goal of this experiment was to demonstrate that Ultrafast Electron Diffraction with MeV electrons can provide sufficient spatial and temporal resolution to take time-resolved snapshots of changing molecular structures during a chemical reaction. As a first experiment, we capture a rotational wavepacket in impulsively aligned nitrogen molecules. We performed a gas-phase electron diffraction experiment using Megaelectronvolt (MeV) electrons, where we captured the rotational wavepacket dynamics of nonadiabatically laser-aligned nitrogen molecules (figure 1). The molecules were aligned with a 40 fs non-resonant laser pulse. Diffraction patterns were recorded as a function of time, and the distribution of molecules was retrieved by taking the Fourier transform of the diffraction patterns. We achieved an unprecedented combination of 100 fs root-mean-squared (RMS) temporal resolution and sub-Angstrom (0.76 Å) spatial resolution that makes it possible to resolve the position of the nuclei within the molecule. In addition, the diffraction patterns reveal the angular distribution of the molecules, which changes from prolate (aligned) to oblate (anti-aligned) in 300 fs. Our results demonstrate a significant and promising step towards making atomically resolved movies of molecular reactions.

Figure 1: MeV gas phase UED experiment set up.

The Figure 2 (below) are the distribution obtained from difference diffraction pattern, in the right panel the molecules are aligned vertically and in the left panel they are aligned in the perpendicular plane. The scale in the figure is in Angstrom, and it shows the angular distribution of the molecules, which changes from prolate (aligned) to oblate (anti-aligned) in 300 fs.

Figure 2: Diffraction patterns taken 310 fs apart.

The second experiment accomplished is to realize Atomic-Level View of Photoexcited I₂ Vibrational Dynamics using MeV gas phase UED. In this work, the photoexcited vibrational dynamics of gas I₂ is probed with MeV UED. Our previous N₂ result demonstrated that MeV UED is capable of providing sub-Angstrom spatial resolution and 100fs RMS temporal resolution simultaneously. This is the first work that we try to resolve structural change in a photochemical process, and could potentially be the first atomically resolved molecular movie of isolated molecules. For a simple diatomic molecule like I₂, the dynamics could already be quite complicated, as we can excite a combination of vibration, dissociation and relaxation to the ground state. In spectroscopy only one process can be studied at a time, but in UED they are studied at the same time. For this reason, UED and spectroscopy provide a different perspective on the same reaction, and a more complete picture can be accomplished by combining the two methods. Figure 3 shows our preliminary result, the measured and simulated diffraction patterns of I₂ with longer bond length. This work could potentially be the first molecular movie in gas phase.

Figure 3 : I₂ bond lengthening(simulation vs. experiment).

To address the current SLAC MeV UED limitation, We propose to carry out a R&D program for new generation MeV-UED in FY2016. The new generation MeV-UED

will open a new frontier, i.e. smaller electron probe (nano-UED), and has higher temporal resolution, faster detector and higher operation efficiency. To fully realize the potential of the new generation MeV-UED, we also propose to increase the ASTA MeV-UED repetition rate from 120 Hz to 360 Hz. To enable the study of irreversible process in material science and biology, we will develop single-shot MeV-UED capability in collaboration with LBNL DOE BES funded detector program.

With smaller probe, better temporal resolution and higher flux, the new generation MeV-UED will have broad impact to the ultrafast and structure biology community. The SLAC nano-UED will represent a paradigm shift as it opens up complementary measurements on the same samples of nanoscale lattice dynamics with nano-UED and of charge/spin dynamics at LCLS using soft x-ray holography. It can provide deep insights into the mechanisms of the lattice response for a wide range of quantum materials and nanostructures.

Publications

FY2015

Weathersby, S. P. *et al.* MeV Ultrafast Electron Diffraction at SLAC. *Rev. Sci. Instrum.* **86**, 073702 (2015).

E. M. Mannebach et al., *“Dynamic structural response and deformations of monolayer MoS2 visualized by femtosecond electron diffraction”*, Nano Letters, 31 August 2015 (10.1021/acs.nanolett.5b02805).
 Jie Yang, Markus et al, *“Diffractive imaging of a molecular rotational wavepacket with femtosecond Megaelectronvolt electron pulses ”* submitted to Nature Communications (2015).

Workshops

none

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	BES AMO
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	N/A
Number of Post Docs supported by LDRD project in FY15?	0
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0
Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0

27.0 Cross-Platform Multiple Length Scale Imaging System for Energy Storage Materials

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Principal Investigator: Johanna Nelson Weker

Project Description

Energy storage devices are complex, hierarchical systems which have operational and failure mechanisms occurring across a wide range of length scales from a few Ångstroms to hundreds of microns. Current *in situ* imaging capabilities at SSRL and Stanford are not able to fully meet the challenges of this broad range of length scales.

The aim of this project is to establish a novel enabling capability within SLAC via two main goals. The first goal is the development of a new sub-5 nm resolution imaging capability in the soft X-ray regime, and the second goal is the creation of a unique, cross-platform *in situ* methodology linking existing and proposed electron and X-ray imaging techniques at Stanford University and SSRL.

The new imaging capability will be achieved through the challenging development of a soft X-ray ptychography, a coherent diffractive imaging technique, with X-ray absorption near edge spectroscopy (XANES) imaging system, which will improve SSRL's soft X-ray imaging resolution from around 40 nm to below 5 nm and give access to oxygen chemistry and the valence states of 3d transition metals. Concurrent to this development will be the design, testing, and implementation of a novel, cross-platform *in situ* cell which will be compatible with soft and hard X-ray imaging systems at SSRL and Stanford's TEM. The ultimate deliverables of this project are to demonstrate *in situ* sub-5 nm resolution ptychographic imaging and to combine this technique with *ex situ* TEM and *in situ* XANES transmission X-ray microscopy (TXM), creating an innovative imaging ecosystem with access to a vast range of chemistries and spatial resolutions.

Accomplishments

The main focus of the first year of this project has been on the design of the soft X-ray ptychography capability through modification of the current scanning transmission X-ray microscope on SSRL Beamline 13-1. A key modification to enable ptychographic imaging is the installation of an area detector to collect the far-field diffraction data. A motorized stage has been designed (Figure 1, right) for the CCD camera to allow movement of the camera in the x, y, and z directions (stages labeled A, B, and C respectively). Movement of the camera along the beam direction (z) is important to allow the adjustment of the sample-to-detector distance as required based on the incident beam energy and the desired resolution. Camera alignment to the beam position will be achieved using motion in the x and y directions. A photodiode will be attached to the side of the camera, offset horizontally in the x direction to prevent obstruction of the CCD and closer to the sample position to maximize signal for STXM measurements. The horizontal linear stage 'A' will therefore also allow fast switching between detection using the camera (ptychography mode) or a photodiode (STXM mode). A coil of flexible stainless steel

tubing (not shown) will be used for water cooling of the camera to allow movement of the z stage while maintaining the connection.

To achieve sub-5 nm resolution, accurate and stable sample positioning with higher reliability than the desired resolution is critical. As in a STXM measurement, the sample is moved in the plane of the beam, creating a raster pattern across the sample and collecting scattering data at each sample position. In a ptychography measurement, each sample position needs to overlap the neighboring sample positions by ~60 % to provide sufficient oversampling to reconstruct the phase. Knowing the sample position used to define the real space constraint in the iterative phase reconstruction algorithms is crucial. To enable this fine motor control, a sample stage has been designed consisting of fine x, y motors on top of coarse x, y motors. A differential laser interferometer system will be used to control the sample position relative to the zone plate which defines the X-ray beam. The interferometer system has four laser beams per axis for the reference and measurement outgoing and incoming signals and requires careful design to incorporate the required mirrors in the available space. Figure 1 (left) shows the design of the zone plate and sample stages along with the incorporation of the interferometer laser reference and measurements beams and necessary mirrors.

Figure 1: Design for zone plate and sample stages and interferometer (left) and the CCD camera stages (right) in the vacuum chamber at SSRL Beamline 13-1.

Computing requirements for the reconstruction of the ptychographic data were also identified with the help of Tolek Tyliczszak and David Shapiro at ALS. The computer with the necessary multicore and GPU configuration has been received from the vendor. The reconstruction software (SHARP CAMERA provided by ALS) was installed on this computer and tested with ptychography data collected at the ALS. The current STXM software was updated to accommodate image acquisition with the CCD camera. Python scripts for data processing have also been developed as part of the SULI internship program.

Due to the required removal of the Beamline 13 undulator for repairs at the beginning of June 2015, one beamtime in May 2015 was available for this project in FY15 during which the operation of the CCD camera was tested. Prior to the beamtime, the CCD camera was installed without motors in the STXM chamber and the STXM's photodiode was remounted such that it could be manually moved in and out of the direct beam (Figure 2, left). The interface between the camera and the data acquisition computer was established using Princeton's WinView imaging software. During this beamtime, a temporary shutter was installed directly upstream of the zone plate so images shorter than the camera's readout time (ca. 0.9 s) could be acquired.

A camera cover was also fabricated and installed to shield the CCD chip from the majority of stray visible and infrared light from the chamber's view ports and the motors' IR encoders, respectively. The beamtime revealed a problem with the current STXM zone plate such that it allows significant direct beam to leak onto the CCD (Figure 2, left inset). During the remaining beamtime we removed the zone plate and attempted ptychography with a pinhole to define the beam footprint on the sample. Example coherent scattering data are shown in Figure 2 (right), showing successful operation of the CCD camera.

Following the beamtime, a number of improvements were identified with respect to the detection set-up including a vacuum compatible shutter, a smaller CCD cover, and a new zone plate. A Si_3N_4 window is also desirable to isolate the STXM chamber from the rest of the beamline to allow ambient (or near ambient) pressure imaging. This will be especially useful in minimizing the design constraints of in situ cells.

Figure 2: Initial optics configuration for May 2015 ptychography beamtime (left). Inset shows CCD image of direct beam leaking through zone plate and OSA, with coherent scattering pattern collected from a Siemens star (right)

In addition to the SSRL beamtime, we have participated in ex situ ptychography and in situ STXM experiments at the ALS (beamline 11.0.2) with the Chueh group to gain experience of practical sides of data acquisition and the use of an in situ liquid cell compatible with soft X-ray measurements as part of the development of the cross platform in situ cell which has been used to successfully collect in situ soft X-ray imaging data.

The plan for FY16 is the installation of beamline hardware to demonstrate sub-5 nm imaging and the successful imaging with the cross platform in situ cell. Designs and hardware procurement for the installation of the motorized CCD stages, sample and optics stages, vacuum compatible fast shutter, smaller CCD cover, and the Si_3N_4 window have now been completed. Installation of the beamline hardware will be carried out to enable collection of ptychography data in December 2015. High resolution imaging will be demonstrated by ex situ measurements in Spring 2016, with imaging using the cross-platform cell planned for Summer 2016.

Publications

FY2015

A. M. Wise, H. Ohldag, W. Chueh, J. Turner, M. F. Toney, and J. Nelson Weker, “Development of a soft x-ray ptychography beamline at SSRL and its application in the study of energy storage materials”, Proceedings of SPIE Volume 9592, X-Ray Nanoimaging: Instruments and Methods II, 95920B (2015); doi:10.1117/12.2188811

Workshops

FY2015

A. M. Wise, *Development of a soft X-ray ptychography beamline at SSRL and its application in the study of energy storage materials*, 23rd International Congress on X-Ray Optics and Microanalysis, Sponsored by DOE, Basic Energy Sciences, Upton, NY, September 14-18 2015

A. M. Wise, *Operando X-Ray Characterization of Metal Oxide Cathodes for Li-ion Batteries*, CalCharge Lawrence Livermore National Laboratory Open House, Sponsored by DOE, Basic Energy Sciences, Livermore, CA, August 25 2015

A. M. Wise, *Development of a soft X-ray ptychography beamline at SSRL and its application in the study of energy storage materials*, SPIE X-Ray Nanoimaging II: Instruments and Methods, San Diego, CA, August 9-13 2015

A. M. Wise, *Development of a soft X-ray ptychography beamline at SSRL and its application in the study of energy storage materials*, Gordon Research Conference on X-Ray Science, Sponsored by DOE, Basic Energy Sciences, Easton, MA, July 26-31 2015

Patents/Invention Disclosures/Copyrights

none

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	JCESR, DOE BES MSE, ARPA-e, EERE
Has follow-on funding been obtained?	No
Amount of follow-on funding (\$K)?	N/A
Number of Post Docs supported by LDRD project in FY15?	1
Number of students supported by LDRD project in FY15?	0
Number of scientific staff/technical staff hired with LDRD funding in FY15?	0
Number of copyrights filed in FY15 and in total?	0/0

Number of invention disclosures filed in FY15 and in total?	0/0
Number of patent applications filed in FY15 and in total?	0/0
Number of patents granted in FY15 and in total?	0/0