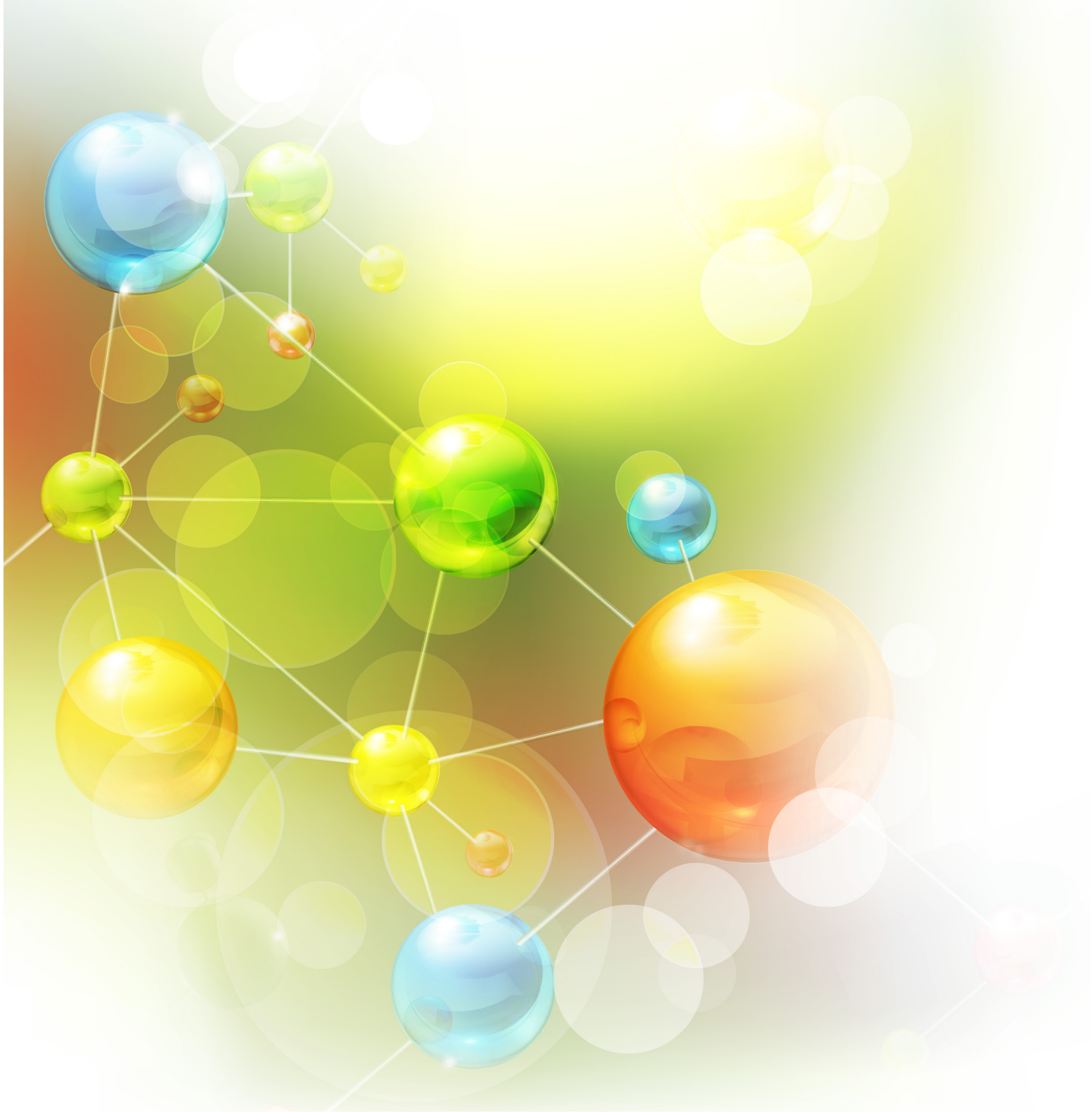
Advanced Photon Source • Center for Nanoscale Materials • Electron Microscopy Center

2014
Users Meeting

PROGRAM AND ABSTRACTS



User Facilities at Argonne National Laboratory

User Contacts

Advanced Photon Source
http://www.aps.anl.gov
630-252-9090
apsuser@aps.anl.gov

Argonne Leadership Computing Facility
http://www.alcf.anl.gov
630-252-0929

Argonne Tandem Linac Accelerator System
http://www.phy.anl.gov/atlas
630-252-4044

Center for Nanoscale Materials
http://nano.anl.gov
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Electron Microscopy Center
http://www.emc.anl.gov
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Table of Contents

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Jim Corsolini (CEP) — Video support

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Ed Russell — Building arrangements, site coordination

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2014 Rosalind Franklin Award
Julian Moosmann
Karlsruhe Institute of Technology

The APS Users Organization has named Julian Moosmann as the winner of the 2014 Rosalind Franklin Young Investigator Award. The award recognizes Moosmann's work to develop methods that have made it possible to obtain time-lapse 3D images of cells and tissues in living vertebrate embryos. The methods will also apply more generally to imaging of materials that have low absorption contrast in conventional x-ray imaging.

Moosmann, a physics Ph.D. student at Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany, is cited as an "original, visionary thinker" who is equally willing to undertake cumbersome experimental work and elaborate numerical simulations. Nominators also commended his scientific maturity, his ability to master techniques from several fields and to work as a team player, and his deep understanding of the concepts and physics behind the experiments.

Moosmann collaborated with his advisor, physicist Ralf Hofmann, and an international team of physicists, beamline scientists, and biologists from KIT, Northwestern University, and the APS to apply the new methods to image the movement of cells within an embryo of the African claw-toed frog (*Xenopus laevis*) over a period of about two hours. The results were published in Nature and the methods in *Nature Protocols*. The initial work was done at APS beamline 2-BM-B, and additional experiments at APS beamline 32-ID confirmed the results.

The work recognized by this award provides an important new modality that could help answer fundamental questions in developmental biology. Although the much-studied *Xenopus laevis* has been the source of many insights about embryonic development, certain questions simply cannot be answered with current technologies. Light microscopes can't show cells inside the optically opaque embryos, and conventional absorption-based x-ray imaging is not sensitive enough, so phase-contrast techniques are needed. But it is still extremely challenging to capture cell movement within the developing embryo without killing it.

Moosmann and Hofmann did not set out to revolutionize developmental biology. They work at ANKA, the synchrotron light source at KIT, and were interested in exploring the fundamental physics and mathematics of x-ray phase-contrast imaging, which exploits differences in a sample's refractive index—and the resulting phase changes in the transmitted x-rays—to create a signal.

One of Moosmann's key advances was to modify the application of the contrast transfer function (CTF), a standard technique used in phase-contrast imaging. He wanted to improve the function's resolution at a greater distance from the sample, that is, at large z. "We decided to focus on propagation-based phase-contrast imaging because of the simplicity of the technique. The setup is free of additional optics and you need only one measurement; there's no scanning or stepping," Moosmann said. They also aimed for a method that would work at larger distances from the sample because in phase-contrast imaging the signal-to-noise ratio improves with distance. This point turned out to be an important advantage because it yields better resolution for less x-ray exposure, so embryos can live longer. It also permits the use of extended sample environments.

The advance depended on close observation of the contrast transfer function. "There is a sinusoidal modulation in the Fourier transform of the intensity," Moosmann explained, "but when the variations in the phase increase, like what would happen as a sample becomes more complex, the contribution from the region around the maxima grew faster than that around the minima." This feature told him that information about the structure of the sample would be concentrated around the maxima. Also, the minima were always in the same place—up to point, at least. When he looked for where the function failed, Moosmann observed a critical transition phenomenon in which the minima shifted rapidly away from their previous positions. In a key step, he realized that below the critical transition, he could safely "crop out" small regions around the minima, leaving most of the information intact.

Such critical transitions are familiar in condensed matter physics, so Moosmann and Hofmann borrowed a theoretical formalism from that field: they proposed that "phase" could be reinterpreted as a "quasiparticle." The same type of formalism is used as a shorthand to represent the vibration of atoms in a solid, for example. In technical terms, Moosmann explains, "There's a dispersion relation between image intensity and phase just as there is between energy and momentum in a solid state material."

It was time for a real-world test. "I had a new algorithm and wanted to test it, so we got some fixed *Xenopus* embryos from Jubin Kashef, a biologist at KIT," Moosmann said. A proof-of-concept experiment at beamline ID19 at the European Synchrotron in Grenoble, France, was a success, yielding a resolution of about a micrometer. "Kashef was impressed with the detail that could be seen deep within the intact embryo," compared to what could be seen with light microscopy, said Moosmann, so they decided to undertake the ambitious step of an *in vivo* experiment using phase-contrast microtomography.

It was a true trial-and-error scenario that demanded on-the-fly understanding of the physics and close collaboration with the beamline staff. "There are so many parameters; we just couldn't simulate them all," Moosmann said. Among them were the heat load, beam energy and bandwidth, exposure dose, pixel size, motion blur, scintillator thickness, number of tomographic projections, scheduling of embryonic development, time lapse between tomograms, and so on. It was a nerve-wracking juggling act.

"On the very last scan of our beam time, the embryo survived two hours," Moosmann said—yielding enough data for the *Nature* paper.

Optimizing the data collection was only the beginning. The image processing and data analysis were another hurdle. "I still had to work really hard to get a good-quality reconstruction of the data, especially since we were at the limits of that setup," Moosmann said. "The main work I'm doing is programming," he added. "There is so much data!"

The result is a set of stunning time-lapse videos of a frog embryo in the gastrulation stage, during which the embryo forms three layers of cells that later become tissues and organs. Among the features shown in unprecedented detail is the formation of the archenteron, or primitive digestive tube. Other images include representations of velocity and direction of the movement of individual cells.

The team achieved a resolution of about a micrometer, or about 1,000 times better than typical medical tomography. However, resolution of the technique is still limited by the coherence of the beam. With the coherence of the APS Upgrade, resolution and efficiency will substantially improve. By using a cone beam and local tomography, it should be possible to reach nanometer resolution, according to Moosmann.

It has been quite a journey for the young German. "I didn't know much about biology. I had no clue when I started this what a blastopore was!" said Moosmann, who expects to complete his Ph.D. this summer. When he isn't learning an unfamiliar discipline or programming numerical simulations or writing algorithms, Moosmann loves climbing, playing squash, and enjoying *really* good food with his girlfriend, a chemist turned professional chef. "I'm a foodie," he admits. But it's clear that his passion of passions is thinking deeply about theory; his first degree (the German diploma) was in theoretical physics, also with Ralf Hofmann. "I've always had a big interest in theoretical concepts. After my diploma I wasn't yet a theoretician; that takes a long time. Now I'm somewhere in between a theoretician and an experimentalist. I'm interested in applying the theory to what you find at the beamline."

Further Reading

Highlight:
Tal Nawy, "Embryos under the X-ray," Nature Methods, **10**, 603 (2013). DOI:10.1038/nmeth.2544

On in vivo *imaging:*
J. Moosmann, A. Ershov, V. Altapova, T. Baumbach, M. S. Prasad, C. LaBonne, X. Xiao, J. Kashef, and R. Hofmann, "X-ray phase-contrast *in vivo* microtomography probes new aspects of *Xenopus* gastrulation," Nature **497**, 374 (2013). DOI:10.1038/nature12116

J. Moosmann, A. Ershov, V. Weinhardt, T. Baumbach, M. S. Prasad, C. LaBonne, X. Xiao, J. Kashef, and R. Hofmann, "Time-lapse X-ray phase-contrast microtomography for *in vivo* imaging and analysis of morphogenesis," Nature Protocols **9**, 294 (2014). DOI:10.1038/nprot.2014.033

"*In vivo* Microtomography of Xenopus Gastrulation" (with data sets), Xenbase, October 17, 2013, http://www.xenbase.org/entry/doNewsRead.do?id=120.

On phase retrieval methods:
J. Moosmann, R. Hofmann, and T. Baumbach, "Single-distance phase retrieval at large phase shifts," Opt. Express 19, 12066 (2011).

R. Hofmann, J. Moosmann, and T. Baumbach, "Criticality in single-distance phase retrieval," Opt. Express **19**, 25881 (2011).

by Jane Marie Andrew
APS User Office.

In 2004, in conjunction with the Advanced Photon Source, the APS Users Organization established the APSUO Rosalind Franklin Young Investigator Award to recognize an important scientific or technical accomplishment by a young investigator (senior graduate student or early career Ph.D.) at, or beneficial to, the APS.

Rosalind Franklin was a brilliant chemist who played a critical but largely unacknowledged role in the discovery of the structure of DNA. While working as a research associate for John Randall at King's College in 1951, Franklin was assigned to study the unwieldy DNA molecule with x-ray crystallography—a technique only just beginning to be used for biological molecules. Her results revealed the position of the sugar-phosphate backbone and the basic helical structure of the molecule; when her x-ray photographs filtered unofficially to John Watson at Cambridge, he immediately saw their implications. Franklin went on to work on the tobacco mosaic virus and the polio virus, but her career came to an untimely end when she died of cancer in 1958 at age 37.

Previous award recipients include Alexis Templeton (2004), Wendy Mao (2006), Oleg G. Shpyrko (2008), Rafael Jaramillo (2010), and Damian C. Ekiert (2012).

2014

Users Meeting

COMPREHENSIVE PROGRAM

Monday, May 12

8:00 – 5:00	Exhibits *Bldg. 402, Gallery (lower level) and Bldg. 402, Atrium*
7:30 – 5:00	Registration *Bldg. 402, Atrium*
12:15 – 1:30	Lunch *Tents outside of lower level Gallery*

Opening Session—Morning
Bldg. 402, Lecture Hall

Session Chair:	**Robert L. Leheny (Johns Hopkins University), APSUO Steering Committee Chair**
8:30 – 8:40	Robert Leheny, APSUO Steering Committee Chair *Welcome*
8:40 – 9:00	Peter Littlewood, Director, Argonne National Laboratory *Welcome from the Laboratory*
9:00 – 9:20	Dr. Michael Knotek, Deputy Under Secretary, Office of the Under Secretary for Science and Energy, DOE *How the Eisenberger-Knotek Report Shaped a Vision for the Nation's Leadership in Synchrotron Science* (Video Presentation)
9:20 – 9:25	Robert Leheny *Introduction of Keynote Speaker*
9:25 – 10:05	Keynote Speaker Katherine Kantardjieff, Dean, College of Science and Mathematics, California State University, San Marcos *Truffles and M&Ms: How the New Digital Age is Reshaping the Future of Science*
10:05 – 10:40	Break
10:40 – 11:05	Stephen Streiffer, Interim Director, Advanced Photon Source *Update on the Advanced Photon Source*
11:05 – 11:25	Andreas Roelofs, Interim Director, Center for Nanoscale Materials *Update on the Center for Nanoscale Materials*
11:25 – 11:40	Dean Miller, Director, Electron Microscopy Center *Update on the Electron Microscopy Center*
11:40 – 12:00	George Srajer, Deputy Director, Advanced Photon Source, Upgrade Project Director *Update on the APS Upgrade*

12:00 – 12:15	Antonio Lanzirotti, University of Chicago *Update on the National User Facility Organization*
12:15 – 1:30	Lunch *Tents outside lower level Gallery*
12:30 – 1:30	Strategic Directions for the APS – Lunchtime talk *Bldg. 401, A1100 (bring you lunch)*

Parallel Facility Plenary Sessions—Afternoon

APS Session
Bldg. 402, Lecture Hall

Session Chair:	**Eric Landahl (DePaul University), APS Users Organization Steering Committee Vice Chair**
1:15 – 1:55	Keynote Speaker Prof. Bruno Scrosati (University of Rome, Italy) *Progress in Lithium-ion and Beyond Lithium-ion Batteries*
1:55 – 2:15	2014 APSUO Rosalind Franklin Young Investigator Award Julian Moosmann (Karlsruhe Institute of Technology) *Challenges in X-ray Phase-contrast* in vivo *Microtomography*
2:15 – 2:55	Przemyslaw Dera (University of Hawaii at Manoa) *Revising Earth Mantle? Mineral Physics and Advances in Extreme Synchrotron Science*
2:55 – 3:25	Break
3:25 – 4:05	Young-June Kim (University of Toronto, Canada) *Spin-orbit-driven Physics in Iridate Materials*
4:05 – 4:25	Invited Student Talk Katherine M. Davis (Purdue University) *X-ray Emission Analysis of the S-state Intermediates of the Photosystem II Protein Complex*
4:25 – 5:05	Thomas O'Halloran (Northwestern University) *Quantitative Subcellular Mapping of Metals Fluxes Reveals New Signaling Pathways in Microbial Physiology and Mammalian Development*
5:05	Adjourn
5:15	Banquet buses leave APS and Guest house at 5:15 sharp!
6:00 – 9:00	Banquet

CNM Session
Bldg. 402, Room E1100-1200

Session Chair: **Steven May (Drexel University), CNM User Executive Committee Chair**

1:30 – 2:15	Keynote Speaker Federico Capasso (Harvard University) *Flat Optics with Metasurfaces*
2:15 – 2:45	David Schuster (University of Chicago) *Hybrid Quantum Computing with Superconducting Circuits*
2:45 – 3:15	Lynn Trahey (Argonne National Laboratory) *Nanostructured Materials in Lithium-ion Batteries*
3:15 – 3:25	Steven May (Drexel University) *Update from CNM User Executive Committee*
3:25 – 3:50	Break
3:50 – 4:20	Rafael Verduzco (Rice University) *Morphology and Charge Separation in All-conjugated Block Copolymers*
4:20 – 4:50	Yongxing Hu (Argonne National Laboratory) *Synthesis and Applications of Multifunctional Nanostructures by Self-assembly*
4:50 – 5:05	Invited Student Talk Chrystian Posada (Missouri University of Science and Technology) *Development of an N-UNCD-based Field Emitter Array for a Flat-panel X-ray Source*
5:05	Adjourn
5:15	Banquet buses leave APS and Guest house at 5:15 sharp!
6:00 – 9:00	Banquet

EMC Session
Bldg. 401, Room A5000

Session Chairs:	**Philipp R. Heck (The Field Museum of Natural History) and Yasuo Ito (Northern Illinois University)**
1:30 – 2:10	Nestor Zaluzec (Electron Microscopy Center) *Prospects for Multi-modal and Multi-dimensional Imaging and Spectroscopy in the AEM*
2:10 – 2:50	John Mansfield (University of Michigan) *Microanalysis and Cultural Heritage: The Melding of Art and Microscopy*
2:50 – 3:30	Pinshane Huang (Cornell University) *Transmission Electron Microscopy of 2D Materials: A Platform for Fundamental Materials Physics Down to the Single Atom Scales*
3:30 – 3:50	Break
3:50 – 4:30	Rhonda Stroud (U.S. Naval Research Laboratory) *Nanoastronomy: A Microscopist's View of the History of the Solar System*
4:30 – 4:50	Invited Student Talk Carlos Alvarez (Northwestern University) *Nanocrystallization in Fluorochlorozirconate Glasses*
4:50 – 5:00	Wrap-up
5:00	Adjourn
5:15	Banquet buses leave APS and Guest house at 5:15 sharp!
6:00 – 9:00	Banquet

Tuesday, May 13

8:00 – 5:00	Exhibits *Bldg. 402, Gallery (lower level) and Bldg. 402, Atrium*
8:00 – 5:00	Registration *Bldg. 402, Atrium*
12:00 – 2:00	Poster setup *(shuttle buses and vans provided throughout the lunch hour to provide transportation between APS, the Guest House, and TCS Bldg. 240)*
12:15 – 1:30	Lunch *Tents outside lower level Gallery*
12:15 – 1:30	CNM Users Executive Committee Meeting *Bldg. 440, Rm. A201*
12:15 – 1:30	APS Partner User Council Meeting *Bldg. 401, Fifth Floor Gallery*

Cross-facility Thematic Workshops

8:50 – 4:50	Workshop A: Beyond Lithium Ion Batteries: Chemistry, Materials, and Characterization (see page 23) *Bldg. 402, Rm. E1100/E1200*
8:30 – 5:00	Workshop B: The APS MBA Upgrade: Introduction and Scientific Opportunities (see page 28) *Bldg. 402, Lecture Hall*
8:30 – 5:15	Workshop C: A Historical Perspective: The First 100 Years of Characterization (see page 30) *Bldg. 446, Auditorium (Advanced Protein Crystallization Facility)*
5:00 – 7:30	Poster Session and Reception *TCS, Bldg. 240 (shuttle buses provided)*

Wednesday, May 14

8:00 – 12:00	Exhibits *Bldg. 402 Gallery and Bldg. 402 Atrium*
8:00 – 12:00	Registration *Bldg. 402, Atrium*
12:00 – 1:30	Lunch *Tents outside lower level Gallery*
12:15 – 1:30	APSUO Steering Committee Meeting *Bldg. 401, Fifth Floor Gallery*

Parallel Facility-specific Workshops*

APS – Workshop 1 (full day) – Bldg. 401, Rm. A1100
Inhomogeneities and Defects in Functional Materials: Future Opportunities with the APS MBA Lattice Upgrade (see page 34)

APS – Workshop 2 (full day) – Bldg. 402, Rm. E1100
Complex Liquid Interfaces (see page 41)

APS – Workshop 3 (full day): – Bldg. 402, Rm. E1200
4D Imaging Applications in Dynamic Studies (see page 46)

APS/CNM – Workshop 4 (morning) – Bldg. 402, Lecture Hall
Imaging at Nanometer and Picosecond Scales: Ultrafast Coherent X-ray Science at a Diffraction-limited Storage Ring (see page 56)

APS – Workshop 5 (afternoon) – Bldg. 401, Rm. A5000
Frontier High-pressure Science at Synchrotron Facilities (see page 59)

APS – Workshop 7 (morning) – Bldg. 401, Rm. A5000
New Advances and Future Opportunities in Phase Contrast Imaging (see page 64)

CNM – Workshop 8 (full day) – Argonne Guest House, Conf. Rm. A
Solar Energy Capture and Conversion at the Nanoscale (see page 69)

APS – Workshop 10 (afternoon): – Bldg. 402, Lecture Hall
Materials for a Sustainable Energy Future: Advances in Structural Science (see page 73)

*Workshops 6 and 9 were withdrawn.

Thursday, May 15

CNM Short Courses

8:30 – 5:00	Course A: Brief Introduction to Scanning Electron Microscopy *Bldg. 440, Rm. A105/106*
8:30 – 12:00	Course B: Introduction to Confocal Raman Microscopy *Bldg. 440, Rm. B108*
8:30 – 12:00	Course C: Using the Hard X-ray Nanoprobe *Sector 26 Control Room*
8:30 – 12:00	Course D: High-performance Computing Techniques for Materials Modeling and Nanophotonics *Bldg. 440, Rm. A201*

Satellite Meeting

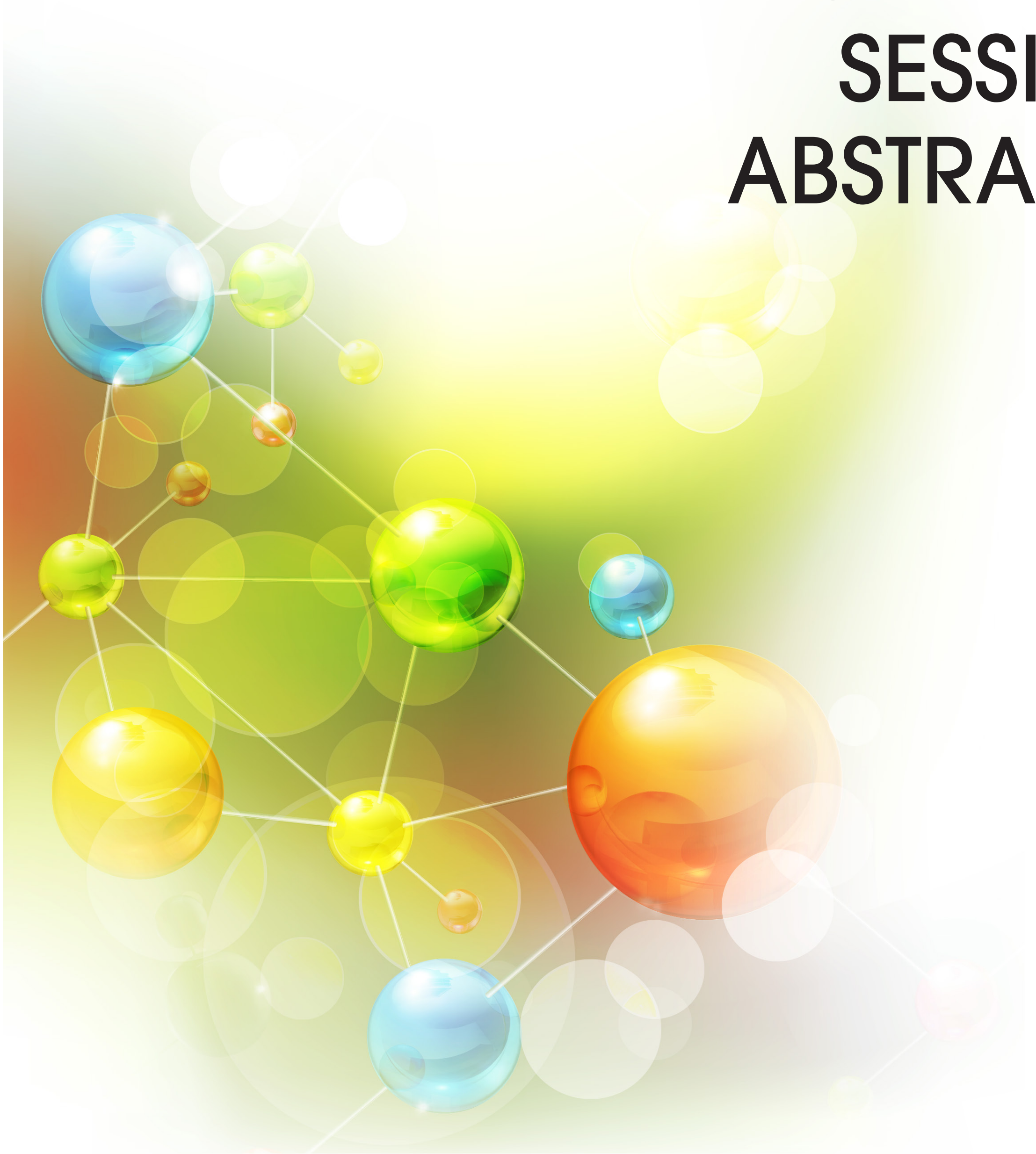
APS/APCF Symposium: Advancement of X-ray Crystallography Using Light Sources

Location: Bldg. 446, Auditorium (Advanced Protein Characterization Facility)

9:00 – 9:30	Stephen Burley (Rutgers University) *IYCr 2014: A Brief History of Macromolecular Crystallography*
9:30 – 10:00	Christine Orengo (University College London) *Protein Fold Space: How Complete Is the Map?*
10:00 – 10:30	Soichi Wakatsuki (SLAC National Accelerator Laboratory and Stanford School of Medicine) *XFELs in Integrated Structural Biology*
10:30 – 10:50	George Srajer (Advanced Photon Source, Argonne National Laboratory) *APS Upgrade: The Future Is Even Brighter*
10:50 – 11:15	Andrzej Joachimiak (Biosciences Division, Argonne National Laboratory) *The Advanced Protein Characterization Facility (APCF): Concept and Development*
11:15 – 12:15	Scientific Opening of APCF and Dedication of Auditorium
12:15	Adjourn

2014 Users Meeting

GENERAL SESSION ABSTRACTS



APS

Progress in Lithium-ion and Beyond Lithium-ion Batteries

Bruno Scrosati

Istituto Italiano di Tecnologia, Sapienza, Roma, Italy
Hemholtz-Institut Ulm, Ulm, Germany

In this talk, new approaches for improving lithium-ion and beyond-lithium-ion batteries will be reported. In particular, advances obtained by developing new chemistries for lithium-ion, lithium-sulfur, lithium-air and sodium batteries are presented. For the first class, we show that the use of optimized battery components, including anode, cathode, and electrolyte, can lead to improvements over the present technology in terms of energy density, rate capability, and cycle life.[1,2] Some recent results obtained on graphene-based lithium-ion batteries will also be reported.[3,4] The challenges in lithium-sulfur and lithium-air batteries and the approaches carried out in our laboratories to address the issues that still prevent the practical development of these systems, will be discussed. For the Li/S battery, we demonstrate the use of solid electrolytes,[5] as well as of polysulphide added liquid electrolytes,[6] as optimized media for improving the control of the lithium sulphide dissolution. We also show that a proper selection of non-lithium-metal, silicon-based anodes can lead to the development of efficient lithium-ion/sulfur systems with expected advances in their safety level.[7] For the Li/air battery, we show that glyme-type electrolytes are stable media and that graphene-oxide-supported ruthenium is a valid catalyst for the oxygen oxidation (OER) process. Also, for this battery, the use of silicon is a promising approach to develop reliable lithium-ion configurations. Finally, the work in progress on sodium ion batteries is presented. We report results obtained in collaboration with Argonne National Laboratory on an electrode configuration involving iron-based materials[8] and on other advanced Na/S battery systems.

[1] R. Verrelli, J. Hassoun, A. Farkas, T. Jacobb, and B. Scrosati, *J. Mater. Chem. A*, 2013, 1, 15329

[2] B.W. Zewde, S. Admassie, J. Zimmermann, C. Schulze Isfort, B. Scrosati, and J. Hassoun, *ChemSusChem* 2013, 6, 1400

[3] O. Vargas, l. Caballero, J. Morales, G.A. Elia, B. Scrosati, and J. Hassoun, *Phys. Chem. Chem. Phys.*, 2013, 15, 20444

[4] J. Hassoun, F. Bonaccorso, M. Agostini, M.G. Betti, C. Mariani, M. Angelucci, V. Pellegrini, R. Cingolani, S., Panero, M. Gemmi, and B. Scrosati, *submitted*.

[5] M. Agostini, Y. Ahiara, T. Yamada, B. Scrosati, and J. Hassoun, *Solid State Ionics*, 2013,244,48

[6] D-J. Lee, M. Agostini, J-W. Park, Y.-K. Sun, J. Hassoun, and B. Scrosati, *ChemSusChem* 2013, 6, 2245

[7] M. Agostini, J. Hassoun, J. Liu, M. Jeong, H. Nara, T. Momma, T. Osaka, Y.-K. Sun, and B. Scrosati, *ACS Applied Materials & Interfaces*, dx.doi.org/10.1021/am4057166

[8] S.-M. Oh, S.-T. Myung, C.-S. Yoon, J. Lu, J. Hassoun, B. Scrosati, K. Amine, and Y.-Kook Sun, *Nano Lett.* 2014, 14, 1620

APS

Challenges in X-ray Phase-contrast *In vivo* Microtomography

Julian Moosmann

ANKA, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

Four-dimensional (time-resolved) imaging techniques are important tools in biology to understand the behavior of cells during embryonic development. Here, we apply x-ray phase-contrast microtomography to capture the early development of the opaque model organism *Xenopus laevis* (African clawed frog) over the course of time and in 3D. First, formation of intensity contrast by means of free-space propagation and linear approximations to the inverse problem of phase retrieval from a single-distance measurement are explained. Then, we describe the experimental conditions for and the constraints imposed by *in vivo* imaging. Driven by high statistical noise in life-cell experiments and large phase variations in the wave front exiting entire embryos, we discuss a departure from linear models of phase retrieval by appealing to perturbation theory and to the concept of quasiparticles. Thus, we can benefit from an increase in signal to noise at large propagation distances. Next, we discuss intricacies of data acquisition and processing, tomographic reconstruction, and image analysis. Finally, we present our results from *in vivo* data of the *Xenopus* frog, were obtained at APS beamlines 2-BM and 32-ID. We were able to reveal a transient ectodermal structure not reported previously. By segmentation and subsequent volume balancing, we could answer a question regarding the formation of a central cavity (the archenteron). Using optical flow techniques, we could visualize the global cell and tissue dynamics, track single cells by time integration, and separate collective from individual cell motion by differential flow.

APS

Revising Earth Mantle? Mineral Physics and Advances in Extreme Synchrotron Science

Przemyslaw Dera

Hawaii Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, Honolulu, HI 96822

In situ high-pressure crystallography has been one of the principal analytical tools of mineral physics research and has significantly contributed to the development of this very fertile field. The concepts of comparative crystal chemistry, isostructural surfaces in the pressure-temperature-composition space, crystal chemical trends, etc., have all been conceived and developed largely based on pioneering *in situ* experiments conducted since the 1970s. Our knowledge of a majority of reversible high-pressure phase transitions and the nature of non-quenchable high-pressure phases comes almost exclusively from *in situ* crystallographic investigations.

Recent technological developments, such as novel detectors, focusing optics, and gas loading systems, as well as developments in synchrotron-based high-pressure crystallographic techniques, have opened new opportunities to explore the behavior of crystals with much smaller sizes (down to below 1 micrometer) to significantly higher pressures (well above 100 GPa), while retaining the main advantages of single-crystal techniques. With the advantage of these new developments, long-standing mysteries in mineral physics, such as the nature of ε-oxygen or $CaCO_3$-III, which puzzled researchers for decades, are starting to be resolved.

Over its long and successful history, crystallography-based mineral physics established the basic mineral behavior and transformation trends along the room-temperature isotherm, as well as the standard mantle geotherm. *In situ* experiments have been focused on studying the equilibrium, stable phases. Structural phase transitions and chemical reactions between the major stable mineral components of the Earth interior have been convincingly linked with the observed seismic velocity discontinuities. At the same time, however, geophysicists gather more and more convincing evidence of additional complexity, featuring significant local heterogeneities in composition, temperature and density. Dynamic geologic environments, such as subduction zones, can also produce conditions that are quite far from the normal mantle geotherm. All these facts fuel new motivation for exploring metastable regimes of compression and metastable transformations, which are often subtle and structurally complex, posing significant challenges for high-pressure crystallography.

This presentation will review recent results obtained at the APS high pressure beamlines, providing new insights into metastable transformations of pyroxenes, one of the dominating mineral families of the Earth mantle, with particular application to cold subducting slabs, and will present an overview of prospects for implementing new experimental methodologies and novel synchrotron instrumentation into extreme conditions science.

APS

Spin-orbit-driven Physics in Iridate Materials

Young-June Kim

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An overview of spin-orbit driven magnetism in iridate materials will be given with the emphasis on experimental investigations using resonant inelastic x-ray scattering (RIXS). Unlike the first-row transition metal compounds, orbital angular momentum is not quenched for the Ir^{4+} ions in iridates. The spin-orbit coupling instead strongly couples spin and orbital moment, giving rise to unusual spin-orbital entangled states. A plethora of exotic topological quantum phases have been predicted to exist in iridate materials, such as Kitaev quantum spin liquid on a honeycomb lattice, Weyl semimetal on a pyrochlore lattice, and high-temperature superconductivity on a square lattice. Recent advances in experimental investigation of these phases will be presented. In particular, the role of RIXS in studying collective magnetic excitations in these compounds will be discussed in detail.

APS

X-ray Emission Analysis of the S-state Intermediates of the Photosystem II Protein Complex

Katherine M. Davis[1], Brendan Sullivan[1], Lifen Yan[1] Irina Kosheleva[2], Robert W. Henning[2], Gerald T. Seidler[3], and Yulia Pushkar[1]

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Large-scale implementation of manmade systems based on artificial photosynthesis to harvest solar energy could lead to abundant chemical storage of solar power in the form of hydrogen. The process of splitting water ($2H_2O \rightarrow O_2 + 4e^- + 4H^+$) during photosynthesis requires a catalyst, the oxygen-evolving complex, or Mn_4Ca cluster, located within the trans-membrane metalloprotein complex photosystem II. Characterization of sub-millisecond reactive intermediates in this system is central to understanding the catalysis involved in water splitting. X-ray emission spectroscopy techniques provide information on the electronic structure of these states.

Following the progression of x-ray induced damage, we demonstrate the feasibility of collecting room-temperature Mn Kβ x-ray emission data on the dark stable S1 state of photosystem II in two different beam modes: continuous monochromatic beam and pulsed pink beam. The dosage/damage relation for continuous beam measurements matches preliminary room-temperature models well. Additionally, the determined damage thresholds, likely representative of other metalloproteins, are sufficient for the analysis of electron dynamics and the catalytic mechanism. Computational modeling of protein damage kinetics in monochromatic mode is extrapolated to higher dose deposition rates. The results support the theory of "detection before destruction" both for pulsed pink beam and free electron laser sources.

To learn more about the water-splitting step in particular, time-resolved Kβ emission laser pump (to advance the catalytic cycle), x-ray probe experiments were conducted in pulsed pink beam mode. For the first time, emission data are presented for the S3 → S0 transition.

Room-temperature data are shown for all S-states. Analysis of the lower states agrees well with limited published results. For the water-splitting transition, we observe immediate Mn reduction, within 50 μs from the final flash. This result likely eliminates two of the five currently supported mechanisms of water oxidation, with radical coupling mechanisms or an OH^- nucleophilic attack left as the strong candidates.

APS

Quantitative Subcellular Mapping of Metal Fluxes Reveals New Signaling Pathways in Microbial Physiology and Mammalian Development

Thomas V. O'Halloran

The Chemistry of Life Processes Institute, and the Departments of Chemistry and Molecular Biosciences, Northwestern University, Evanston, IL 60208

Bacterial, fungal, and eukaryotic cells must acquire significant quantities of several different transition metal ions for use in a multitude of essential enzymes; however, recent studies have shown that dramatic time-dependent fluctuations in intracellular metal availability control key steps in development, proliferation, differentiation, and growth. Quantitative single-cell x-ray fluorescence microscopy experiments at a variety of APS beamlines, including the new bionanoprobe, are rapidly emerging as some of the most powerful tools to define these key developmental fluctuations in a quantitative manner. We are using these approaches in conjunction with other physical methods, including confocal fluorescence and STEM microscopy, to understand how zinc fluxes control physiological decisions in the earliest stages of mammalian development, including oocyte maturation, fertilization, and early embryonic development. In parallel studies of the malaria-causing parasite, *P. falciparum*, we find that large swings in zinc content, i.e., zinc fluxes, are essential in the blood stage of infectious cycle. These zinc fluxes, which involve movement of from millions to billions of metal ions between compartments of a single cell, or between the intracellular and extracellular environment, are key regulatory events in both infectious disease and mammalian development.

CNM

Nanostructured Materials in Lithium-ion Batteries

Lynn Trahey

Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439

Electrochemical cycling of battery couples (i.e., lithium metal vs. electrode of interest in "half cell" configurations) is an important and routine method for characterizing battery performance. However, to gain deeper insight into the mechanisms underlying performance degradation, new methods aimed at nanoscale interrogation are necessary. This talk will highlight some of the research being performed on lithium-ion battery materials at the Center for Nanoscale Materials. Both advanced anodes and cathodes have been investigated with nanotomography and fluorescence at the hard X-ray Nanoprobe beamline. Recently, single particles of the Argonne-developed high-energy lithium- and manganese-rich, nickel-manganese-cobalt (LMR-NMC) oxide cathode material were imaged *ex situ* to see and quantify the changes with cycling. Drastic differences in the porosity, surface area, and transition metal ratios are evident and correlate well with changes seen via other techniques; thus, we now have a fuller picture of the failure mechanisms happening on the electrode scale. This work and the prospect of *in situ* analysis will be presented.

CNM

Morphology and Charge Separation in All-conjugated Block Copolymers

Rafael Verduzco

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Recent work has demonstrated the potential of all-conjugated block copolymers for solution-processed photovoltaic devices, with power conversion efficiencies near 3%. However, optoelectronic properties and structure-property-processing relationships are poorly understood for this class of materials. Here, we present systematic studies on the processing, morphology, and optoelectronic properties of model all-conjugated block copolymer systems. First, through systematic variations of the polymeric side-chains, we explore the role of enthalpic interactions on thin film morphology. In contrast to coil-coil block copolymers, all-conjugated block copolymers exhibit morphology dominated by crystallization rather than micro-phase segregation. In some cases, solvent annealing gives rise to liquid crystal ordering. We also show that all-conjugated block copolymers with polar side-chains have a stronger driving force for self-assembly through micro-phase segregation. Next, we explore the role of the block linker on charge

separation and performance. Recent photophysical studies have demonstrated the potential detrimental effects of low-energy charge-transfer states in donor-acceptor block copolymers. Here, we show that all-conjugated block copolymers that vary only in the linker between conjugated polymer blocks exhibit dramatically different photovoltaic performance and optoelectronic properties. This result suggests that the linker between polymer blocks is predominant in charge separation processes. Finally, we show that block copolymer additives significantly improve the performance of bulk heterojunction photovoltaics. The performance improvement is due to both morphology changes and improved charge-separation in a ternary donor-donor-acceptor system.

CNM

Synthesis and Applications of Multifunctional Nanostructures by Self-assembly

Hongxing Hu

Argonne National Laboratory, Argonne, IL 60439

Controlled assembly of nanoparticles into multifunctional structures is of great interest because of their novel properties and promising applications. However, it is difficult to synthesize desired structures (especially nanostructures with asymmetric configurations under precise control) with high purity and yield through conventional approaches. Here we demonstrate a generic strategy to prepare functional nanostructures using magnetic colloidal substrates, on which tailored surface modifications and controlled physical confinements are applied. The modularity of our approach facilitates the fabrication of multifunctional nanostructures with varying sizes, shapes, compositions, and surface chemistry. Such potential applications as active surface-enhanced Raman scattering (SERS) substrates and photo-enhanced catalysts have been demonstrated. It sheds light on the versatility of our strategy in rationally designing and synthesizing multifunctional nanostructures, especially structures with asymmetric configurations having tailored properties and functionalities.

CNM

Development of an N-UNCD–based Field Emitter Array for a Flat-panel X-ray Source

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As an alternative to conventional x-ray sources, a flat-panel transmission x-ray source is being developed. A field emitter array (FEA) prototype to be incorporated as a cold cathode in the flat-panel x-ray source was fabricated for this work. Using the particle-in-cell code OOPIC Pro, an initial FEA was designed through simulations. On the basis of the simulation results, a FEA prototype was fabricated using conventional microfabrication techniques. Planar nitrogen-incorporated ultrananocrystalline diamond (N-UNCD) films were used as field emitters. This N-UNCD–based FEA prototype was composed of nine pixels distributed in a 3 × 3 square array, with a pixel size of 225 × 225 µm and a 500-µm pitch. Each pixel was composed of a N-UNCD–based cathode and a free-standing copper grid used as extraction grid. Field emission from each pixel could be addressed individually. Emission currents per pixel on the order of 0.05–3.0 µA were obtained for extraction fields between 4 and 20 V/µm. Delamination issues were found in the microfabrication of the first FEA prototype. Consequently, a second-generation N-UNCD–based 3 × 3 FEA was designed and fabricated. In this design, the free-standing grid was replaced by a tungsten layer composed of a matrix of 11 × 11 extraction gates. Each extraction gate had a circular aperture of 6 µm in diameter. These design changes solved the delamination issues found for the first prototype. Also, for an extraction field of 7 V/µm, an emission current around 0.14 µA per pixel was measured; this value is higher than the 0.08 µA per pixel obtained from the initial FEA prototype at the same extraction field.

This work was supported by DARPA under Grant No. N66001-12-1-4237. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of DARPA. Use of the Center for Nanoscale Materials (CNM) for device fabrication was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. Special thanks to D. Rosenmann and L. Stan for their support with metal depositions at the CNM.

EMC

Microanalysis and Cultural Heritage: The Melding of Art and Microscopy

John F. Mansfield

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In museums and art galleries around the world, conservation scientists strive to restore and maintain culturally and historically important pieces of art without significantly changing their chemistry, structure, and, of course, appearance. Early attempts at conservation often resulted in damage to pieces rather than repair, and modern conservators have embraced the microstructural and microanalytical tools that are available to materials scientists to improve their techniques. In addition, the analytical tools can also be used to aid in determining the provenance of works that are of unknown origin.

Members of the University of Michigan Electron Microbeam Analysis Laboratory, in collaboration with the Detroit Institute of Arts (DIA), the Henry Ford Museum, and other individual researchers at the University of Michigan have undertaken a wide range of cultural heritage studies, a number of which will be highlighted in this presentation. Examples will include the following:

- The study of the structure and composition of pigments present in layers of paint on a 1907 white steam-powered touring car from the collection of Henry Ford, now in the Henry Ford Museum in Dearborn, Michigan. The principal goals here were to determine the original color of the car and to what extent it had been overpainted.
- A systematic chemical analysis of paint fragments extracted from a possible Monet from the collection of the DIA, to determine the true provenance of the painting.
- Chemical, morphological, and crystallographic analysis of pigments present in small fragments of paint extracted from a painting of Christ as Salvator Mundi from the DIA that shares its subject with a number of other very similar paintings, in particular a piece in a private collection in Europe that is attributed to Leonardo da Vinci. The intention here was to establish whether the painting was a 19th century copy or a work contemporary with da Vinci.

In each case samples have been examined by optical microscopy, Fourier transform infrared microspectroscopy, environmental scanning electron microscopy, and x-ray energy dispersive spectrometry (XEDS). In some instances, samples have been prepared for electron diffraction and XEDS analysis in the transmission electron microscope and scanning transmission electron microscope by focused ion beam sectioning.

EMC

Transmission Electron Microscopy of 2D Materials: A Platform for Fundamental Materials Physics Down to the Single-atom Scales

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Two-dimensional (2D) materials are ideal systems for showcasing and pushing the limits of the latest developments in atomic-resolution transmission electron microscopy (TEM). In atomically thin films, such as graphene, inherent challenges of TEM acquisition and interpretation, such as electron channeling, multiple scattering, and projection artifacts, are minimized. These characteristics mean that, more than in any other system, transmission electron microscopy and spectroscopy provide powerful, yet flexible tools to probe structure, bonding, and chemistry in 2D materials down to the single-atom scale. Moreover, applying electron microscopy to the 2D world opens up two new and promising avenues of materials research.

First, we can gain new insight into some of the oldest and most fundamental challenges in materials science. What is the atomic structure of glass? What are the atomic-scale mechanisms for bending, breaking, and melting in disordered and complex systems? Using a new 2D form of SiO_2, we show that it is possible to image atoms in disordered solids, track their motions in response to local strain, and directly visualize their phase transitions—a 80-year-old dream in glass science.

Second, we can build and probe the systems that are created when 2D materials are grown, stacked, twisted, and strained into novel structures. Our studies of graphene, hexagonal boron nitride, and molybdenum disulfide answer such questions as the following. What is the structure of grain boundaries in materials that are only a single atom thick? And how do defects, interfaces, and disorder impact the properties of materials where electrons are confined to a 2D plane? These studies are critical for exploring the advantages and potential limitations in incorporating 2D systems into applications such as flexible electronics and layered photovoltaic devices.

EMC

Nanoastronomy: A Microscopist's View of the History of the Solar System

R.M. Stroud

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Microscopy of meteorites and other extraterrestrial materials at the nanoscale is important for understanding the evolution of stars, the formation of the solar system, and the inventory of materials delivered to the early Earth that helped produce a habitable planet. A wide variety of extraterrestrial materials are available for study in the laboratory, including meteorites; interplanetary dust; and returned lunar, solar wind, comet, asteroid, and interstellar dust samples. The most primitive samples contain rare grains (at the parts per million level) that formed prior to the solar system. These grains condensed around aging stars, were ejected from their parent stars into the interstellar medium, and were incorporated into the molecular cloud that collapsed to form the solar nebula. The histories of the grains' condensation and subsequent processing are recorded, with varying fidelity, in the grains' isotopic and elemental compositions, crystal structures, and morphologies. The cosmochemical origin of an individual grain, e.g., in the solar system, in the interstellar medium, or in a supernova, red giant, or other class of star, can be determined from its isotope composition. The conditions of condensation, e.g., pressure, temperature, and gas composition, can be determined from the grain crystal structure and elemental composition. Processing signatures, such as radiation damage or shock alteration, can also be recorded in the grain structure. The most powerful constraint comes from coordinated isotope-structure studies of the same grain using a combination of ion microprobe and transmission electron microscopy methods.

EMC

Nanocrystallization in Fluorochlorozirconate Glasses

Carlos Alvarez[1,2], R. Lee Leonard[3], Julie King[3], Jacqueline Johnson[3], and Amanda Petford-Long[1,2]

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Heat-treating fluorochlorozirconate (FCZ) glasses nucleates $BaCl_2$ nanocrystals in the glass matrix, resulting in a nanocomposite glass ceramic that has optical properties suitable for use as a medical imaging plate.[1] Understanding the way in which the nanocrystal nucleation proceeds is critical to controlling the optical behavior. The nucleation and growth of nanocrystals in FCZ glass ceramics was investigated with *in situ* x-ray diffraction (XRD) heating experiments and transmission electron microscopy (TEM). These experiments showed that the nucleation of hexagonal $BaCl_2$ nanocrystals first occurs at 220°C and undergoes a phase transformation to the orthorhombic phase at 280°C. The morphology of the $BaCl_2$ crystals changed with phase from spherical to spheroidal nanocrystals. With extended heat treatments, the $BaCl_2$ nanocrystals continue to grow and coalesce to micron-sized crystals, potentially damaging their optical performance. Through the use of different heat treatments it was found that the nucleation and phase transformation processes are kinetically controlled processes.

[1] J.A. Johnson, S. Schweizer, and A.R. Lubinsky, *J. Am. Ceram. Soc.* **90**, 693–698 (2007).

2014

Users Meeting

WORKSHOP AGENDAS AND ABSTRACTS

Tuesday, May 13
Cross-facility Thematic Workshops

Workshop A
Beyond Lithium Ion Batteries: Chemistry, Materials, and Characterization

Location: Bldg. 402, Rm. E1100/E1200

Organizers: Christopher S. Johnson and Khalil Amine (for APS), Elena Shevchenko (for CNM), and J.G. Wen (for EMC) (all Argonne National Laboratory)

While lithium ion batteries are renowned in energy storage applications, there is a cap in energy density because of the limited capacity inherent to intercalation electrodes. Research interest in battery chemistries beyond lithium ion such as lithium-sulfur (Li/S), lithium-air (Li/air), multivalent (Mg, Al), and Na-ion systems are now gaining momentum. Na-ion batteries in particular are prominently developing at a rapid pace for immediate applications in energy storage.

This APS/CNM/EMC cross-facility workshop will address the discovery and spectroscopic/microscopic characterization of new active materials and electrolytes, the optimization and improvement of standard materials, and chemical/electrochemical reactions/interfaces and their mechanisms.

8:50 – 9:00	Christopher Johnson and Khalil Amine (Argonne National Laboratory) *Welcome*
9:00 –9 :40	Josh Thomas (Uppsala University) *The Search for a Safe and Cheap LIB Cathode Material for EV and Sustainable Energy Storage Applications*
9:40 – 10:20	*David G. Kwabi (Massachusetts Institute of Technology)* *The Influence of Superoxide on Decomposition Reactions in Lithium-oxygen Batteries*
10:20 – 10:50	Break
10:50 – 11:30	Jordi Cabana (University of Illinois at Chicago) *High-resolution Chemical Imaging of Phase Transformations during Electrochemical Reactions*
11:30 – 12:00	Jun Lu (Argonne National Laboratory) *A Nanostructured Cathode Architecture for Low Charge Overpotential in Lithium-Oxygen Batteries*
12:00 – 1:40	Lunch
1:40 – 2:20	Lynden Archer (Cornell University) *Nanoporous Hybrid Materials – Structure, Transport Phenomena and Applications in Secondary Lithium Metal Batteries*
2:20 – 3:00	David Prendergast (Lawrence Berkeley National Laboratory) *First-principles Understanding of Electrochemical Systems and their X-ray Absorption Spectra*
3:00 – 3:30	Break

3:30 – 4:00 Xin Li (Massachusetts Institute of Technology)
The Structures and Properties of Layered Sodium Compounds

4:00 – 4:40 Donghai Wang (Pennsylvania State University)
Understanding Chemical Interaction in Functional Carbon-Sulfur Composites as Cathode for Lithium-Sulfur Batteries

4:40 – 4:50 Christopher Johnson and Khalil Amine (Argonne National Laboratory)
Summary and Final Comments

4:50 Adjourn

WKA

The Search for a Safe and Cheap LIB Cathode Material for EV and Sustainable Energy Storage Applications

Josh Thomas

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The development of larger, more efficient, safer, cheaper, and necessarily "greener" Li-ion batteries (LIBs) for electric vehicle (EV) and stationary sustainable energy storage applications continues to present a pivotal challenge to battery researchers the world over. Progress has been slow—and we cannot be overly proud of the progress made in the last two decades. There are several underlying reasons for this, not least the availability and cost of raw materials. Several millions of tons per year of active cathode material will be required if we are to achieve the long-term goal of a worldwide transition from internal combustion engines to EVs and the wide-scale implementation of renewable energy sources.

In this context, the absence of an ideal cathode material with a sufficiently high energy density is arguably the most serious bottleneck facing us. A significant breakthrough came with the development of polyanion-based cathode materials: typically, the phosphates and silicates, e.g., $LiFePO_4$ [1] and Li_2FeSiO_4 [2]. These materials are, in principle, expected to be both cheaper and safer than the conventional LIB transition metal–oxide cathode materials, such as $LiCoO_2$ and $LiMn_2O_4$. A negative feature of these materials is, however, their generally poor electronic conductivity—a problem that is normally addressed by reducing particle size into the nanoscale range and promoting ionic transport through the use of various particle-surface coatings. Judicious doping strategies, often based on DFT model calculations, are also desirable for these essentially electronically insulating materials. Arguably the most promising cathode materials for large-scale applications involve the Li-M-SiO_4 family of silicates, typically Li_2FeSiO_4. Recent advances in our efforts to address the challenge of scaling up the synthesis of these materials—along with the exploitation of a two-electron reaction—will be described, along with examples taken from our use of solid-state, solvo-thermal, precipitation, solution, microwave, and combustion methods.

[1] A.K. Padhi et al., *J. Electrochem. Soc.*, 144, 1609 (1997).

[2] A. Nytén et al., *Electrochem. Commun.*, 7, 156 (2005).

This work has been supported by the Global Climate and Energy Project of Stanford (GCEP), the Swedish Energy Agency (STEM), VINNOVA and the Swedish Science Research Council (VR).

WKA

The Influence of Superoxide on Decomposition Reactions in Lithium-oxygen Batteries

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Non-aqueous lithium–oxygen batteries have been estimated to deliver gravimetric energy higher than that of conventional lithium-ion batteries at comparable gravimetric power. Fundamentally understanding reaction mechanisms and associated intermediates during lithium-oxygen cell operation is critical for implementing practical batteries with high reversibility and long cycle life. Understanding the specific origin of parasitic reactions in rechargeable lithium-oxygen batteries is important for designing systems with high round-trip efficiency and long cycle life. We discuss how superoxide-like species facilitate both solvent and Li_2O_2 decomposition in a dimethylsulfoxide (DMSO)-based electrolyte. The reactivities of electrochemically formed Li_2O_2, and chemically synthesized Li_2O_2 and KO_2 with DMSO are examined in detail via a variety of structural and spectroscopic measurements. We observe that in the presence of DMSO, electrochemically formed Li_2O_2 gradually decomposes into LiOH. From separate chemical studies, it is shown that the presence of superoxide ions enhances this transformation. This work highlights the importance of decoupling electrochemical reactions from chemical decomposition processes in lithium-oxygen batteries and the unique role of the superoxide phase in accelerating parasitic reactions.

WKA

High-resolution Chemical Imaging of Phase Transformations during Electrochemical Reactions

Jordi Cabana

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Battery electrodes are hierarchically complex structures formed by different components whose distribution determines the final properties. These structures must enable fast ion and electron transport. As a consequence, they are usually composite films of a redox active material with carbon and a polymer binder, cast onto a metal foil current collector. Ion transport is ensured by the presence of pores that provide points of contact between the electrolyte and the active material throughout the depth of the electrode. Because these hierarchies are assembled at scales much larger than a few nanometers, tools that can probe multiple levels of complexity are required to fully determine the parameters that control performance. Direct visualization of phase distribution within an active particle or an electrode is challenging. Because reactions at an electrode involve redox phase transformations, the state of charge can easily be correlated to composition. The field has a need for tools that can access chemical speciation at nanoscale spatial resolutions while also providing fields of view spanning up to several hundreds of microns. Because thermodynamic pathways can be controlled by the presence of electrical potential, the harvesting of a sample from a cycled battery, while providing a useful preliminary insight, can lead to misleading results because components may relax into a different state that is more stable under open circuit conditions. Therefore, measurements performed during device operation (*in operando*) are preferred.

This presentation will discuss recent advances in the development of imaging tools to follow oxidation state changes in a battery active electrode material. Data from tools with different chemical and spatial sensitivities will be discussed, with an emphasis on spectromicroscopy using synchrotron radiation.

WKA

A Nanostructured Cathode Architecture for Low Charge Overpotential in Lithium–Oxygen Batteries

Jun Lu[1], Yu Lei[2], Kah Chun Lau[3], Xiangyi Luo[1], Jianguo Wen[4], Dean Miller[4], Jeffrey W. Elam[2], Larry A. Curtiss[3], and Khalil Amine[1,5]

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The lithium–oxygen battery, of much interest due to its very high energy density, presents many challenges, one of which is a high charge overpotential that results in large inefficiencies. Here we report a cathode architecture based on nanoscale components that results in a dramatic reduction in charge overpotential (to ~0.2 V). The cathode utilizes atomic layer deposition of palladium nanoparticles on a carbon surface with an alumina coating for passivation of carbon defect sites. The low charge potential is enabled by the combination of palladium nanoparticles attached to the carbon cathode surface, a nanocrystalline form of lithium peroxide with grain boundaries, and the alumina coating (which prevents electrolyte decomposition on carbon). High-resolution transmission electron microscopy provides evidence for the nanocrystalline form of lithium peroxide. The new cathode material architecture provides the basis for future development of lithium–oxygen cathode materials that can be used to improve the efficiency and extend the cycle life of this class of batteries.

WKA

Nanoporous Hybrid Materials: Structure, Transport Phenomena, and Applications in Secondary Lithium Metal Batteries

Lynden A. Archer

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Secondary batteries capable of reliably storing and delivering large amounts of electrical energy are key components in many contemporary and emerging technologies, such as electric vehicles, autonomous aircraft, and advanced robotics. Batteries based on lithium metal anodes are understood to be among the most promising for achieving high specific electrochemical storage capacities and high cell voltages. Development of a practical rechargeable lithium metal battery (LMB) remains a challenge because of uneven lithium deposition and dendrite formation during repeated cycles of charge and discharge.

Known consequences of unstable electrodeposition in LMBs include accumulation of electrically disconnected regions of the anode (so-called “dead lithium”), thermal runaway of the cell, and internal short circuits, which limit cell lifetime and may pose serious hazards if a flammable, liquid electrolyte is used in a LMB. Lithium-ion batteries (LIBs) are designed to eliminate the most serious of these problems by hosting the lithium in a graphitic carbon substrate, but this configuration is not entirely immune from uneven lithium plating and dendrite formation. Specifically, the small potential difference separating lithium intercalation *into* graphite versus lithium plating *onto* graphite means that a too quickly charged or overcharged LIB may fail by mechanisms similar to those in an LMB.

Using a continuum transport model for electrodeposition in a structured electrolyte in which a fraction of the anions are fixed in space, the talk will show that electrodeposition at the lithium anode can be stabilized through rational design of the electrolyte and salt. Building upon these ideas, the talk will explore structure and transport in novel nanoporous hybrid electrolyte configurations designed to stabilize the lithium metal anode against dendritic electrodeposition and premature failure. Finally, the talk will explore an application of these electrolyte/separator designs to full-cell LMBs to evaluate the stability conditions deduced from theory.

WKA

The Structures and Properties of Layered Sodium Compounds

Xin Li and Gerbrand Ceder

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The layered sodium compounds with O_3 stacking, $\mathrm{NaT}\mathit{M}\mathrm{O}_2$, where TM stands for the transition metals and their mixings, form one of the most important types of the sodium battery materials. This class includes $NaMnO_2$ and $NaCoO_2$ with high capacities; $NaCrO_2$, $NaFeO_2$, and $NaNiO_2$ with high voltages; and $NaTiO_2$ and $NaVO_2$ in the anode voltage range. Mixing these compounds can sometimes combine the advantages for the battery performance, as is the case with $Na(Fe_{0.5}Co_{0.5})O_2$. However, we still lack a fundamental understanding of the mechanisms that dominate these different characteristics, which is essential for further materials design.

We study the structure and property relations of these compounds and some new compounds. In particular, we have studied a superstructure of $NaMnO_2$, $Na_{0.625}MnO_2$, by a combination of DFT, TEM, STEM-EELS, SXRD and neutron diffraction*. The superstructure includes ordering of the Mn^{4+} stripes and the Jahn-Teller active Mn^{3+} stripes; ordering of the Na and Na vacancies with some of the Na ions occupying the unusual highly distorted octahedral site; and magnetic stripe ordering at low temperature. The effect of the cooperative Jahn-Teller distortion is directly visualized on the atomic scale by STEM.

**Accepted by Nature Materials.*

WKA

Understanding Chemical Interaction in Functional Carbon–Sulfur Composites as Cathode for Lithium–Sulfur Batteries

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Li–S batteries have a high theoretical specific energy of 2600 Wh/kg, which makes them promising as a next-generation electrochemical energy storage system. Li–S systems operate by electrochemical conversion of sulfur through a multistep redox reaction, forming different lithium sulfide products. The formation of soluble polysulfide and insoluble, insulating Li_2S contributes to poor sulfur utilization and cycling efficiency, as well as capacity fading. As one important component of sulfur cathodes, the carbon host plays a key role in the electrochemical performance of lithium–sulfur batteries. The presentation will discuss development of Li–S batteries, with emphasis on applications of new carbon–sulfur composites with the capability for chemical adsorption of sulfur/polysulfides, as well as demonstration of improved performances in Li–S batteries. Fundamental reaction mechanisms in the new electrode materials and electrolyte to address the challenges will be also discussed.

Workshop B
The APS MBA Upgrade: Introduction and Scientific Opportunities

Location: Bldg. 402, Lecture Hall

Organizers: Dean Haeffner and Jonathan Lang (APS)

This workshop is intended to introduce the APS user community to the latest information on the proposed APS MBA Upgrade. There will be a mixture of talks emphasizing the vastly improved scientific capabilities (especially in the use of x-ray coherence) and talks describing various technical areas that are relevant for beamlines to fully utilize the low-emittance lattice. Subjects for the scientific capabilities talks will include coherent diffractive imaging (CDI), ptychography, and x-ray photon corellation spectroscopy. Technical subjects include accelerator design (from a user's point of view), optics, detectors, and x-ray theory.

8:30 – 8:40	Dean Haeffner (Advanced Photon Source) *Welcome*
8:40 – 9:15	Oleg Shpyrko (University of California, San Diego) *Science Opportunities with the APS MBA Upgrade*
9:15 – 9:50	Dennis Mills (Advanced Photon Source) *Synchrotron Radiation Primer*
9:50 –10:15	Break
10:15 – 10:40	Glenn Decker (Advanced Photon Source) *APS-U MBA Accelerator Description*
10:40 – 11:15	Efim Gluskin (Advanced Photon Source) *APS-U Insertion Devices*
11:15 – 11:50	Chris Jacobsen (Advanced Photon Source) *Science Opportunities with the APS MBA Upgrade*
11:50 – 1:30	Lunch
1:30 – 2:00	Stephan Hruszkewycz (Advanced Photon Source) *Science Opportunities with the APS MBA Upgrade*
2:00 – 2:30	Ruben Reininger (Advanced Photon Source) *Codes for Simulating Performance of Beamlines Using the MBA*
2:30 – 3:00	Lahsen Assoufid (Advanced Photon Source) *Beamline Optics for the APS MBA Lattice*
3:00 – 3:30	Break

3:30 – 4:00	Raymond Conley (Advanced Photon Source) *Thin Film Optics for the Future APS*
4:00 – 4:30	Robert Bradford (Advanced Photon Source) *Detectors for the APS MBA Upgrade*
4:30 – 5:00	Panel Discussion
5:00	Adjourn

Workshop C
A Historical Perspective: The First 100 Years of Crystallography

Location:	Bldg. 446, Auditorium (Advanced Protein Characterization Facility)
Organizers:	Robert Fischetti (APS), Keith Moffat (University of Chicago), and Lahsen Assoufid (APS)

In 1912 Max von Laue published a paper on the discovery of the diffraction of x-rays from crystals, for which he received the 1914 Nobel Prize in Physics. Almost immediately William Lawrence Bragg and his father William Henry Bragg began investigating the phenomenon. They derived and validated the expression that bears their name and explains the diffraction of x-rays from crystals, for which they were awarded the 1915 Nobel Prize in Physics. These seminal works ushered in an era of applying crystallography as a tool to study the structure of matter. This series of lectures by renowned crystallographers will present both a historical perspective and some recent advances in x-ray crystallography.

8:30 – 8:35	Robert Fischetti (Advanced Photon Source) *Opening Remarks*
8:35 – 8:40	Stephen Streiffer (Interim Director, Advanced Photon Source) *Welcome from the APS*
8:40 – 8:45	Peter Littlewood (Director, Argonne National Laboratory) *Welcome from the Laboratory*
8:45 – 9:15	Dennis Mills (Advanced Photon Source) *X-ray Diffraction from Crystals: In the Beginning...*
9:15 – 10:05	Philip Coppens (University of Buffalo) *The Old and the New: The Expanding Scope of Chemical Crystallography*
10:05 – 10:30	Break
10:30 – 11:20	Brian Matthews (University of Oregon) *From Bragg's Hometown to the MRC, Cambridge: Early Experiences in Protein Crystallography*
11:20 – 12:10	Stephen Harrison (Harvard University) *The Beginnings of Virus Crystallography*
12:10 – 1:30	Lunch
1:30 – 2:20	Michael Rossmann (Purdue University) *The First 58 Years of Protein Crystallography: From Haemoglobin to Mimivirus*
2:20 – 3:10	Keith Moffat (University of Chicago) *The Foundations of CHESS and Time-resolved Crystallography*

3:10 –3:35	Break
3:35 – 4:25	Erin Adams (University of Chicago) *Molecular Insights into Immune Recognition: How Crystallography Has Transformed Our Understanding of T Cell Recognition*
4:25 – 5:15	Ada Yonath (Weizmann Institute of Science) *Can Structures Lead to Better Therapeutics?*
5:15	Adjourn

WKC

The Old and the New: The Expanding Scope of Chemical Crystallography

Philip Coppens

Chemical Crystallography Laboratory, Chemistry Department, University at Buffalo, SUNY,
Buffalo, NY 142600-3000

The talk will cover developments in chemical and chemistry-related crystallography with which I have been closely or peripherally involved. They include very early attempts at the study of chemical reactions in crystals, x-ray analysis of charge density distributions, structure determination of modulated crystals using superspace, chemical reactions within supramolecular frameworks, and, more recently, time-resolved studies of microsecond-lifetime excited molecular states with both monochromatic and Laue techniques, performed first at the National Synchrotron Light Source at Brookhaven National Laboratory and in the last few years at APS. The developments were made possible because of the dramatic increase in our technical capabilities, which nobody could even envision in the early days. They have revolutionized the nature of diffraction research in the last half of the crystallographic century.

WKC

From Bragg's Hometown to the MRC, Cambridge: Early Experiences in Protein Crystallography

Brian W. Matthews

Institute of Molecular Biology, University of Oregon, Eugene, OR 97403-1229

I grew up in Adelaide, Australia, and took my Ph.D. at the University of Adelaide, where Henry Bragg had been head of the Physics Department and Lawrence Bragg had been a student. My postdoctoral experiences included three years at the Medical Research Council (MRC) Laboratory, Cambridge, in the group of David Blow, participating in the determination of the structure of alpha-chymotrypsin, one of the earliest known protein structures. The talk will focus on experiences from that era.

WKC

The Beginnings of Virus Crystallography

Stephen Harrison

Harvard Medical School, Boston, MA 02115

Virus crystallography began in the late 1930s with crystallization of tomato bushy stunt virus (TBSV) by Bawden and Pirie and recording of diffraction from TBSV crystals and tobacco mosaic virus paracrystals by Bernal and Fankuchen. In 1956, Don Caspar recorded a small-angle precession photograph from TBSV crystals that gave conclusive evidence for icosahedral symmetry. In 1965, I joined Caspar's laboratory as a doctoral student, with the goal of determining the TBSV structure. The talk will describe some stages of that project, including published concepts (by Rossmann and Blow, especially) that influenced the strategy used, collaborators (Crowther, Bricogne) and co-workers who made essential contributions, and developments in technology and computation that made virus structure determination possible.

WKC

The First 58 Years of Protein Crystallography: From Haemoglobin to Mimivirus

Michael Rossmann

Department of Biological Sciences, Purdue University, West Lafayette, IN 47907-2054

I will relate my experiences of working on the determination of the haemoglobin structure with Max Perutz, the structure determination of dehydrogenases and the discovery of the nucleotide binding fold, the first plant and the first animal structures, the structure of lipid-containing alpha and flaviviruses, bacteriophages, very large double-stranded DNA viruses and pleomorphic viruses such as mumps and measles. I will discuss the earlier development of x-ray crystallography and the more recent development of electron microscopy for the determination of biological macromolecular assemblies.

WKC

The Foundations of CHESS and Time-resolved Crystallography

Keith Moffat

Department of Biochemistry & Molecular Biology, Center for Advanced Radiation Sources, and the Institute for Biophysical Dynamics, The University of Chicago, Chicago, IL 60637

Synchrotron and storage ring x-ray sources have transformed experimental crystallography over the last 40 years. Planning for the Cornell High Energy Synchrotron Source (CHESS) began in 1976 when it became clear that the high-energy physics program would build a 6-GeV, NSF-funded, electron-positron colliding beam storage ring whose bending magnets and a six-pole electromagnetic wiggler could be splendid (but parasitic) x-ray sources. CHESS began operations in 1980, followed shortly by MacCHESS, its NIH-funded macromolecular crystallography component. Our early crystallographic studies revealed that typical polychromatic, Laue x-ray exposures on a stationary protein crystal were very short, which necessitated redevelopment of Laue diffraction and opened the possibility of ultrafast time-resolved crystallography, which had previously been only a dream.

WKC

Molecular Insights into Immune Recognition: How Crystallography Has Transformed Our Understanding of T Cell Recognition

Erin Adams

Department of Biochemistry and Molecular Biology, University of Chicago, IL 60637

The vertebrate immune system has evolved a myriad of ways to detect and destroy infection and disease in the host. This ability relies upon a network of specialized cells, some of which express rearranged receptors (antibodies and T cell receptors) that exhibit amazing diversity and are thus well-positioned to recognize novel antigens. Crystallography has been instrumental in defining the molecular rules of engagement of these receptors. I will review how three-dimensional structures have given us the ability to understand these rules and how variations on this theme are further used to differentiate between self and non-self during immune surveillance.

WKC

Can Structures Lead to Better Therapeutics?

Ada Yonath

Department of Structural Biology, Weizmann Institute, Rehovot 76100, Israel

Ribosomes, the universal cellular machines that translate the genetic code into proteins, are targeted by many antibiotics that paralyze them by binding to their functional sites. The three-dimensional structures of ribosomes from genuine pathogens and nonpathogenic models in complex with ribosomal antibiotics revealed their binding modes, inhibitory actions, and synergism pathways. They also indicated the principles of differentiation between patients and pathogens, suggested species-specific mechanisms leading to bacterial resistance, and paved ways for improvement of existing antibiotics, as well as for the design of advanced therapeutics capable of minimizing antibiotics resistance.

Wednesday, May 8
Facility-specific Workshops

APS Workshop 1
Inhomogeneities and Defects in Functional Materials: Future Opportunities with the APS MBA Lattice Upgrade

Location: Bldg. 401, Rm. A1100

Organizers: Zhonghou Cai, Ross Harder, Barry Lai, Wenjun Liu, Jörg Maser, and Stefan Vogt (APS)

Inhomogeneities and defects, both intrinsic and engineered, have significant impact on the properties of materials and devices. Engineered defects, such as dopants in semiconductor materials or well-defined strain fields, can be beneficial in tuning the properties of functional materials or the performance of electronic devices to desired parameters. At the same time, contaminants or structural defects such as dislocations can alter the structural and electronic properties of materials, leading to reduced performance and material failure.

This workshop will focus on understanding inhomogeneities and defects and their impact on the structure and properties of advanced functional materials by deploying x-ray microscopic techniques with compositional and structural sensitivity. The workshop will particularly emphasize future needs in characterization and analysis capabilities and will explore unique opportunities enabled by the APS MBA lattice upgrade. Specific topics will include defects in photovoltaic materials, nanoelectronic devices, and in complex condensed matter systems such as InGaAs semiconductors, BiFeO3 multiferroics, and strongly correlated transition metal oxides such as VO2. The workshop will encompass characterization of individual defects by x-ray fluorescence, x-ray diffraction and coherent diffraction imaging, and of mesoscale and micro-scale structural and functional impact of local defects. The common theme in all of these systems is that inhomogeneous local interactions give rise to fundamentally interesting and technologically important physical phenomena. Spatially resolved x-ray techniques provide essential structural information for understanding these fundamental materials properties.

The workshop is intended to explore unique new opportunities enabled by the APS MBA lattice upgrade, including nanometer scale x-ray probe sizes, significantly increased coherent flux, and enhanced high-energy microscopy capabilities.

8:50 – 9:15	Stefan Vogt (Advanced Photon Source, Argonne National Laboratory) *Introduction: Unique Opportunities for X-ray Microscopy with the APS MBA Upgrade*
9:15 – 9:50	Yong Chu (NSLS-II, Brookhaven National Laboratory) *Nanoscale X-ray Imaging Capabilities of the Hard X-ray Nanoprobe (HXN) at NSLS-II*
9:50 – 10:25	Tonio Buonassisi (Massachusetts Institute of Technology) *Opportunities in Photovoltaic Research with a Diffraction-limited Storage Ring*
10:25–10:50	Break
10:50 – 11:25	Michael Chabinyc (University of California, Santa Barbara) *Challenges in Energy Conversion Using Complex Blends of Organic Semiconductors*
11:25 – 12:00	Lynn Trahey (Argonne National Laboratory) *Challenges and Opportunities for Imaging Battery Materials at the APS*
12:00 – 1:30	Lunch

1:30 – 2:05	Lyle Levine (Arizona State University) *Using Microbeam Diffraction to Characterize the Impact of Thermal Cycling on the Evolution of Stresses in Cu Through-Silicon Vias*
2:05 – 2:40	Felix Hofmann (University of Oxford) *X-ray Microbeam Characterization of Atomic-scale Material Defects*
2:40 – 3:00	Bradley West (Arizona State University) *X-ray Characterization of Defects in Thin Film Solar Cells: What Can We See and Potential Moving Forward*
3:00 – 3:20	Break
3:20 – 3:55	Venkat Gopalan (Pennsylvania State University) *Accessing Metastable States with Large Property Enhancements in Functional Oxides*
3:55 – 4:30	Stephan Hruszkewycz (Argonne National Laboratory) *Coherent Bragg Diffraction Studies of Local Structure in Nano-structured Thin Films*
4:30 – 4:50	Andrew Ulvestad (University of California, San Diego) *Understanding* Operando *Battery Nanomechanics: Lensless Strain Mapping via* In situ *Coherent X-ray Diffractive Imaging*
4:50 –5:10	Wrap-up
5:10	Adjourn

WK1

Nanoscale X-ray Imaging Capabilities of the Hard X-ray Nanoprobe (HXN) at NSLS-II

Yong S. Chu, Hanfei Yan, Evgeny Nazaretski, Sebastian Kalbfleisch, Xiaojing Huang, Ken Lauer, Kazimierz Gofron, Nathalie Bouet, Juan Zhou, Li Li, Weihe Xu, Hui Yan, Brian Mullany, Dennis Kuhne, James Biancarosa, and Mathew Vescovi

National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973

The Hard X-ray Nanoprobe (HXN) Beamline at NSLS-II, to be fully constructed in summer of 2014, is expected to explore new frontiers of x-ray microscopy, virtually eliminating a long-standing resolution gap between x-ray and electron microscopy. Its initial goal is to achieve a 10-nm spatial resolution by using novel x-ray nanofocusing optics called multilayer Laue lenses (MLL), while continuing efforts will be made to enhance the resolution down to ~5 nm within the next several years. The scanning x-ray microscopy capabilities offered by the HXN x-ray microscope are ideally suited for nanoscale materials science investigations. In particular, it offers multi-modality imaging capabilities for analyzing material composition (through x-ray fluorescence), material morphology (through differential phase contrast imaging and ptychography), and crystalline material properties (through nanodiffraction and Bragg ptychography), so that comprehensive structural investigation can be completed in parallel. Moreover, the HXN microscope is designed to provide *in situ* regulation of sample temperature from ~95K to ~1200K. Recently, an 11-nm focusing has been achieved using MLLs, and the preliminary x-ray performance results demonstrated high instrument stability for the HXN x-ray microscope. The presentation will summarize the recent progress of the HXN Beamline and the early science applications.

WK1

Opportunities in Photovoltaic Research with a Diffraction-limited Storage Ring

Rafael Jaramillo[1], Jasmin Hofstetter[1], Ashley E. Morishige[1], Rupak Chakraborty[1], Sin Cheng Siah[1], Sergio Castellanos[1], Mallory Ann Jensen[1], Barry Lai[2], Jörg Maser[2], David P. Fenning[1,3], Mariana Bertoni[4], and Tonio Buonassisi[1]

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[3] Department of Nanoengineering, University of California, San Diego, La Jolla, CA 92093
[4] Arizona State University, Tempe, AZ 85281

The multi-bend achromat (MBA) lattice upgrade presents a unique opportunity for the APS to extend its scientific leadership by increasing the throughput of its microprobe capabilities by up to 10,000x. For energy materials research, including photovoltaics, the principal advantages of the MBA lattice stem from the 100x increase in brightness, particularly at hard x-ray energies. This increased brightness should directly enable the following advances:

1. Nanoscale imaging with nanosecond temporal resolution, allowing *in situ* studies of chemical reactions in real materials under real processing and operating conditions. One can envision how *in situ* studies of grain nucleation and secondary-phase precipitate formation could reveal mechanism and rate constants that inform predictive simulations of defect kinetics, thus accelerating the effort to understand and optimize novel materials for energy applications. More generally, when coupled with novel instrumentation for *in situ* studies, this increase in data acquisition rate enables real-world inquires and multidimensional data sets of complex processes in experimentally accessible times.
2. Unprecedented bulk chemical sensitivity and spatial resolution, with impurity detection limits estimated as low as sub-parts per billion, and extended defect ptychography, enabling a complete characterization of a heterogeneous material's "defect DNA."
3. Mesoscale imaging with macroscale statistics, enabled by faster data acquisition. Coupled with improvement in optics and detectors, this brightness gain will enable an orders-of-magnitude increase in the speed of data acquisition. This upgrade should enable true hierarchical imaging, involving multiple levels of data acquisition from millimeters to tens of nanometers. One can envision zooming in and out with the ease expected of modern scanning electron microscopes, but with orders of magnitude higher bulk chemical sensitivity enabled by photon-in, photon-out techniques that avoid Bremsstrahlung background (e.g., x-ray fluorescence and x-ray absorption spectroscopy). Such capabilities could prove invaluable in studying heterogeneous materials for energy applications, including thin-film solar cell devices. When integrated with combinatorial materials and device synthesis tools, such analytical capabilities could accelerate the pace of novel materials discovery.

Throughout the talk, I will highlight opportunities to increase user productivity by several orders of magnitude by adopting a user-centered design (UCD) framework for lattice and beamline upgrades. To realize a UCD process, performance metrics beyond traditional hardware-centered specifications must be considered. Our research groups' experiences suggest that the ease and speed of data acquisition and processing are more strongly linked to user productivity than hardware performance specifications, suggesting that software and hardware should be integrated during the design phase. If a UCD framework is adopted, data analysis techniques currently considered "boutique" (e.g., ptychography) have the potential to become standard, allowing even novice users to extract maximum publishable data per unit of beam time.

WK1

Challenges in Energy Conversion Using Complex Blends of Organic Semiconductors

Michael Chabinyc

Materials Department, University of California, Santa Barbara, CA 93106-5050

Organic semiconducting materials provide the ability to form low-cost, thin film electronic devices. In many applications, such as solar cells, complex blends of organic semiconductors are used to achieve high performance. In bulk heterojunction (BHJ) solar cells, an electron donating and an electron accepting material meet in bicontinuous nanoscale phase-separated network, making characterization difficult. The nature of the electronic states in these materials is determined by their microstructure and impurities making physical characterization of significant importance. The current state of understanding of the operation of organic BHJs will be presented along with opportunities for future research and outstanding needs for characterization methods.

WK1

Challenges and Opportunities for Imaging Battery Materials at the APS

Lynn Trahey

Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439

Advanced Li-ion and "beyond" Li-ion (Li-S, Li-air) battery materials can interrogated at the APS in a variety of ways. *In situ* imaging experiments are particularly sought, yet offer considerable challenges in sample preparation and beam-induced side reactions. This talk will summarize the fundamental research questions regarding Li-ion, Li-air, and Li-S research and highlight some of the *ex situ* and *in situ* imaging experiments that have been performed at the APS. Opportunities that would be afforded with better spatial resolution and faster data collection rates will be presented in the context of research on lithium-based energy storage systems.

WK1

Using Microbeam Diffraction to Characterize the Impact of Thermal Cycling on the Evolution of Stresses in Cu Through-Silicon Vias

Lyle E. Levine[1], Chukwudi Okoro[2], and Ruqing Xu[3]

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[2] Semiconductor and Dimensional Metrology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899
[3] Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

The fluctuation in temperatures during the lifetime of microelectronic devices is one of the main causes of their failure. Microbeam x-ray diffraction is being used to explore the mechanism behind these failures by measuring full stress tensors along the length of copper through-silicon via (TSV) interconnects. Two test conditions were analyzed: "as received" and 1000 thermal cycles. Thermal cycling produced drastic changes in both the diagonal and off-diagonal stress components. For example, mean hydrostatic stresses within the 1000-cycled Cu TSV were found to be eight times greater than the "as-received" Cu TSV stresses. These stress changes are the "smoking gun" that allows quantitative investigation of the root causes of critical device failures. These measurements are severely photon limited. The MBA lattice upgrade promises radical improvements that should enable *in situ* measurements of these changes during device operation.

WK1

X-ray Microbeam Characterization of Atomic-scale Material Defects

F. Hofmann[1], D. Nguyen-Manh[2], B. Abbey[3,4], C. E. Beck[5], W. Liu[6], J. K. Eliason[7], R. Xu[6], S. Dudarev[2], and Y. Liu[8]

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[4]Melbourne Centre for Nanofabrication, Melbourne, Victoria 3168, Australia
[5]Department of Materials, University of Oxford, Oxford, OX1 3PJ, UK
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[8]Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

Atomic-scale defects play a central role in determining the mechanical and functional properties of many materials systems. X-ray micro- and nanodiffraction are powerful tools for the study of these defects, making it possible to probe larger material volumes and affording excellent strain resolution. They are thus a perfect complement to electron microscopy techniques that allow nanoscale imaging of material structure. Here key results from two recent microdiffraction studies of atomic-scale defects will be presented.

The first concentrates on the structural modifications due to inert gas retention. In particular, we consider the tungsten-helium system, which is of importance for armor components in future fusion reactors. By using microbeam Laue diffraction, we characterize the lattice swelling associated with helium-retaining defects. The results are analyzed with the help of density functional theory (DFT) calculations to reveal the relative contributions of interstitial and substitution helium storage mechanisms. Our DFT calculations also suggest significant changes in elastic modulus due to retained helium. Surface acoustic wave measurements show encouraging agreement with these predictions, providing essential insight into the complex behavior of helium-retaining defects.

Secondly, we report the first microbeam Laue diffraction measurements of a single, isolated misfit dislocation in a GaAs/InGaAs/GaAs membrane.[1] The membrane geometry allows a direct comparison of the x-ray-measured dislocation structure with transmission electron micrographs, showing excellent agreement. We are further able to quantify the lattice rotations and strain fields associated with an individual dislocation. The measured profiles are consistent with those expected from anisotropic elastic calculations, constituting one of the few experimental validations of this fundamental theory.

On the basis of the experimental uncertainty in the single dislocation measurements, we estimate the conditions required for the 3D measurement of dislocation strain fields in thicker samples more representative of the material bulk. We find that smaller x-rays beams than currently available at any microbeam Laue instrument are needed. Fortunately, the optics required to produce these beams are already well within reach of present technology. The availability of nanofocused polychromatic x-ray beams would open up myriad opportunities for material defect characterization, some of which will be discussed.

[1] F. Hofmann, B. Abbey, W. Liu, R. Xu, B. F. Usher, E. A. Balaur, Y. Liu, Nat. Commun. 4, 2774 (2013)

WK1

X-ray Characterization of Defects in Thin Film Solar Cells: What Can We See and Potential Moving Forward

Bradley West

School of Electrical Computer and Energy Engineering, Arizona State University, Tempe, AZ 85287

Thin film chalcopyrite solar cells have become the subject of increasing interest for deployment of large-scale photovoltaic systems. Not only does its high absorption coefficient allow for less material use compared to traditional silicon technologies, but film deposition on flexible substrates also enables lightweight modules and roll-to-roll manufacturing, decreasing substantially the balance of systems costs. Copper indium gallium selenide—Cu(In,Ga)

Se$_2$ or CIGS—modules, in particular, achieved a breakthrough in 2011 in module shipments and installations, generating 1.2GW of demand and being forecast to reach 2.3GW in 2015, according to several market research firms. While laboratory-scale devices have reached record efficiencies of 20.8%, surpassing multicrystalline silicon, modules have yet to surpass 16% efficiency.[1] It is believed that 7% (absolute) efficiency is lost due to bandgap variability that originates from compositional changes and also from electrostatic potential variations at charged extended defects, such as grain boundaries.[2]

In this talk we will discuss our work to directly correlate electrical performance (EBIC/XBIC) to elemental distribution (XRF) at extended defects and throughout the thickness of the absorber layer. Investigations carried out in plan view and in cross section suggest that copper-poor regions at grain boundaries correlate with decreased electrical activity and that compositional variations in gallium through the thickness dominate the overall generation of the solar cell. We will also discuss the potential of the MBA lattice upgrade for future research avenues related to defect characterization in thin film photovoltaic absorbers.

[1] ZSW Press Release 18/2013.

[2] S. Siebentritt, "What limits the efficiency of chalcopyrite solar cells?" *Solar Energy Materials and Solar Cells*, **95**(6), 1471–1476 (2011).

WK1

Accessing Metastable States with Large Property Enhancements in Functional Oxides

Tom T. A. Lummen[1], N. Shukla[1], G. Stone[1], M. Holt[2], S. Kalinin[3], H. Wen[4], J. Freeland[4], D. G. Schlom[5], Suman Datta[1], and Venkatraman Gopalan[1]

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[5]Cornell University, Ithaca, NY 14850

Much of the theory and experimentation in materials science and condensed matter physics focuses on predicting ground states with interesting phenomena and functional properties, largely through searching the materials space for complex chemical compositions. However, even in well-known, simple chemistries, there are often other higher energy states that are close to these ground states and that may show significantly superior properties, and yet these phases do not appear in the thermodynamic phase diagram. An opportunity exists to exploit these phases for practical applications if these states can be meta-stabilized by stresses, fields, atomic-scale heterostructure design, surfaces, and interfaces.

In this talk, I will focus on functional oxides. In classic ferroelectrics, such as $BaTiO_3$ and $KNbO_3$ single crystals, we have discovered monoclinic phases that are not found in the theormodynamic phase diagrams but are meta-stabilized by stresses and fields naturally arising through a domain microstructure. These phases exhibit up to 4x enhancement in piezoelectric and nonlinear optical properties. Nanoscale xray diffraction imaging techniques play a key role in discovering these phases. As a second example, I will discuss transient monoclinic states that arise across a metal insulator transition in VO_2, as probed by x-ray, optical, and terahertz pump-probe techniques. These phases are stabilized, and coupled charge oscillators are demonstrated; thus, these phases could open the possibility of computing architectures based on non-Boolean logic.

WK1

Coherent Bragg Diffraction Studies of Local Structure in Nano-structured Thin Films

Stephan Hruszkewycz

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

Coherent focused x-ray Bragg diffraction techniques, such as scanning probe diffraction microscopy and Bragg ptychography, are well suited for studying structural heterogeneity in extended crystalline thin films. With relatively short acquisition times and nanoscale resolution, images of structured films can be generated with a wide variety of structural contrast mechanisms. Here, we will discuss our recent work in mapping structure and defects in InGaN/GaN multi-layer devices using nanodiffraction techniques. We will also discuss the prospects of leveraging the capabilities of an upgraded APS for coherent Bragg ptychography studies of local strain distributions in this and other wide bandgap semiconductor device materials critical to our energy future.

WK1

Understanding Operando Battery Nanomechanics: Lensless Strain Mapping via *In situ* Coherent X-ray Diffractive Imaging

Andrew Ulvestad

Department of Physics, University of California, San Diego, La Jolla, CA 92093-0319

Lithium ion batteries are the dominant power source for mobile devices, are increasingly used in hybrid and fully electric cars, and are promising candidates for both stationary and mobile storage in a smart electrical grid that incorporates intermittent renewable energy sources. To fulfill their powerful promise, electrodes with increased capacity, faster charge rates, and minimal capacity fade must be developed. Understanding the nanomechanics of lithium ions and the resulting strain distribution at the level of an individual particle is a crucial step and key to achieving these ambitious goals. Here we reveal strain evolution of a single $LiNiMnO_4$ spinel cathode particle in a coin cell battery under operando conditions during (dis)charge cycles with coherent x-ray diffractive imaging (CXDI). We show that CXDI is convenient, noninvasive, and capable of imaging the strain distribution in full three-dimensional detail. We use strain to deduce Li intercalation maps and key material properties and to map the potential energy landscape of the structural phase transition. This demonstration opens a new, powerful avenue for studying the nanomechanics of battery strain, phase transitions, and capacity fade under operando conditions at the nanoscale in a wide range of electrochemical energy storage systems.

APS Workshop 2
Complex Liquid Interfaces

Location: Bldg. 402, Rm. E1100

Organizers: Ivan Kuzmenko and Joseph Strzalka (APS)

Liquid interfaces are relevant to many of the energy and environmental challenges facing our nation. For example, extractant-mediated ion transport of radionuclides from nuclear waste occurs at the liquid-liquid interface. Related interfacial processes are of great importance for liquid membrane separation processes used for environmental cleanup of toxic metals. Heterogeneous chemistry at the liquid surface of sea salt aerosols controls many reactions, such as those believed responsible for depletion of ozone in the lower troposphere at high latitudes in the spring. Monolayers of biomolecules on the surface of aqueous solutions are used to model processes such as signaling, electron transfer, and optical responses that are important for the development of biomolecular materials with novel properties. Ionic liquid interfaces are relevant for lubrication, electrochemistry and heat transfer. More generally, liquid interfaces provide model systems to study self-assembly, interfacial orientation and forces, molecular interactions, and chemical reactivity in a wide range of materials. Although there is great interest in understanding and improving processes at complex liquid interfaces, we are only starting to probe the attendant complex and dynamic interfacial phenomena. This workshop will focus on the advantages of current and anticipated capabilities of synchrotron x-ray scattering, along with complementary neutron methods, to address these issues .

8:45 – 9:00	Welcome and Introductory Remarks
9:00 – 9:40	Bridget Murphy (Kiel University, Germany) *Liquid-Liquid Interfaces:* In situ *Electrodeposition X-ray Studies*
9:40 – 10:20	Wei Bu (University of Illinois at Chicago) *Intermediate State in Extractant-mediated Transport of Ions across Oil/Water Interfaces*
10:20 – 10:50	Break
10:50 – 11:30	David Vaknin (Ames Laboratory) *Surface-sensitive X-ray Spectroscopy and Diffraction from Liquid Interfaces*
11:30 – 12:10	Pulak Dutta (Northwestern University) *Ions at Aqueous Interfaces: Biomineralization and More*
12:10 – 1:30	Lunch
1:30 – 2:10	Tonya Kuhl (University of California, Davis) *New Insights into the Structure of Supported Lipid Membranes*
2:10 – 2:50	Sushil Satija (National Institute of Standards and Technology) *Conformational Transition of Membrane-Associated Terminally Acylated HIV-1 Nef Protein*
2:50 – 3:20	Break
3:20 – 4:00	Binhua Lin (University of Chicago) *Structural Evolution and Relaxation of Supported Nanoparticle Monolayers under Lateral Stress*

4:00 – 4:40	Masa Fukuto (Brookhaven National Laboratory) *Towards Scanning Transmission X-ray Scattering Microscopy for Liquid Surfaces*
4:40 – 5:00	Wrap-up and Concluding Remarks
5:00	Adjourn

WK2

Liquid-Liquid Interfaces: *In situ* Electrodeposition X-ray Studies

Bridget Murphy

Ruprecht Haensel Laboratory/Institut für Experimentelle und Angewandte Physik,
Christian-Albrechts-Universität zu Kiel, Germany

Paints, milk, and sun-cream—mixtures of immiscible liquids are part of our everyday life. Additionally, liquid–liquid interfaces offer exciting opportunities for material synthesis. To investigate these processes, we used x-ray scattering methods to achieve the first *in situ* atomic-scale observation of crystal formation at the fluidic interface. In studies at PETRA III of liquid mercury in contact with a salt solution containing fluorine, bromine, and lead ions, we found that a 7.6-Å–thick crystalline PbFBr layer forms at the interface. This layer acts as a template for a new epitaxial growth process assigned to the combined action of electrostatic and short-range chemical interactions.

For *in situ* studies of such interface processes with atomic resolution, we have developed the LISA liquid interface diffractometer at PETRA III beamline P08 in the last few years. This beamline allows detailed surface-scattering studies of liquid–liquid interfaces while the sample remains stationary, providing the utmost mechanical stability. Using this instrument, as well as a liquid diffractometer at the Advanced Photon Source (Argonne, USA) beamline 9-ID, we investigated the initial stages of crystal growth at model Hg–electrolyte interfaces. We used a NaF base electrolyte containing Pb^{2+} and Br^{-} ions and controlled the phase formation reaction electrochemically via a Faradaic reaction. Pb amalgamates into Hg at potentials ≤ 0.70 V, whereas at more positive potentials the amalgamated lead is released into the electrolyte. The potential-dependent variations in the structure of the Hg–electrolyte interface were studied by x-ray reflectivity and diffraction.

WK2

Intermediate State in Extractant-mediated Transport of Ions across Oil/Water Interfaces

Wei Bu[1], Hao Yu[1], Guangming Luo[1], Mrinal K. Bera[1], Binyang Hou[1], Binhua Lin[3], Mati Meron[3], Ivan Kuzmenko[4], Mark R. Antonio[2], L. Soderholm[2], and Mark L. Schlossman[1]

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[2]Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439
[3]Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637
[4]XSD, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Selective extraction of metal ions from a complex aqueous mixture into an organic phase is used to separate toxic or radioactive metals from polluted environments and nuclear waste, as well as to produce industrially relevant metals, such as rare earth ions. Selectivity arises from the choice of an extractant amphiphile, dissolved in the organic phase, which interacts preferentially with the target metal ion. The extractant-mediated process of ion transport from an aqueous to an organic phase takes place at the aqueous/organic interface; nevertheless, little is known about the molecular mechanism of this process in spite of its importance. Although state-of-the-art x-ray scattering is uniquely capable of probing molecular ordering at a liquid/liquid interface with sub-nanometer spatial resolution, utilizing this capability to investigate interfacial dynamical processes of short temporal duration remains a challenge.

We demonstrate a method to immobilize an interfacial intermediate state during the transport of rare earth erbium ions and determine its nanoscale structure with synchrotron x-ray reflectivity and fluorescence measurements. Contrary to the common expectation that monolayers of extractant amphiphiles at the aqueous/organic interface underlie the transport process, these measurements reveal a counterintuitive interfacial arrangement of extractants, namely, an inverted bilayer, whose head groups complex and shield ions from the organic phase. This novel molecular arrangement is a two-dimensional condensed phase of ion-extractant complexes that are an intermediate state in the extraction process. EXAFS measurements of the bulk organic phase indicate that ion extraction proceeds by desorption of ion-extractant complexes from the interface into the bulk phase. The aforementioned inverted bilayer was not observed in a solvent extraction system with a divalent ion (strontium) but was found in the presence of another trivalent ion (yttrium), implying that the valence of the target metal ion has a strong effect on the interfacial conformation.

WK2

Surface-sensitive X-ray Spectroscopy and Diffraction from Liquid Interfaces

David Vaknin and Wenjie Wang

Ames Laboratory and Physics and Astronomy Department, Iowa State University, Ames, IA 50011

Surface-sensitive x-ray diffraction in combination with spectroscopy techniques from organic functional films at vapor/aqueous interfaces will be reviewed. We have extended standard methods, such as XANES, to monitor ion-specific binding at charged surfaces. For instance, examination of same-charge multivalent ions to charged surfaces indicates different binding paths for La^{3+} compared to Fe^{3+}. We will also report our recent examination of Compton scattering from liquid surfaces as a possible interfacial probe.

The work at Ames Laboratory was supported by the Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC02-07CH11358.

WK2

Ions at Aqueous Interfaces: Biomineralization and More

Pulak Dutta

Department of Physics and Astronomy, Northwestern University, Evanston, IL 60208

Living organisms use biomolecular surfaces to attract dissolved ions and grow designed arrays of crystals, which are used to provide mechanical strength, sensing capabilities, etc. The nonintuitive phenomenon of charge inversion in colloidal particles has been attributed to ordering of counterions. The attachment of metal ions to surfactant molecules is the basis for a number of methods used to separate impurities from water. This talk will describe our studies of dissolved metal ions under floating monolayers and discuss the potential relevance to the above-mentioned processes.

WK2

New Insights into the Structure of Supported Lipid Membranes

Tonya L. Kuhl

Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616-5294

Over the past several decades, supported lipid membranes have been used as model systems of cellular membranes, to investigate various membrane interactions, and as platforms for development of biosensors. Precise structural characterization by x-ray reflectivity and grazing incidence diffraction at the solid-liquid interface offers a wealth of insight into membrane organization, self-assembly, and domain formation, as well as into how membranes respond to changes in their environment. In this talk, I will discuss some recent advances in our understanding of supported membranes, including (1) high-resolution details regarding the inorganic-organic interface; (2) changes in the membrane structure with fabrication method, temperature, and solution conditions; and (3) a novel, "textured" lipid phase induced by specific multivalent protein binding to membrane embedded receptors. The talk will particularly highlight the importance of x-ray scattering techniques for structural characterization of single lipid bilayers.

WK2

Conformational Transition of Membrane-associated Terminally Acylated HIV-1 Nef Protein

Sushil Satija

NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899

Although methods such as x-ray crystallography and nuclear magnetic resonance are available to determine the structure of folded proteins in solution, the precise position of folded domains relative to a membrane remains largely unknown. We use neutron and x-ray reflection methods to measure the displacement of the core domain of HIV Nef from lipid membranes upon insertion of the N-terminal myristate group. Nef is one of several HIV-1 accessory proteins and an essential factor in AIDS progression. Upon insertion of the myristate and residues from the N-terminal arm, Nef transitions from a closed-to-open conformation that positions the core domain 70 Å from the lipid head groups.

Work done in collaboration with Bulent Akgun, John Engen, Michael Kent, Hirsh Nanda, Gregory Pirrone, and Xiaomeng Shi.

WK2

Structural Evolution and Relaxation of Supported Nanoparticle Monolayers under Lateral Stress

Binhua Lin

Center for Advanced Radiation Sources and James Franck Institute, University of Chicago, Chicago, IL 60637

I will discuss the structural response to lateral compression of self-assembled nanoparticle monolayers supported on the surface of water (Langmuir monolayers). Synchrotron x-ray scattering and various microscopy techniques, such as optical microscopy, atomic force microscopy (AFM), and others, are used to characterize both the structural and morphological evolution and the dynamics of such quasi-two-dimensional (q2D) particle films under stress. For the study of the structural evolution, gold (Au) and silver (Ag) nanoparticle monolayers are used for the measurements. When they are compressed beyond the collapse point, both Au and Ag nanoparticle monolayers undergo a similar sequence of buckling to wrinkling, followed by a localized folding transition. Gold monolayers buckle into a trilayer, whereas Ag monolayers buckle into a bilayer. We propose a nanoparticle-crinkling model that describes the buckling mechanism for both types of monolayers. For the study of dynamics, iron oxide nanoparticle monolayers are used for the measurements. When the compression of the monolayer is stopped at a target surface pressure, the structural relaxation of the monolayer is indicated both by the decay of its surface pressure and by the dynamic structure autocorrelation functions derived from x-ray photon correlation spectroscopy (XPCS) measurements. An anomalous slow structural relaxation is observed at the interparticle length scale, suggesting a nondiffusive dynamics resulting from nanoparticle rearrangement under internal stress.

WK2

Towards Scanning Transmission X-ray Scattering Microscopy for Liquid Surfaces

Masafumi Fukuto

Brookhaven National Laboratory, Upton, NY 11973-5000

As the need for functionality raises the complexity of self-assembly systems, the ability to probe both local structure and heterogeneities, such as phase-coexistence and domain morphologies, will become essential to controlling self-assembly processes, including those at liquid surfaces. The traditional x-ray scattering methods for liquid surfaces, such as reflectivity and scattering at grazing incidence, are not well suited to spatially resolving lateral heterogeneities because of their large illuminated footprint. A possible alternative approach is to use scanning transmission x-ray scattering to simultaneously probe local intermolecular structures and heterogeneous domain morphologies on liquid surfaces. To test the feasibility of this approach, we recently carried out transmission SAXS/WAXS studies of Langmuir films on a water meniscus surface. Our results, together with continual improvement in the brightness and spot size of x-ray beams available at synchrotron facilities, raise the possibility of using scanning transmission x-ray scattering to characterize heterogeneous structures at liquid surfaces.

APS Workshop 3
4D Imaging Applications in Dynamic Studies

Location:	Bldg. 402, Rm. E1200
Organizers:	Xianghui Xiao (APS) and Mark Rivers (University of Chicago)

State-of-the-art synchrotron-radiation-based micro- and nano-computed tomography (SR-CT) provides high spatial and temporal resolutions, making SR-CT an ideal tool for real-time characterization of many dynamic phenomena in biology, geoscience, and materials science.

In the past few years, fast SR-CT has seen significant development at many synchrotron facilities around the world. This workshop brings together experts from the scientific user community and beamline scientists to present their recent work and to discuss prospects for *in situ*/*in vivo* phase-contrast imaging and 4D tomography.

Speakers representing battery research, materials science and engineering, geosciences, and biology will be invited to present both their current work and proposals for future directions. Beamline experts from other synchrotron facilities will also contribute.

The participants will have the opportunity to define a roadmap for joint activities and research projects that exploit state-of-the-art x-ray imaging capabilities recently made available at the APS. The roadmap will also help guide imaging activities in the APS Upgrade.

8:30 – 8:35	Welcome
8:35 – 9:05	Peter Voorhees (Northwestern University) *Dendritic Growth in 4D*
9:05 – 9:35	Nik Chawla (Arizona State University) In situ *Materials Science: Probing Microstructural Evolution of Metallic Materials in Real Time*
9:35 – 9:55	Wen-lu Zhu (University of Maryland) *Real-time Pore Structure Evolution during Olivine Carbonation*
9:55 – 10:15	Brian Patterson (Los Alamos National Laboratory) In situ *Compression Imaging of Polymer Foams Using Laboratory and Synchrotron X-ray Computed Tomography*
10:15 – 10:35	Walid Mohamed (Argonne National Laboratory) *Influence of Nano-layer Coating on Corrosion Resistance of Nuclear Cladding*
10:35 – 11:05	Coffee break
11:05 – 11:25	Wayne Chen (Purdue University) *Damage Assessment during Individual Sand Particle Failure at Different Loading Rates*
11:25 – 11:45	Yujie Wang (Shanghai Jiaotong University) *Dynamic X-ray Imaging Application for the Study of Granular Materials*
11:45 – 12:05	Jake Socha (Virginia Tech) *How Beetles Induce Tracheal Collapse: A Multi-linked System*

12:05 – 1:10	Lunch
1:10 – 1:40	Lynn Trahey (Argonne National Laboratory) *Challenges and Opportunities for Imaging Battery Materials at the APS*
1:40 – 2:00	Fikile Brushett (Massachusetts Institute of Technology) *Full-field Synchrotron Tomography of Nongraphitic Foam and Laminate Anodes for Lithium Ion Batteries*
2:00 – 2:20	Wilson Chiu (University of Connecticut) In situ *Synchrotron-based Transmission X-ray Microscopy of Solid Oxide Fuel Cell Materials*
2:20 – 2:40	Di-Jia Liu (Argonne National Laboratory) *Spatiotemporal Study of Li-O_2 Battery under Cycling Using Microfocused X-ray Diffraction and Tomographic Methods*
2:40 – 3:10	Coffee break
3:10 – 3:40	Dula Parkinson (Lawrence Berkeley National Laboratory) *Dynamic Tomography at the Advanced Light Source*
3:40 – 4:00	Marco Voltolini (Lawrence Berkeley National Laboratory) *The Emerging Role of 4D Synchrotron X-ray Microtomography in Climate and Fossil Energy Studies* (abstract)
4:00 – 4:20	Patrick La Riviere (University of Chicago) *Material Identification in Dynamic Pink Beam Studies Using Dual-layer Scintillators*
4:20 – 4:40	Stuart Stock (Northwestern University) *X-ray Imaging and Scattering during Dynamic Loading of Bone*
4:40 – 5:00	Singanallur Venkatakrishnan (Purdue University) *Model-based Iterative Reconstruction for Synchrotron X-ray Tomography*
5:00 – 5:20	Discussion
5:20	Adjourn

WK3

Dendritic Growth in 4D

J.W. Gibbs[1], A. Mohan[2], A. Shahani[1], B. Gulsoy[1], C. Bouman[2], X. Xiao[3], and P.W. Voorhees[1]

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[3] Argonne National Laboratory, Argonne, IL 60439

With the advent of high-energy x-ray sources, it is now possible to follow microstructural evolution in three dimensions and as a function of time (4D). The ability to observe and quantify the evolution of the solidification process in metals provides fundamentally new insights into this complex phase transformation. A key to acquiring 4D data is for the time between each 3D reconstruction to be small on the time scale for the evolution of the interfaces. Using a novel view sampling method and reconstruction approach, we show that it is possible to decrease the time step between 3D reconstructions by at least factor 16, with no change in the time needed to acquire a single projection or decrease in spatial resolution. By using this approach, we have investigated dendritic growth in Al-Cu. Because we measure the 3D morphology of the dendrite, it is possible to characterize the morphology of a growing dendrite using methods that are valid regardless of its shape. These parameters naturally provide characteristic length scales for interface patches with different shapes, as well as quantification of the 3D shape of a growing dendrite. Examples of the 4D results and insights into the 3D evolution of a single growing Al dendrite will be given. In addition, a multimodal x-ray imaging approach for systems in which the atomic density contrast is small and where accurate interfacial morphology is required will also be discussed. This method has also been applied to follow the evolution of solid-liquid mixtures consisting of initially faceted Si solid particles in an Al-Si liquid.

WK3

In situ Materials Science: Probing Microstructural Evolution of Metallic Materials in Real Time

N. Chawla

School of Materials, Arizona State University, Tempe, AZ 85287-6106

The field of materials science and engineering (MSE) is based on the fundamental principle that microstructure controls properties. Traditionally, the study of material structure has been limited by sectioning and postmortem observations. This approach is often inaccurate or inadequate for solving many fundamental problems. It is also often laborious and time-consuming. Advances in experimental methods, analytical techniques, and computational approaches have now enabled the development of *in situ* techniques that allow us to probe the behavior of materials in real time. The study of microstructures under an external stimulus (e.g., stress, temperature, environment) as a function of time is particularly exciting. Examples include an understanding of time-dependent deformation structures, phase transformations, compositional evolution, magnetic domains, etc.

X-ray synchrotron tomography provides a wonderful means of characterizing damage in materials nondestructively. In this talk, I will describe experiments and simulations in which we address the critical link between microstructure and deformation behavior of metallic materials by using a three-dimensional (3D) virtual microstructure obtained by x-ray synchrotron tomography. The approach involves capturing the microstructure by novel and sophisticated *in situ* tensile testing in an x-ray synchrotron, followed by x-ray tomography and image analysis and 3D reconstruction of the microstructure. Case studies on fundamental deformation phenomena, such as cyclic fatigue and stress corrosion cracking in aluminum alloys and metallic composites, will be presented and discussed.

WK3

Real-time Pore Structure Evolution During Olivine Carbonation

Wen-lu Zhu[1], Florian Fusseis[2], Harrison Lisabeth[1], and Xianghui Xiao[3]

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[3]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

In situ carbonation of mafic or ultramafic rocks has been proposed as a promising method for long-term, secure sequestration of carbon dioxide. To assess its full potential, as well as its risks, as an economically viable method for carbon capture and storage, rigorous estimates of the mineral carbonation rate in olivine are needed. Existing chemical kinetics data indicate that many factors, such as pH, pressure, temperature, ionic activity, reaction surface area, etc., affect the mineralization rate. In practice, the flux and fluid distribution through pore space may control the overall rate and extent of carbonation. Therefore, mechanical constraints on fluid-rock interaction must be taken into account. In this study, we constructed a state-of-the-art pressure vessel that is transparent to x-rays. Sodium bicarbonate ($NaHCO_3$) solution was injected into porous olivine aggregates, and olivine carbonation at reservoir pressure and temperature conditions was investigated. Microtomography experiments were conducted at 2-BM at the Advanced Photon Source. At a constant confining pressure of 12 MPa and a temperature of 200°C, the real time pore structure evolution of olivine aggregates undergoing mineral carbonation was captured at 30-minute intervals for ~150 hours (5 days). The microtomography data show a substantial increase in surface roughness. At 200°C, dissolution is *ubiquitous*. Crystal growth became visible after 48 hours. Both dissolution and precipitation contribute to the increase of surface roughness. In general, mineral carbonation of olivine results in a net volume increase. The observed disintegration of the sinter olivine aggregates at a later stage of pore evolution could result from reaction-driven cracking. Dissolution and stress corrosion due to subcritical crack growth are other contributing factors. The *in situ* and real-time microtomography investigation of the evolution of pore structure provides a powerful new approach in studying mineral carbonation.

WK3

In situ Compression Imaging of Polymer Foams Using Laboratory and Synchrotron X-ray Computed Tomography

Brian M. Patterson[1], Nikhilesh Chawla[2], Jason Williams[2], Xianghui Xiao[3], Mathew Robinson[4], Zachary Smith[1], Kevin Henderson[1], and Nikolaus Cordes[1]

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Understanding the effects of material composition, geometry, aging, and processing upon the overall material performance requires a detailed understanding of their initial morphology and how the morphology changes under external stimuli. Laboratory-based x-ray CT systems can image polymer foams as they are compressed, in an interrupted *in situ* modality. From these images, we can measure and compare the initial structure and how a foam structure responds to an applied load. Morphological measures such as void size, shape, distribution, percent void volume, and even the Poisson ratio can be tracked as a result of age degradation, compression set, or radiation damage. However, because of the lengthy (1-2 hours) image acquisition time, the initial response of the material to the applied load is not captured.

Third-generation synchrotron light sources, such as the APS, afford materials researchers unprecedented x-ray flux to help unravel these complex materials science challenges. By coupling this high flux with a high-speed camera, we can obtain x-ray radiographs every millisecond and collect tomographic data in ~1 second. Adding a sample compression cell makes it possible to study the dynamic *in situ* deformation of polymeric foams at a 10^{-2} strain rate. In this study, synchrotron x-ray tomography at beamline 2-BM was used to capture the morphology changes in polymeric foam materials during dynamic compression that cannot be captured in the laboratory.

WK3

Influence of Nanolayer Coating on Corrosion Resistance of Nuclear Cladding Materials

Walid Mohamed, Di Yun, Kun Mo, Mike Pellin, and A.M. Yacout

Nuclear Engineering Division, Argonne National Laboratory, Argonne, IL 60439

After the Fukushima nuclear accident, enhancing the corrosion resistance of nuclear cladding materials, such as Zr-2, Zr-4 and Zirlo, became a more urgent challenge than ever before. Different approaches have been attempted, among which the creation of a diffusion barrier of oxygen through the cladding materials is of high interest. In this study, nano-layer, ceramic thin film deposited via atomic layer deposition (ALD) is evaluated as a proposed diffusion barrier to enhance corrosion resistance of typical nuclear cladding materials. The development of an oxidation layer on coated Zirlo was investigated *in situ* utilizing the tomography capability available at beamline 2-BM at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL); the influence of the coating on the corrosion resistance of Zirlo will be presented.

WK3

Damage Assessment During Individual Sand Particle Failure at Different Loading Rates

Wayne Chen

**School of Aeronautics and Astronautics and School of Mechanical Engineering, Purdue University,
West Lafayette, IN 47907-2045**

Fracture of individual sand particles under compressive loading at different loading rates was investigated by using x-ray imaging at APS. High-speed x-ray phase contrast imaging (PCI) at beamline 32-ID-B was utilized to study the damage mechanisms in dry and wet sand particles under dynamic compressive loading. A modified Kolsky bar setup was used to apply controlled dynamic compression on two contacting sand particles. Pulverization was observed as the sole mode of failure for dry sand particles. Under wet conditions, one of the particles was observed to break into large sub-particles that pulverized upon further loading. Three-dimensional x-ray tomography at beamline 2-BM-B was used to assess the failure of sand particles under static compressive loading. Breaking into large sub-particles followed by pulverization was observed under static compressive loading. The order of pulverization for the particles was observed to be random in all experiments. The x-ray imaging capabilities from low to high speeds available at APS provide the necessary tools to understand the failure process of sand particles over a wide range of loading rates.

WK3

Dynamic X-ray Imaging Application for the Study of Granular Materials

Yujie Wang

Physics Department, Shanghai Jiao Tong University, P.R. China

It is important to understand both static and dynamic properties of a granular system. Studying granular systems with x-ray imaging technology, including x-ray computed tomography (CT) and ultrafast x-ray projection imaging, has great advantages. Because of the penetrating properties of x-rays, internal structures of a granular system can be obtained. We used x-ray CT technology to study packing problems with various granular systems, such as monodispersed hard spheres, wet spheres, rods, and polydispersed foams. At the same time, ultrafast x-ray phase contrast imaging technology based on synchrotron radiation provides a projective realization of evolving systems and is thus one of the few experimental methods that can probe dynamic properties of granular systems. Using the above technology, we implement dynamic projective tracking of a 3D granular gas, granular pipe flow, and a granular system under shaking. With these dynamic systems, we studied energy partition problems in granular systems and analyzed such concepts as effective temperatures, dynamic heterogeneity, and self-organized criticality in the granular jamming transition. This experimental work will contribute to revealing some important properties of granular systems.

[1] X.D. Zhang, C.J. Xia, X.H. Xiao, and Y.J. Wang, *Chin. Phys. B* **23**, 044501 (2014).

[2] C.J. Xia, K. Zhu, Y.X. Cao, H.H. Sun, B.Q. Kou, and Y.J. Wang, "X-ray tomography study of the random packing structure of ellipsoids," *Soft Matter* **10**, 990 (2014).

WK3

How Beetles Induce Tracheal Collapse: A Multi-linked System

Jake Socha and Hodjat Pendar

Department of Engineering Science and Mechanics, Virginia Tech, Blacksburg, VA 24061

Some insects are known to augment their respiration via rhythmic tracheal compression, in which parts of the tracheal system collapse and reinflate on a second time scale. A significant decrease in the volume of tracheal tubes during compression transports air out of the body and likely mixes air within the tracheal system, thereby enhancing gas exchange. Multiple mechanisms have been suggested to explain tracheal collapse, including collapse by contraction of surrounding muscles, abdominal or thoracic pumping, auto-ventilation by leg or wing movement, and hemolymph transport. None of these hypotheses have been investigated in detail, and the mechanism of tube collapse in most insect species remains unknown. To determine the mechanism of collapse in beetles, we have

been probing multiple physiological processes that are correlated with tube collapse to explore possible mechanical linkages in the system. We use synchronous measurements of body movement, pressure, and CO_2 to quantify internal and external processes while tracheae collapse. These measurements have revealed the relationship of collapse with abdominal pumping, hemolymph pressure, gut movement, and CO_2 release. Simultaneous pressure pulses of differing magnitude throughout the body suggest that the abdominal pump helps to produce pressure, which is mediated by gut movements and regional compartmentalization. This research demonstrates how the use of multiple coordinated processes can result in collapse of tracheal tubes and the augmentation of gas exchange.

This work has largely been funded by the NSF (0938047) and the Institute for Critical Technology and Applied Science (Virginia Tech).

WK3

Challenges and Opportunities for Imaging Battery Materials at the APS

Lynn Trahey

Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439

Advanced Li-ion and "beyond" Li-ion (Li-S, Li-air) battery materials can interrogated at the APS in a variety of ways. *In situ* imaging experiments are particularly sought, yet offer considerable challenges in sample preparation and beam-induced side reactions. This talk will summarize the fundamental research questions regarding Li-ion, Li-air, and Li-S research and highlight some of the *ex situ* and *in situ* imaging experiments that have been performed at the APS. Opportunities that would be afforded with better spatial resolution and faster data collection rates will be presented in the context of research on lithium-based energy storage systems.

WK3

Full-field Synchrotron Tomography of Nongraphitic Foam and Laminate Anodes for Lithium-ion Batteries

Fikile R. Brushett[1], Lynn Trahey[2], Xianghui Xiao[3], and John T. Vaughey[2]

[1]Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139
[2]Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439
[3]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Translating the success of rechargeable lithium-ion batteries (LIBs) in the consumer electronics market to the transportation market requires doubling the battery energy density without increasing cost or sacrificing safety. To that end, a key challenge is replacing the graphitic carbon negative electrode, which has a limited capacity (372 mAh/g), with metals, metalloids, or intermetallic compounds that offer significantly higher capacities (>1000 mAh/g) while operating at similar potentials. Despite their advantages, these materials have yet to supplant graphitic carbon as the dominant commercial material because of the mechanical and chemical problems that accompany lithium insertion and removal. Gaining a better understanding of electrode microstructure and, more specifically, the electrically and chemically driven changes to that structure over the electrode's lifetime is critical to designing next-generation energy storage systems.

Nondestructive methods that allow researchers to gather high-resolution quantitative information on a material's physical properties from inside a working device are increasingly in demand from the scientific community. Synchrotron-based micro-computed x-ray tomography (microCT) enables the fast full-field interrogation of complex materials with high spatial resolution (1-10 μm) and over large geometric volumes (on the order of 1 mm^3). Moreover, variations in x-ray absorption enable identification of different phases and elements and their distribution throughout the sample. To date, research efforts have focused on characterizing present day LIB materials; microCT is perhaps even better suited for investigating high-capacity metal and metalloid active materials because, compared to graphite, these materials have high x-ray absorption and undergo large volume changes during charge and discharge. Here we employ synchrotron-based microCT to characterize the physical changes in next-generation LIB anode materials and architectures. In this work, Cu_6Sn_5 coated on a three-dimensional copper foam was used to model a high-power electrode, while laminated silicon particles were used to model a high-energy electrode. The electrodes were illuminated *in situ* and *ex situ*, respectively, at beamline 2-BM of the Advanced Photon Source. Evolutions in electrode porosity and volume-specific surface area were investigated and showed large differences depending on the electrode architecture. The determination of these physical parameters should provide guidance for electrode-level modeling and simulation as well as for material design. This work represents one of the first reports of full-field synchrotron tomography on high-capacity battery materials under operating conditions.

WK3

In situ Synchrotron-based Transmission X-ray Microscopy of Solid Oxide Fuel Cell Materials

Wilson K. S. Chiu

Department of Mechanical Engineering, University of Connecticut, Storrs, CT 06269-3139

Substantial losses can arise in the solid oxide fuel cell (SOFC) because of degradation during operation. This presentation will focus on the development of *in situ* x-ray imaging and spectroscopy techniques that will allow the direct observation of the SOFC under operational conditions to provide further fundamental understanding of degradation. Progress on *in situ* x-ray imaging of 3D microstructural and chemical changes in SOFC materials using synchrotron-based transmission x-ray microscopy will be presented, with a long-term goal to develop hard x-ray *in situ* techniques to further the understanding of SOFCs and enhance their long-term performance and reliability to enable SOFCs as a viable technology for efficient and sustainable energy conversion.

This work is supported by the National Science Foundation (Award CBET-1134052) and an Energy Frontier Research Center on Science Based Nano-Structure Design and Synthesis of Heterogeneous Functional Materials for Energy Systems (HeteroFoaM Center) funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (Award DE-SC000106).

WK3

Spatiotemporal Study of Li–O_2 Battery under Cycling using Microfocused X-ray Diffraction and Tomographic Methods

Jiang-Lan Shui[1], John S. Okasinski[2], Peter Kenesei[2], Jonathan D. Almer[2], and Di-Jia Liu[1]

[1]Chemical Sciences and Engineering Division and [2]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Li-O_2 batteries have generated a great deal of interest for vehicular applications because of their high theoretical energy storage capacity. Many studies have been carried out in an attempt to understand the fundamental chemical processes in Li-O_2 batteries. The reports so far have been segmented into investigations of the individual regions of the battery—cathode, anode and separator—mostly at the post-mortem state because of the limitations of the characterization methods used.

We have adopted a holistic approach in studying electrochemical processes and mechanisms of the Li-O_2 battery using operando methods. In particular, we introduced the use of microfocused synchrotron x-ray diffraction (μ-XRD) and tomographic techniques for spatiotemporal study of the phase and structural changes in Li-O_2 batteries. These tools offered some unique capabilities to probe battery properties under actual discharge-charging conditions. In this presentation, we will discuss our recent operando investigation of Li-O_2 batteries under cycling condition in real time. The cells were fabricated on the basis of the most representative design and materials at present. We were able not only to reveal individually the changes at anode, cathode, and separator but also to provide a holistic view of the regional chemical processes and their interdependence to the overall battery performance during the multiple discharge-charge cycles.

The work performed at Argonne is supported by DOE under Contract No. DE-AC02-06CH11357 by UChicago Argonne, LLC.

WK3

Dynamic Tomography at the Advanced Light Source

Dilworth Y. Parkinson and Alastair A. MacDowell

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Berkeley, CA 94720

The Hard X-ray Tomography Beamline at the Advanced Light Source (Beamline 8.3.2) has worked closely with a number of users over the past years to develop dynamic tomography capabilities. This talk will review a selection of these experiments.

WK3

The Emerging Role of 4D Synchrotron X-ray Microtomography in Climate and Fossil Energy Studies

Marco Voltolini[1], Jonathan Ajo-Franklin[1], Shan Dou[1,3], Jill Geller[1], Abdelmoula Haboub[2], Alastair MacDowell[2], Dilworth Parkinson[2], and Lin Zuo[4]

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X-ray microtomography has been a valuable tool for the scientists involved in fossil energy research during the last decade. The characterization of reservoir rock microstructures and the ability to see the distribution of oil and brine in them has already shown its potential. In the last few years, a significant effort has been made to upgrade such studies from many points of view. Now it is no longer a scan-and-visualize process for a given sample: New, sophisticated software tools have been developed to *quantify* the morphological features and/or to model the behavior of the sample under certain conditions (see especially advances in "digital rock physics"). On the more "instrumental" end, where imaging synchrotron beamlines play a leading role, new tools have been developed to make the collection of datasets, faster, of better quality, higher resolution, etc. In the context of these new improvements, the addition of a fourth dimension in XR-microtomography experiments has been possible with the development of proper experimental setups, such as sample chambers used to maintain the sample at non-room conditions, modifying temperature or pressure, etc. This additional dimension is of course of paramount importance in studies related to climate change and fossil energy, since the systems studied are not static in nature, but dynamic. The ability to follow in real time the dynamics of these systems opens new opportunities for the Earth scientist to obtain a better knowledge of the key features that rule those processes. This better comprehension can allow the development of new models to describe the phenomena or the improvement of some processes from an industrial point of view.

The presentation will show a selection of experiments concerning the topics of climate change and fossil energy done by the authors. Each experiment will show a different fourth dimension and its contribution to obtain new knowledge about the processes involved. All the experiments have been carried out at the 8.3.2 beamline at the Advanced Light Source at the Lawrence Berkeley National Laboratory.

– *High temperature: pyrolysis of an oil shale.* This experiment shows the evolution of an oil shale during heating. The evolution of the microstructure and the variation of attenuation values can provide useful information to better understand the phenomenon and the potential of oil shale recovery.

– *Low temperature: freezing brine and sand*. Permafrost evolution is a crucial process in the context of greenhouse gas emission in the atmosphere. The classical models describing the nucleation and growth of ice do not work properly, especially when modeling the propagation of ultrasonic waves in a frozen sand pack. We have imaged the evolution of a similar system and found that the microstructure of the frozen pack is much more complex than expected, partially invalidating the classical models.

– *High pressure: $scCO_2$ geological sequestration.* In the field of CO_2 capture and storage, geological sequestration is the process of choice to eventually store the largest amount of CO_2. With a cell capable of flow, at reservoir P/T conditions, we have studied the effect of pressure variation in the behavior of the trapped CO_2 and developed a model to predict the invasion of supercritical CO_2 in reservoir rocks. Examples of drainage-exsolution-imbibition cycles in the Domengine sandstone will be shown.

–*Uniaxial stress: closing a fracture in a shale filled with proppant.* Hydraulic fracturing in gas shales is becoming more and more important for deriving fuel from deposits that could not be exploited economically prior to the application of this technique. While hydraulic fracturing is applied successfully in the field, the basics of its mechanisms are still poorly understood and there are opportunities to further optimize the process. We show the development of a fracture, filled with proppant, in a Mancos Shale sample subject to unconfined uniaxial stress and the knowledge acquired from the experiment (especially prediction of fractures and the role of the proppant in crack formation).

– *Chemical dissolution: limestone dissolution subject to a CO_2-saturated solution flow.* The pH of CO_2-saturated aqueous solutions is low enough to severely attack limestones. We have imaged a Bedford limestone sample while subject to dissolution (in flow conditions) and obtained a sequence of datasets at different dissolution stages. From these data we have been able to describe the dissolution mechanisms involved in the process and to model the variation of entry pressure due to the evolution of the pore space.

The new opportunities to study dynamic systems in 3D opened by the recent evolution of synchrotron beamlines are still awaiting full exploitation with the improvement from both the instrumental side (higher x-ray fluxes available with new storage rings and insertion devices, faster detectors, new sample chambers, etc.) and software side (models taking advantage of supercomputing units, new reconstruction algorithms, etc.), and the results obtained so far highlight the importance of following this path.

WK3

Material Identification in Dynamic Pink-beam Studies Using Dual-layer Scintillators

Patrick La Riviere

Department of Radiology, University of Chicago, Chicago, IL 60637

We are exploring the use of dual-layer, dual-color scintillators that would allow some measure of x-ray spectral sensitivity when performing rapid imaging using pink- or white-beam configurations. The spectral sensitivity permits material identification and even quantification in radiographic or tomographic acquisitions. The key idea is to layer two scintillators that emit different colors of optical light. The light can be detected with a color camera or, preferably, by using a dichroic mirror to create two separate optical channels. When such a multilayer detector is illuminated by a polychromatic spectrum, the first layer will preferentially stop lower energy x-rays and the deeper layers, higher energy x-rays, leading to limited but perfectly registered spectral resolution. We will present some of our preliminary experimental results obtained using a custom multilayer scintillating detector in conjunction with a color CCD camera. We found that our dual-layer detector provided a significant amount of spectral separation and allowed identification of different materials.

WK3

X-ray Imaging and Scattering during Dynamic Loading of Bone

Stuart R. Stock

Feinberg School of Medicine, Northwestern University, Chicago, IL 60611

Bone is a complex composite of collagen fibrils reinforced with mineral nanoplatelets of carbonated hydroxyapatite (cAp). The tissue is hierarchically structured and has a remarkable combination of toughness and strength. Combining imaging and internal strain measurements on the same sample provides a powerful approach for understanding the interactions of the different spatial scales in bone. Although there have been many x-ray imaging and scattering studies of bone, particularly trabecular bone, under load, very little has been done with *in vivo* or *in situ* x-ray imaging while bone is loaded at physiological strain rates. This talk outlines why such imaging will provide new insights into bone quality that cannot be gained under static conditions, what might be required to perform such dynamic studies, and challenges (including radiation damage to specimens) that must be overcome.

WK3

Model-based Iterative Reconstruction for Synchrotron X-ray Tomography

Singanallur Venkatakrishnan

College of Engineering, Purdue University, West Lafayette, IN 47907

Characterizing materials at the micro- or nanometer scale can have unprecedented impact on areas ranging from energy to medicine. Synchrotron x-ray tomography is widely used to characterize materials in 3D as well as to study the temporal evolution of 3D volumes. Traditional algorithms used for tomography require large amounts of data at a reasonably high signal-to-noise ratio for accurate reconstructions. Furthermore, many of the data sets have outliers that are due to properties of the sample or non-idealities in the detector; these outliers result in strong artifacts when traditional methods are used. In this talk, I will present a model-based iterative reconstruction (MBIR) approach for tomographic modalities relevant to scientific imaging. MBIR involves combining a statistical model for data formation with a statistical model for the image to formulate the reconstruction as an estimation problem. First, I will introduce an MBIR method that can model the non-idealities in the synchrotron x-ray imaging system. This method yields 3D reconstructions that have significantly fewer streaks and ring artifacts than those produced with traditional approaches. Furthermore, the MBIR method can account for missing sets of views in the data set (the "missing wedge problem"). Next, I will present an MBIR algorithm for *in situ* synchrotron x-ray (4D) tomography that can achieve significantly higher temporal resolution that the traditional approaches. The method combines a novel data-collection strategy with an MBIR technique to attain reconstructions with high temporal resolution.

APS/CNM Workshop 4
Imaging at Nanometer and Picosecond Scales: Ultrafast Coherent X-ray Science at a Diffraction-limited Storage Ring

Location: Bldg. 402, Lecture Hall

Organizers: Haidan Wen (APS), Ross Harder (APS), Alec Sandy (APS), and Ian McNulty (CNM)

The unprecedented increase of coherent x-ray flux at diffraction-limited storage rings presents great opportunities for mesoscale science at the intersection of nanometer length and picosecond time scales. We will bring together experts and potential users to explore the frontier of ultrafast coherent x-ray science and to develop a roadmap that will exploit the synergy of time-resolved and coherent x-ray capabilities of the proposed APS upgrade. This workshop will focus on new science enabled by combining stable, tunable, coherent x-ray probes for nanoscale x-ray imaging and correlation spectroscopy, together with advanced ultrafast optical, electrical, and mechanical excitation. Instrumentation and data analysis, driven by scientific needs, will also be discussed. The goal of this workshop is to leverage Argonne's strengths in coherent x-ray imaging and time-resolved x-ray science to cultivate a vibrant community that embraces the APS Upgrade for transformational science.

8:45 – 9:00	Linda Young (APS, Argonne National Laboratory) *Welcome & Introductory Remarks*

Session I — Chair: Brian Stephenson

9:00 – 9:30	Peter Abbamonte (University of Illinois at Urbana-Champaign) *Attosecond Imaging of Collective Dynamics Using Standing Wave Inelastic X-ray Scattering with a Transversely Coherent Source*
9:30 – 10:00	Paul Evans (University of Wisconsin–Madison) *Opportunities for Coherent X-ray Scattering in the Dynamics of Electronic Materials*
10:00 – 10:30	David Johnson (University of Oregon) *Controlling Reactions at Solid-Solid Interfaces: Access to New Materials with Designed Nanoarchitecture*
10:30 – 10:50	Break

Session II — Chair: Peter Abbamonte

10:50 – 11:20	Jesse Clark (SLAC National Accelerator Laboratory) *Coherent Diffraction Imaging of Dynamics at the Nano- and Mesocale*
11:20 – 11:50	Mark Sutton (McGill University) *New Opportunities for XPCS with the MBA Lattice*

Session III — Chairs: Haidan Wen and Ross Harder

11:50 – 12:10	Discussion and conclusion
12:10	Lunch

WK4

Opportunities for Coherent X-ray Scattering in the Dynamics of Electronic Materials

Paul G. Evans

Materials Science and Engineering, University of Wisconsin–Madison, Madison, WI 53706

Coherent x-ray scattering techniques can be combined with time-resolved and ultrafast x-ray scattering techniques to yield new insight into the fundamental physical phenomena underpinning the properties of emerging electronic materials. We will discuss briefly recent progress in separate coherent scattering and ultrafast x-ray diffraction studies of complex oxide ferroelectric and multiferroic materials. Coherence techniques are particularly useful in probing the arrangement and dynamics of ferroelectric/dielectric superlattices exhibiting self-organized nanoscale domain patterns. Coherent scattering can be combined with pump-probe techniques to study the evolution of the domain pattern in applied electric fields. We discuss the statistical interpretation of initial pump-probe coherent scattering experiments and describe opportunities for improved studies at future light sources with a high degree of transverse x-ray coherence.

WK4

Controlling Reactions at Solid–Solid Interfaces: Access to New Materials with Designed Nanoarchitecture

David C. Johnson

Materials Science Institute and Department of Chemistry, University of Oregon, Eugene, OR 97403-1253

We have shown that by controlling the composition of an amorphous intermediate, obtained via several different approaches, it is possible to control nucleation to obtain new metastable binary and ternary compounds. A significant challenge is determining the structure of these new materials without the ability to prepare a single crystal. By introducing more than one diffusion distance, one can control local composition on an angstrom length scale; we have used this approach to control solid-state reaction pathways, leading to the self-assembly of new nanostructured compounds consisting of two or more compounds with different crystal structures that are precisely interleaved on the nanoscale [1]. By avoiding compounds on equilibrium phase diagrams, we have prepared hundreds of new metastable compounds with designed nanostructure, including structural isomers. Many of these materials have unprecedented physical properties, including the lowest thermal conductivities ever reported for a fully dense solid [2], systematic structural changes dependent on nanostructure [3,4], and unusual electrical behavior[5]. The designed precursors also enable diffusion to be followed and quantified over distances of less than a nanometer, providing insights into the mechanism that gives control of the nanoarchitecture of the final product. Understanding how these compounds self-assemble from the designed precursors would provide valuable insight enabling the more rapid synthesis of compounds containing new constituents. We believe the ability to prepare entire families of new nanostructured compounds and controling carrier concentrations permits a new "thin film metallurgy" or "nanochemistry" in which nanostructure and composition can both be used to tailor physical properties, interfacial structures can be determined for precisely defined constituent thicknesses, and interfacial phenomena and modulation doping can be exploited systematically.

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[5] Daniel B Moore, Matt Beekman, Sabrina Disch, David C. Johnson, "Synthesis and Structural Characterization of the First Telluride Misfit Layer Compounds: $[(PbTe)_{1.17}]_m(TiTe_2)_n$", Angew. Chem. Int. Ed., **52** (2014), accepted.

WK4

Coherent Diffraction Imaging of Dynamics at the Nano- and Mesoscale

Jesse N. Clark

Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

There is a fundamental interest in studying picosecond dynamics at the nano- and mesoscale in particles and structures, as it provides insight into their mechanical and thermal properties out of equilibrium and during phase transitions. I will discuss several coherent diffraction imaging techniques that can be used to study dynamics with high temporal (ps) and spatial (nm) resolution. Current opportunities and limitations will be discussed, as well as the new science that can be enabled with diffraction-limited storage rings.

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APS Workshop 5
Frontier High-pressure Science at Synchrotron Facilities

Location:	Bldg. 401, Rm. A5000
Organizers:	Lin Wang and Maria Baldini (HPSynC)

The APS has been one of the world-leading synchrotron facilities in frontier research in extreme conditions, specifically in high compression. Recently, several novel *in-situ* high-pressure synchrotron techniques involving imaging, scattering, and spectroscopy have been developed and together have promoted new science in extreme conditions. In order to push the applications of these new techniques, leading to higher scientific impact and a more diverse user community, this workshop will highlight the latest breakthroughs in synchrotron techniques and scientific discoveries achieved with facilities at APS, as well as exploring emerging scientific opportunities related to the future capabilities of the new dynamic compression beamline at APS.

Session I Chair:	**Lin Wang** *(Center for High Pressure Science & Technology Advanced Research, Carnegie Institution for Science)*
1:10 – 1:15	Welcome
1:15 – 1:45	Hans-Rudolf Wenk (University of California, Berkeley) In situ *Observation of Texture Changes in Metals at High Pressure and Temperature: Experiments and Data Analysis*
1:45 – 2:15	Ercan Alp (Argonne National Laboratory) *Inelastic and Nuclear Resonant Scattering under High Pressure at the APS*
2:15 – 2:45	Maria Baldini (HPSynC, Carnegie Institution for Science) *High-pressure Behavior of VO_2: A PDF Study*
2:45 – 3:15	Yuejian Wang (Oakland University) *Carbon Allotropes under Pressure*
3:15 – 3:45	Break
Session II Chair:	**Maria Baldini** *(HPSynC, Carnegie Institution for Science)*
3:45 – 4:15	Brent Fultz (California Institute of Technology) *Activation Volume and Polaron Dynamics in $LiFePO_4$*
4:15 – 4:45	Guoyin Shen (Geophysical Laboratory, Carnegie Institution of Washington) *Materials under Fast Compression and Decompression*
4:45 – 5:15	Daniel Haskel (Argonne National Laboratory) *Recent Progress in High-pressure Studies of Magnetism Using Polarized X-ray Techniques*

5:15 – 5:45	Wenge Yang (High Pressure Science and Technology Advanced Research, P.R. China) In situ *Nanoscale Imaging of Strain and Phase Separation under High Pressure*
5:45	Adjourn

WK5

In situ Observation of Texture Changes in Metals at High Pressure and Temperature: Experiments and Data Analysis

Hans-Rudolf Wenk

Earth and Planetary Science, University of California, Berkeley, CA 94720-4767

Under an applied stress, crystals often undergo orientation changes and develop texture that is responsible for anisotropy in polycrystalline aggregates. Distinct preferred orientation patterns can also be produced during phase transformations. With the advent of new experimental and analytical techniques at synchrotron sources, such changes can be observed *in situ* at high pressure and temperature with a multianvil apparatus such as D-DIA (currently up to 10 GPa) or diamond anvil cells (up to 300 GPa). These techniques permit recording of x-ray diffraction images that contain information about phases, stress and pressure conditions, and preferred orientation of component crystals. This information can be extracted quantitatively with the Rietveld method. Here the method will be illustrated with two examples: slip and mechanical twinning in hexagonal metals and the martensitic transition from ductile hexagonal alpha zirconium at low pressure to brittle hexagonal omega zirconium at high pressure, with a remarkable orientation memory.

WK5

Inelastic and Nuclear Resonant Scattering under High Pressure at the APS

E.E. Alp, W. Bi, J.Y. Zhao, A. Alatas, T.S. Toellner, A. Said, and B. Leu

Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Elastic, thermal, and electronic properties of materials show substantial modification as a function of pressure and temperature. Inelastic x-ray scattering (IXS) and nuclear resonant scattering (NRS) have emerged as techniques of choice to quantitatively measure accompanying changes in sound velocity, shear velocity, specific heat, Gruneisen constant, anisotropy, isotope fractionation, overall modification to phonon density of states, valence and spin state, and magnetism.

Two beamlines at the APS, 3-ID and 30-ID, have some unique and dedicated capabilities for the high-pressure community, in addition to HPCAT at Sector 16. Two dedicated spectrometers (HERIX-3 and HERIX-30) with a resolution of 2.2 and 1.5 meV, respectively, are instrumented with microfocusing capabilities to facilitate diamond-anvil-cell studies. A unique high-pressure/high-temperature laser heating facility, combined with x-ray diffraction, inelastic nuclear resonant scattering (NRIXS), and synchrotron Mössbauer spectroscopy (SMS) with dedicated capabilities for Kr, Fe, Eu, Dy, and Sn nuclear resonances, has been developed. Recent research results will be presented.

Work performed in collaboration with J. Bass (UIUC), J. F. Lin (University of Texas, Austin), J. Jackson and B. Fultz (Caltech), D. Shim (ASU), T. Duffy (Princeton), J. Schilling (WUSL), J. Tse (U. of Saskatchewan), and their collaborators.

Use of the APS is supported by DOE under contract No: DE-AC02-06CH11357. Use of Sector 3 at the APS was partially supported by COMPRES, the Consortium for Materials Properties Research in Earth Sciences under NSF Cooperative Agreement EAR 06-49658.

WK5

High Pressure Behavior of VO2: A PDF Study

M. Baldini[1], P. Postorino[2], L. Malavasi[3], C. Marini[4], K. V. Chapman[5], and H-K. Mao[6]

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[2] Department of Physics, Sapienza University, 00185 Roma, Italy
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VO_2 undergoes a sharp metal-insulator transition with an impressive resistance change of five orders of magnitude near room temperature (340 K) at ultrafast time scales. Although VO_2 has been investigated over the last three decades, the role played by electron-electron correlations and by lattice structure in driving the insulator-to-metal transition (IMT) still needs to be clarified.

The temperature-driven IMT is accompanied by a structure change from a monoclinic insulating phase (M1) to a tetragonal (rutile structure) metallic phase (R). A pressure-induced insulator-to-metal transition was observed in VO_2 at 12 GPa. The structural changes associated with pressure-driven IMT are more subtle than the ones observed for increasing temperature. Here we present pair distribution function measurements up to 22 GPa. The pressure dependences of the V-V and V-O bond lengths and of the lattice parameters were obtained by refining the PDF and the x-ray diffraction data, respectively. The pressure-driven IMT is not related to the symmetrization of the V-V chain, confirming the preeminent role of the e-e correlation.

WK5

Carbon Allotropes under Pressure

Yuejian Wang

Physics Department, Oakland University, Rochester, MI 48309

As a ubiquitous element in nature, carbon has far-reaching implications for a variety of topics, including climate change, clean energy, new technology, and the origin of life, because of its capability to form numerous essential materials by substantially different bonding means. Even carbon itself can form a host of allotropes, including diamond, graphite, graphene, fullerene, and carbon nanotubes. Each of them has been the focus of global attention in fundamental science and industrial development, and every year enormous amounts of money and time are invested to learn more about them. Because pressure is a reliable variable to tune the crystal structure of materials, we can use high pressure to discover even more carbon allotropes which perhaps do not exist at ambient conditions. It has long been known that there exists a pressure point beyond which graphite transforms into another allotrope. However, its crystal structure and the kinetics of the transformation have been intensively debated over decades. In the talk, a brief review of the history of the identification of the high-pressure carbon allotrope will be given. Another component of the talk is graphene, a single layer of carbon atoms, which shows quite unusual features. The forefront of high-pressure study of graphene will be discussed.

WK5

Activation Volume and Polaron Dynamics in $LiFePO_4$

Brent Fultz, Sally Tracy, and Lisa Mauger

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Pasadena, CA 91125

Valence fluctuations of Fe^{2+} and Fe^{3+} ions were studied in a solid solution of Li_xFePO_4 by nuclear resonant forward scattering of synchrotron x-rays while the sample was heated in a diamond-anvil pressure cell. The compound $LiFePO_4$, with an olivine structure, is used as a cathode material in rechargeable Li batteries, but it is an insulator at low temperatures. Its low electrical conductivity is an issue for its use as an electrode. Polaron hopping is the mechanism of charge transfer between Fe^{2+} and Fe^{3+} ions in $LixFePO_4$, and polaron hopping is the mechanism of electrical conductivity in $LiFePO_4$.

Mössbauer spectrometry is sensitive to the valence of Fe, showing distinct spectral signatures of Fe^{2+} and Fe^{3+} at low temperatures. At higher temperatures, when the valence changes at rates of 1 to 100 MHz, these spectral components become blurred and merge together. The temperature dependence of this process can be used to obtain an activation energy for charge hopping in Li_xFePO_4, and such measurements have been performed for several years.

In a new development, we studied polaron hopping in Li_xFePO_4 by making measurements on samples under pressure in a heated diamond-anvil cell. We measured synchrotron Mössbauer spectra on Li_xFePO_4 at the Advanced Photon Source. The spectra were analyzed for the frequencies of valence fluctuations using the Blume-Tjon model of a system with a fluctuating Hamiltonian. The polaron hopping frequencies were analyzed to obtain activation energies and activation volumes. The temperature of polaron hopping increased considerably under pressure, showing a positive “activation volume.” For samples of conventional bulk $Li_xFePO_{4,}$ the activation volume is approximately 6 $Å^3$ at pressures to 17 GPa.

The activation volume is a measure of the local atomic distortion required for the polaron to move between Fe sites, so its magnitude can indicate the rate-controlling process. The very large activation volume of +6 $Å^3$ is typical of ion diffusion, not that of isolated polarons (which are usually small and negative). We explain our results with strong correlations in the motions of polarons and Li^+ ions that alter the dynamics of both. The strengths of the interactions between polarons and ions are estimated by a Monte Carlo simulation of their coupled dynamics. This interpretation has practical implications. It is known that the Li^+ ions have one-dimensional channels for diffusion in olivine Li_xFePO_4, and the ion diffusion is sensitive to impurities that block the ion channels. The wide scatter in reported electrical conductivity in Li_xFePO_4 likely reflects the interactions of polarons and Li^+ ions.

WK5

Materials under Fast Compression and Decompression

Guoyin Shen, Stanislav Sinogeikin, and Jesse Smith

HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, IL 60439

Phase transformation pathways are strongly influenced by the time dependence of the driving mechanism (compression, thermal transfer, strain, irradiation, etc.). Various compression rates drive rich new physics, novel chemistry, exceptional energy materials, and new routes of materials synthesis and have become an important impetus in studying the metastability, phase growth, and transition kinetics of materials. In this talk, we will outline recently developed capabilities at HPCAT at the Advanced Photon Source for studying materials behavior under fast compression and decompression, including both single event loading or unloading and multiple, repetitive ramping events. A few recent studies will be highlighted.

WK5

Recent Progress in High-pressure Studies of Magnetism Using Polarized X-ray Techniques

Daniel Haskel

Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

The high brilliance of synchrotron radiation, coupled with its energy tunability and polarization control, has enabled the implementation of element- and orbital-specific x-ray magnetic circular dichroism (XMCD) as a probe of magnetic ordering at high pressure in the diamond anvil cell (DAC). I will describe recent instrumentation developments allowing high-pressure XMCD measurements to be carried out in a much more expanded parameter space ($H < 6.5$ Tesla, $T > 1.4$ K, $P < 1$ Mbar) than previously available at APS. While these developments extend the use of XMCD to studies of strongly anisotropic ferro/ferrimagnets, canted anti-ferromagnets, and paramagnetic substances at high pressure, collinear AFM order cannot be probed by XMCD. To address this limitation, we show the first implementation of x-ray resonant magnetic scattering measurements using a panoramic DAC. The new instrumentation/probe developments are illustrated with studies of the novel high-pressure magnetic ground state in a layered Sr_2IrO_4 "iridate" sample.

Work at Argonne is supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC-02-06CH11357.

WK5

In situ Nanoscale Imaging of Strain and Phase Separation under High Pressure

Wenge Yang, Junyue Wang, and Ho-kwang Mao

High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, P.R. China

Over the last few decades, both synchrotron radiation techniques and high pressure research have made great progress. Advanced synchrotron capabilities with high spatial resolution, high flux, high energy resolution, and high coherence provide us many new avenues to conduct advanced high pressure research. In this talk, we will mainly focus on new developments in nanoscale imaging techniques for measuring internal strain distribution and pressure-induced phase separation in three dimensions. In the high pressure community, the coherence of the synchrotron beam has been largely ignored because of the complicated sample environment for data interpolation. We have developed a practical "mutual coherence function" to overcome the influence from the sample condition and extrapolated the full coherent diffraction imaging results from a single crystal nanoparticle. The 3D internal strain evolution as a function of applied pressure shows clearly the nanoscale plastic flow cross the nanograin and gives us information on the fundamental deformation mechanism of individual nanocrystals under pressure. The advanced synchrotron optics also provides us 3D tomography resolution on the scale of tens of nanometers, which in return provides detailed structural characterization of materials at extreme conditions. By choosing an incident x-ray energy near the absorption edge, the pressure-induced valence transition can be mapped at the tens of nanometer scale in 3D, which provides crucial information on the HP-LP phase boundary. Several new experimental results will be presented and the outlook for future work will be discussed.

APS Workshop 7
New Advances and Future Opportunities in Phase Contrast Imaging

Location:	Bldg. 401, Rm. A5000
Organizers:	Les Butler (Louisana State University) and Lahsen Assoufid (APS)

X-ray Talbot grating interferometry is a new phase-contrast imaging method that simultaneously provides three different modalities: absorption, differential phase, and scattering or dark-field contrast. Since its initial implementation in the x-ray regime more than a decade ago, use of this technique has rapidly expanded. The technique has proven to be extremely versatile and useful in many areas requiring static or high-speed phase-contrast imaging and tomography of large specimens at a relatively low dose, such as biomedical applications. Applications are also developing rapidly in materials and environment research, as well in other areas, such as industrial nondestructive testing. Recently, the method has been shown to be a valuable tool for at-wavelength testing and quantitative characterization of coherence/wavefront-preserving optics, a capability that is essential for diffraction-limited sources currently being planned or under construction worldwide. This half-day workshop will provide an ideal opportunity to bring experts together from diverse fields to discuss the latest developments in both instrumentation and applications, as well as future prospects.

8:00 – 8:30	Han Wen (National Institutes of Health) *Advances in Information Retrieval in Grating-based Phase Contrast Imaging*
8:30 – 9:00	Friedrich Prade (Technical University of Munich, Germany) *Materials Science Applications of X-ray Grating Interferometry*
9:00 – 9:30	Les Butler (Louisiana State University) *Comparison of Stepped and Single-shot Grating-based Interferometry for Differential Phase Contrast Imaging of Flame Retardant/Polymer Blends*
9:30 – 10:00	Dan Stutman (Johns Hopkins University) *Talbot-Lau X-ray Phase-Contrast Research at Johns Hopkins*
10:00 – 10:30	Break
10:30 – 11:00	Shashi Marathe (Argonne National Laboratory) *Characterization of X-ray Beam Coherence along Multiple Directions Using Single-phase-grating Interferometer*
11:00 – 11:30	Joachim Schulz (Microworks GmbH, Germany) *X-ray Grating Fabrication using the LIGA technology for Interferometry-based Differential Phase Contrast Imaging*
11:30 – 12:00	Hongchang Wang (Diamond Light Source, UK) *At-wavelength Metrology of Hard X-ray Optics*
12:00	Adjourn

WK7

Advances in Information Retrieval in Grating-based Phase Contrast Imaging

Han Wen

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Grating or grid-based x-ray phase contrast imaging detects both wavefront distortion and intensity attenuation as the x-ray beam propagates through the object of interest. The information about the phase and amplitude of the wavefront is encoded into the detected intensity image in ways that require additional steps to retrieve. I will give an introduction to the common methods that have been used and describe the latest advances for robust measurements in phase contrast imaging, where instrument instability and uncertainties need to be addressed.

WK7

Materials Science Applications of X-ray Grating Interferometry

Friedrich Prade, Michael Chabior, and Franz Pfeiffer

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Grating-based x-ray phase contrast imaging has been extensively applied in medical research in recent years because of the additional contrast channels this technique provides besides the standard absorption contrast. Although the differential phase contrast allows one to visualize soft tissue that usually suffers from weak absorption contrast, microstructures that are too small to be resolved in absorption imaging can be analyzed with dark-field contrast.[1] However, up to now, less effort has been devoted to establishing this technique in such research areas as materials research and nondestructive testing. To close this gap, we applied grating-based x-ray phase contrast imaging to analyzed two very well-known construction materials, namely cement and fiber-reinforced plastics. The mechanical properties of both materials are determined primarily by their microstructures, which can be characterized by dark-field imaging as already mentioned.

In the case of cement, the process of hardening and the final mechanical properties are strongly related to the development of crystalline structures that form due to the hydration of the cement material. Our studies reveal that *in situ* information about these hydration processes, which change the cement microstructure, can be extracted directly from the dark-field signal.

But besides its sensitivity to sample microstructure, the dark-field signal also depends on the relative orientation between these structures and the gratings. Building on that relationship, a new technique called x-ray tensor tomography has been recently developed to obtain three-dimensional information on the orientation of the microstructures within the sample.[2] As our studies on the characterization of fiber-reinforced materials show, this technique allows us to reconstruct the fiber orientation in a three-dimensional sample.

[1] F. Pfeiffer, et al., Nature Materials 7, 2008

[2] A. Malecki, et al., Europhysics Letters 105, 2014

WK7

Comparison of Stepped and Single-shot Grating-based Interferometry for Differential Phase Contrast Imaging of Flame Retardant/Polymer Blends

Leslie G. Butler[1,*], Shashidhara Marathe[2], Lahsen Assoufid[2], M. Bolaji Olatinwo[1], and Kyungmin Ham[3]

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We have been investigating the performance of flame retardants in polymer blends.[4] This study has used both previously burnt samples and samples that are burnt during x-ray imaging. The static samples are compatible with both stepped and single-shot interferometry while the burning samples were imaged only with single-shot interferometry. The single-shot method is nicely compatible with 2D radiography movies of the burning process. Herein, we compare the relative performance of both interferometry methods for the polymer blend project. With a highly coherent X-ray source such as an undulator at beam line 32-ID-C at the Advanced Photon Source, one has the option of at least two different modes for grating-based x-ray interferometry. These are the classical stepped two-grating system and the direct detection of interferograms from single-phase grating. The first technique makes use of a π or π/2-phase shift grating followed by an absorption analyzer grating. Alternatively, a single grating can be held in a fixed position and interferometric data can be collected in a single image.[1–3]. Here we compare the stepped two-grating system with that of single-grating, single-shot interferometry.

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[1] H. A. Barnett et al., Synchrotron x-ray tomography for 3D chemical distribution measurement of a flame retardant and synergist in a fiberglass-reinforced polymer blend, J. Phys. Chem. B 2010, 114, 2–9.

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WK7

Talbot-Lau X-ray Phase Contrast Research at Johns Hopkins

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The Talbot-Lau (T-L) grating interferometer enables x-ray differential phase contrast (DPC) imaging with low-coherence conventional x-ray tubes, being thus attractive for medical and other applications. We studied several variations of the conventional T-L interferometer design. First, to extend the T-L method to high x-ray energy, we developed a symmetric interferometer having gratings inclined at a glancing angle of incidence (GAI). This simple setup enables achieving high fringe contrast up to 80 kVp or more. The high GAI contrast in turn enabled us to demonstrate for the first time DPC-CT of soft tissues with clinically compatible x-ray dose and energy. Industrial and security applications of the GAI appear also possible.

Further on, we studied high-magnification T-L interferometry for electron-density diagnostics in high-energy-density plasmas. High-magnification refraction radiography with laser-driven backlighters can help understand inertial-confinement fusion experiments, for instance. For plasma diagnostics using a single radiographic image, we develop moiré fringe deflectometry. We also extended the T-L method below 10 keV by using membrane and free-standing gratings.

Lastly, we explored using grazing incidence microperiodic mirrors instead of gratings in the T-L interferometer. The mirrors make it possible, in principle, to achieve very small interferometer periods over a broad energy range, at the price of a narrow field of view in one dimension.

The possibility of using these designs for DPC imaging of materials under extreme conditions will also be examined.

WK7

Characterization of X-ray Beam Coherence along Multiple Directions Using Single-phase-grating Interferometer

Shashidhara Marathe[1,], Xianbo Shi[1], Michael J. Wojcik[1], Naresh Kujala[1], Ralu Divan[2], Suresh Narayanan[1], Alec Sandy[1], Albert T. Macrander[1], and Lahsen Assoufid[1]

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Knowledge of the x-ray beam transverse coherence for coherence-based imaging experiments is important not only for selecting appropriate experimental conditions but also for post-processing of the data.[1] With the planned upgrades to the present third-generation synchrotron radiation sources, a three orders increase in the coherent flux is anticipated. Therefore, it becomes even more important to understand both the beam coherence and the effect of the x-ray optics that deliver this beam on the beam coherence. Recently, x-ray grating Talbot interferometry has been shown to be a promising new technique to measure the beam coherence and beam wavefront.[2]

Here we describe a single phase-grating interferometry technique to measure the beam coherence along multiple directions simultaneously. Previously, we have shown that by using a two-dimensional checkerboard phase-grating interferometer the beam coherence of a bending magnet beamline can be measured along four different directions simultaneously together with the local beam coherence.[3] We will discuss the results obtained by application of this technique for measuring beam coherence of the 8-ID-I beamline of the APS with one and two undulators in the beam.

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WK7

X-ray Grating Fabrication Using the LIGA Technology for Interferometry-based Differential Phase Contrast Imaging

Joachim Schulz[1], Stefan Hengsbach[2], Jan Meiser[2], Pascal Meyer[2], Jürgen Mohr[2], and Marco Walter[1]

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Grating-based x-ray phase contrast imaging has attracted significant interest since its demonstration at a tube source in 2006. The key elements of this technique are the gratings, whose fabrication needs highly specialized techniques, such x-ray or laser lithography and subsequent electroforming. Demands on the gratings, such as an increased grating height, larger grating areas, or a better visibility performance, are challenging and drive our research work. To fulfill this multitude of demands, a series of improvements have been implemented into the fabrication process.

- Larger grating area: Improved mask techniques and a newly developed stitching process make it possible to fabricate gratings for large-area phase contrast setups. Gratings allowing for fields of view of about 100 mm × 100 mm are currently under development, and gratings with 100 mm diameter have been successfully tested.

- Higher gratings: Improvements in grating design, such as the sunray or unit cell design, were established and successfully tested to reduce the residual mechanical stress in the resist structures. The limitation of 120 µm grating height was overcome by using higher energy x-ray sources for the lithography. These improvements allow us to manufacture gratings with heights up to 220 µm and periods down to 4.8 µm.
- Better visibility and uniformity: To increase the imaging performance of the gratings, a set of improvements has been implemented, including the use of thinner substrates (less absorption), bent gratings to overcome shadowing at beam setups with a smaller cone, new layouts with minimized support structures to increase visibility and to resist stress. Advanced fabrication adjustments helped to increase process stability and finally grating yield. A performance parameter for characterizing the homogeneity of visibility has been introduced, allowing for a better comparison between different gratings and for benchmarking of design and process iterations.
- Smaller grating periods: First tests and simulations were performed to evaluate the fabrication of gratings with periods of 2.0 µm or less. The presentation will discuss today's capabilities in high-quality grating fabrication for application use, highlighting the actions that served best in keeping grating deviations small. It will also describe planned activities to push the limitations further.

WK7

At-wavelength Metrology of Hard X-ray Optics

Hongchang Wang, Kawal Sawhney, John Sutter, Simon Alcock, and Sebastien Berujon
Diamond Light Source, Harwell Science and Innovation Campus, Didcot, OX11 0DE, UK

One present challenge of the synchrotron community is to achieve diffraction-limited hard x-ray optics. The successful exploitation of the intense synchrotron light produced depends to a significant extent on the quality and performance of the optics employed on these beamlines. This requires development of precise, accurate and repeatable metrology. As well as optical tests in the metrology lab, extensive work is being carried out at Diamond to perform at-wavelength (using x-rays) metrology, which is considered a major pathway for surpassing the present optics performance. Two at-wavelength metrology methods have been established and further developed on B16, Diamond's test beamline. One is based on the grating shearing interferometer, whereas the other is based on the x-ray speckle tracking technique. Various x-ray optics, such as compound refractive lenses, Fresnel zone plates, and x-ray mirrors, have been investigated by using both methods [1-4]. The two techniques are both capable of measuring the surface profile of hard x-ray reflective optics with nanometer height accuracy and sub-millimetre lateral resolution [5,6]. Furthermore, we have also demonstrated that these techniques can be used for the online and fast optimization of active, nanofocusing mirrors on modern synchrotron beamlines [7]. An overview of the development of at-wavelength metrology at Diamond will be presented, including representative examples of its application.

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CNM Workshop 8
Solar Energy Capture and Conversion at the Nanoscale

Sponsored by
OCI Company Ltd.

Location: Argonne Guest House, Conf. Rm. A

Organizers: Maria Chan, Seth Darling, and Stephen Gray (CNM)

Solar energy remains the most promising renewable energy source. Many solar energy capture and conversion systems, including but not limited to inorganic, dye-sensitized and organic photovoltaics, and solar fuels, are at the forefront of materials research. A fundamental understanding at the nanoscale of the processes of photon capture, electronic excitations and charge transport, as well as the effects of structural and chemical variations of the materials on these processes, is integral for progress. This full-day workshop will provide a forum for presentation and discussion of current research advances in this fast-paced, topical area.

8:55 – 9:00	Welcome and Introductory Remarks
9:00 – 9:40	Shannon Riha (Argonne National Laboratory) *Enabling Thin Film Photovoltaics via Atomic Layer Deposition*
9:40 – 10:20	Mariana Bertoni (Arizona State University) *Nanoscale Defects in Silicon Solar Cells: Understanding the Impact of Processing Conditions*
10:20 – 10:50	Break
10:50 – 11:30	Robert Klie (University of Illinois at Chicago) *Atomic-resolution Study of Energy Conversion and Storage Materials*
11:30 – 12:10	Su-Huai Wei (National Renewable Energy Laboratory) *First-principles Study of Defects in Solar Cell Absorbers: The Case of CdTe*
12:10 – 1:30	Lunch
1:30 – 2:10	Giulia Galli (University of Chicago) *Understanding and Predicting Materials for Solar Energy Conversion: Insights from Quantum Simulations*
2:10 – 2:50	Michelle Povinelli (University of Southern California) *Nanophotonic Solutions for High-performance Solar Cells*
2:50 – 3:20	Break
3:20 – 4:00	Mool Gupta (University of Virginia) *Control of Micro/Nanoscale Surface Morphology to Enhance the Performance of Photovoltaic, Solar Thermal and Thermophotovoltaics Systems*
4:00 – 4:40	Wei Chen (Argonne National Laboratory) *Understanding the Role of Additives in Improving the Performance of Polymer:Fullerene Bulk Heterojunction Solar Cells*

4:40 – 5:00	Wrap-up and Concluding Remarks
5:00	Adjourn

WK8

Enabling Thin Film Photovoltaics via Atomic Layer Deposition

Shannon C. Riha

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

Atomic layer deposition (ALD) is an attractive low-temperature, layer-by-layer deposition method based on self-limiting surface reactions. As a result of the self-limiting growth mechanism, ALD provides exceptional control over nanoscale architectures and device composition and is further ideal for tuning dopant density, spacing, and location in 3D. These traits make ALD uniquely suited for depositing moisture-barrier layers, passivation layers, and active layers in devices, where precisely controlled films are required. Therefore, ALD is emerging as a technique of choice for the microelectronics industry and is starting to make an impact in the photovoltaics and organic LED industries. Here I will address the opportunities for ALD in photovoltaic applications.

At the core of making efficient photovoltaic devices from ALD materials is a complete understanding of the photophysical properties of these thin films. Therefore, I will focus not only on using ALD for photovoltaic materials but also on some important findings we have uncovered through collaborations with the nanophotonics group in Argonne's Nanoscience and Technology Division. Of particular interest to our group are two chalcogenide systems, namely Cu_2S and $V:In_2S_3$. Cu_2S has a rich history in photovoltaics, and in the 1980s Cu_2S/CdS heterojunction devices reached ~10% power conversion efficiency. Despite such rapid success, an incomplete understanding of the optoelectronic stability—resulting from uncontrolled stoichiometry, interfaces, and defects—has prevented the practical utilization of stoichiometric Cu_2S. Starting with clean chemistry, preventing surface oxidation, and limiting Cu diffusion into adjacent layers may be the key to enabling stable Cu_2S-based photovoltaics.

The second part of the talk will address using ALD to enable a new type of photovoltaic technology, namely, intermediate-band (IB) solar cells. Designed to achieve a large photocurrent and high output voltage, IB solar cells have a theoretical efficiency of 63%, surpassing the Shockley-Queisser limit. $V_{0.25}In_{1.75}S_3$ has recently been identified as a promising IB material, having an ideal bandgap of 2.0 eV and significant sub-bandgap absorption. The challenge, however, lies not only in collecting and converting red and near-IR photons, but also in retaining the high voltage of a large-gap device. While developing clean chemistry for In_2S_3 ALD is the first necessity, addressing the demands above will also require precise control over the vanadium dopant location and chemical control of defects and interfaces.

WK8

Nanoscale Defects in Silicon Solar Cells: Understanding the Impact of Processing Conditions

Mariana Bertoni

School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, AZ 85287

The performance of full-size solar-cell devices is normally controlled by nanometer-sized defects that can take the form of impurity clusters, precipitates, point defects, and structural misorientations (such as grain boundaries and dislocations). More importantly, the level of interaction among defects is governed by the processing conditions required to assemble the devices.

In this talk we will illustrate the impact that processing conditions have on dislocation clusters with different recombination strengths as well as on grain boundaries. The latter give rise to an unexpected photoluminescence trend, which evolution was followed throughout the cell processing.

Band-to-band photoluminescence (BPL) and sub-bandgap PL (subPL) were collected for the entire silicon wafers. Interestingly, a reversal of the subPL intensity in various regions of the wafer is observed right after the deposition of the antireflective coating (ARC). Regions with low subPL intensity before ARC exhibit high subPL intensity afterwards, and the opposite holds true for other regions of the wafer. We correlate our fluorescence findings to high-resolution cathodoluminesce spectroscopy, electron beam–induced current, and dark lock-in-thermography to elucidate the origin of this phenomenon.

WK8

First-principles Study of Defects in Solar Cell Absorbers: The Case of CdTe

Su-Huai Wei

National Renewable Energy Laboratory, Golden, CO 80401

One of the most important issues in semiconductor physics is to control charge carriers through doping, because effectivness of semiconductors as electrical and optical devices depends critically on their doping properties. For example, CdTe is one of the leading materials for low-cost, high-efficiency solar cell absorbers, because of its suitable band gap of 1.5 eV, high optical absorption, and ease of growth. However, CdTe solar cells have a relatively low efficiency (~19%) compared with the theoretical limit (~30%). One of the main reasons is because of the low majority carrier concentration of CdTe and low carrier lifetime caused by defect-induced carrier recombination. Therefore, to improve the solar conversion efficiency of CdTe, it is necessary to understand and control its doping properties. Using first-principles band structure methods, we systematically studied the defect properties in CdTe, including calculation of the defect formation energies and transition energy levels of intrinsic and extrinsic point defects and defect complexes, grain boundaries, defect diffusion barriers, and carrier concentration as function of atomic chemical potentials and temperature. From the calculated results, we investigate the limiting factors for p-type and n-type doping in CdTe and the potential nonradiative recombination centers. Possible approaches to significantly increase the doping limits and reduce the recombination centers, as well as passivation of grain boundary defect levels, are discussed. General understanding of the chemical trends of defect properties in thin-film solar cell absorbers will also be discussed.

The work is supported by the US DOE/EERE under Contract No. DE-AC36-08GO28308.

WK8

Understanding and Predicting Materials for Solar Energy Conversion: Insights from Quantum Simulations

Giulia Galli

Institute for Molecular Engineering, University of Chicago, Chicago, IL 60637

We will discuss some progress in predicting materials for solar energy conversion by using *ab initio* calculations, in particular semiconducting nanocomposites and silicon-based clathrates. We will also address the problem of building much needed tighter connections between computational and laboratory experiments.

WK8

Control of Micro/Nanoscale Surface Morphology to Enhance the Performance of Photovoltaic, Solar Thermal, and Thermophotovoltaic Systems

Mool C. Gupta

Department of Electrical and Computer Engineering, University of Virginia, Charlottesville, VA 22904-4743

The control of surface morphology is highly important for the enhancement of solar power conversion efficiency or generation of thermal heat. For example, in photovoltaics, surface recombination and optical surface reflection losses can reduce the power conversion efficiency. In solar thermal receivers, it is desired to have extremely high sunlight absorption over a broad spectral range but minimum thermal losses due to infrared radiation emission. In thermophotovoltaic systems, extremely high sunlight absorption is required, but thermal emission needs to occur in a narrow spectral range to match the solar cell bandgap. By controlling the surface morphology at the micro- or nanoscale, optical absorption and thermal emission can be controlled to make highly efficient devices for solar power conversion. In this talk, we will provide various examples of surface morphology used to control the light absorption and thermal emission in order to enhance the efficiency of solar power conversion.

WK8

Understanding the Role of Additives in Improving the Performance of Polymer:Fullerene Bulk Heterojunction Solar Cells

Wei Chen

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Institute for Molecular Engineering, University of Chicago, Chicago, IL 60637

Solar cells based on the polymer:fullerene bulk heterojunction (BHJ) represent one of the most promising technologies for next-generation solar energy conversion because of their low cost and scalability. In the last 10 years, the highest power conversion efficiency (PCE) obtained from polymer:fullerene BHJ solar cells has risen from 2.5% to 12% through the development of new materials. However, when organic solar cells are manufactured in large area with high-throughput techniques, the efficiencies are much lower, usually below 3.5%. This performance gap is standing in the way of market penetration for this technology. One of the primary reasons for the gap is the poor control of morphological changes in the active layer when shifting from spin coating in the laboratory to high-throughput techniques on a commercial scale.

Incremental changes in organic photovoltaic (OPV) materials will not get us where we need to go. To close this performance gap, a thorough understanding of the complex processing-structure-performance relationships in OPV devices is required. Among several strategies that are most often used to tune the nanomorphology of the polymer:fullerene active layer, the use of processing additives has proved to be one of the most effective methods. The incorporation of a small percentage of solvent additives results in a nearly doubling of device efficiency. So far, the role of processing additives in improving OPV performance remains unclear. In this work, by taking advantage of resonant soft x-ray scattering (RSoXS) and energy-filtered transmission electron microscopy (EFTEM), we have determined that the solvent additives induce the change in the formation mechanism of polymer:fullerene nanomorphologies in the process of film casting. The superior performance of polymer:fullerene BHJ solar cells is attributed to hierarchical nanomorphologies with optimum crystallinity and nanoscale intermixing of copolymers with fullerenes. Progress established in the course of these studies on the effects of solvent additives outlined above will serve as the foundation for further improving the efficiency of polymer solar cells to realize their large-scale commercial use.

APS Workshop 10
Materials for a Sustainable Energy Future: Advances in Structural Science

Location: Bldg. 402, Lecture Hall

Organizers: Angus Wilkinson (Georgia Tech), Gregory Halder (APS), Peter Chupas (APS), and Randall Winans (APS)

The great challenge for the coming decades will be to develop technologies that can accommodate the ever increasing demands for energy resources in an economically and environmentally sustainable way. With concerns over climate change and the long-term availability of fossil fuels scientist and engineers from diverse backgrounds are focusing on materials research to achieve this goal of a sustainable energy future. The wide-range of structural characterization tools offered by x-ray and neutron scattering sciences are vital to both the discovery of new materials as well as developing a thorough understanding of how energy-related materials function. Of particular importance are *in situ* studies of these materials using multiple scattering techniques in order to extract all critical structural information.

The suite of "*in situ*"-enabled structural science tools available at the APS provides the opportunity to perform such multi-approach investigations. These include facilities for powder diffraction, pair distribution function, and small angle scattering, as well as high-resolution and high-throughput instrumentation. These tools serve a large number of users and have considerable impact due to the importance and diversity of the energy-related scientific challenges being addressed. Further advancement of these capabilities is vital if we are to adequately meet the scientific demands associated with the efficiency of materials discovery (materials genome), and to align future instrument developments with the APS Upgrade project.

This half-day workshop will examine the current state of the art in instrumentation and scientific applications, and look forward with a view to developing plans for the next generation of structural science capabilities that address key energy-related problems, including new battery, solar, and fuel cell technologies; hydrogen and methane storage; carbon sequestration; and nuclear energy. A broad cross section of speakers from the user community will be charged with discussing how scattering is aiding research in their area(s) of interest and what the opportunities are for future capability improvements that will have a high scientific impact.

1:30 – 1:40	Peter Chupas and Randall Winans (Argonne National Laboratory) *Opening Remarks and Overview of Current Capabilities at APS*
1:40 – 2:05	David M. Tiede (Chemical Sciences & Engineering Division, Argonne National Laboratory) *Determining Domain Structures of Amorphous Metal-oxide Water-splitting Catalysts for Artificial Photosynthesis*
2:05 – 2:30	Craig Brown (NIST Center for Neutron Research) *Structural Studies of Adsorbates in Porous Media*
2:30 – 2:50	Andrey Yakovenko (X-ray Science Division, Argonne National Laboratory) *Study of Metal–Organic Frameworks via Analysis of Difference Envelope Density*
2:50 – 3:20	Break
3:20 – 3:45	Kenneth R. Poeppelmeier (Department of Chemistry, Northwestern University) *Accelerated Discovery of Materials*

3:45 – 4:10	Andrew Herring (Chemical and Biological Engineering Department, Colorado School of Mines) *Using* In situ *SAXS to Elucidate Phase-separated Morphology and Dynamics in Next-generation Ionomers for Polymer-membrane-based Electrochemical Conversion Devices*
4:10 – 4:35	Karena Chapman (X-ray Science Division, Argonne National Laboratory) *Decoupling Mesoscale Effects in Electrochemical Energy Storage with Hard X-ray Tools*
4:35 – 4:45	Wrap-up and concluding remarks
4:45 – 5:00	Workshop report preparation (organizers)
5:00	Adjourn

WK10

Determining Domain Structures of Amorphous Metal-oxide Water-splitting Catalysts for Artificial Photosynthesis

David M. Tiede, Gihan Kwon, Diego Fazi, and Oleksandr Kokhan

Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439

The successful development of artificial leaves for solar energy conversion will depend on the availability of efficient water-splitting catalysts. One promising class of catalysts, which has generated widespread interest, is based on electrochemically processed, self-assembled, amorphous films of transition metal oxides. They offer a synthetic approach that bridges the gap between molecular and crystalline oxides and offer opportunities for functional optimization on a per-metal-atom basis. Notable success has been achieved in the development of a range of cobalt-, nickel-, iron-, and iridium-based catalyst films. Resolution of the fundamental chemistry underlying the assembly, repair, and catalysis of these amorphous metal oxides can provide information needed for the design of efficient molecular catalysts that are based on first-row transition metals. Toward this end, we have investigated domain structures within amorphous catalyst films grown from Co and Ir molecular precursor complexes using synchrotron high-energy (60 keV) x-ray scattering and atomic pair distribution function (PDF) analyses. The results demonstrate that the films are composed of ligand-terminated, molecular-dimensioned metal-oxo clusters. For these catalyst films based on Co-phosphate and Ir, the longest atom pair distance is 11.4 Å and 7.1 Å, with the domains accurately modeled as selected mineral lattice fragments, comprised of 13 and 5 metal atoms, respectively. It is suggested that the models represent the population-averaged distribution of metal-oxide clusters in the films. The Ir-oxide catalyst film is distinguished by the remarkably small domain size and homogeneity. The auxiliary ligands are proposed to play a critical role in determining metal-oxo cluster size and provide secondary proton-accepting chemistry that enhances catalytic activity compared to the corresponding nanocrystalline metal-oxides. This work suggests chemical principles and experimental approaches applicable to catalyst design in artificial photosynthesis. Ongoing work is investigating in operando catalyst film structure and molecular catalysts.

WK10

Structural Studies of Adsorbates in Porous Media

Craig M. Brown[1,2]

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Adsorption of molecules in functionalized and high-surface-area microporous materials is of technological importance in a multitude of areas ranging from chemical separations to energy storage. Over the past several years we have focused our research efforts on understanding the properties of metal-organic frameworks (MOFs) [1]

and zeolites [2] for storage and separation of industrially important small molecules, such as hydrogen, oxygen, carbon dioxide, noble gases, and short-chain organics. Besides the geometrical and porosity control in either class of materials, the properties of metal–organic frameworks can be tuned to optimize electrostatic interactions by exposing open metal cation sites, while zeolites can be tailored through Si-Al content with choice of charge-balancing cations.

Here, we discuss the different requirements for performing these experiments at x-ray compared to neutron sources and reflect on the information potentially obtainable in both cases. The results illustrate the power, and limitations, of diffraction in elucidating many of the governing characteristics of these material properties and the interactions with the guest molecules.

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[2] T.-H. Bae, M.R Hudson, J. Mason, W.L. Queen, J. Dutton, K. Sumida, K. Micklash, S. Kaye, C.M. Brown, and J.R. Long, "Evaluation of Cation-exchanged Zeolite Adsorbents for Post-combustion Carbon Dioxide Capture," Energy Environ. Sci., 2013, 6, 128.

WK10

Study of Metal–Organic Frameworks via Analysis of Difference Envelope Density

Andrey A. Yakovenko[1,2], Mario Wriedt[2], Zhangwen Wei[2], Gregory J. Halder[1], and Hong-Cai Zhou[2]

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Synthesis of polycrystalline vs. single-crystalline porous materials, such as metal-organic frameworks (MOFs), is usually beneficial because of shorter synthetic time and higher yields. Also, polycrystalline materials often have higher surface area, which is very important for gas adsorption and storage applications. However, the structural characterization of these materials by x-ray powder diffraction can be complicated. An even more difficult task is to track structural changes in MOFs during *in situ* experiments. Hence, recently we designed several successful techniques for the structural investigation of porous MOFs.

These methods are based on the analysis of structure envelope density maps. These maps can be easily generated from the structure factors of a few (1 to 10) of the most intense low-index reflections. However, the most interesting results have been found by using difference envelope density analysis. They are made by taking the difference between observed and calculated structure envelope densities. This approach allows us to study guest-related issues of MOFs, such as tracking activation of MOFs and gas loading and determining interpenetration and positions of ligand substituents. In the presentation, this technique will be described and explained using several examples.

WK10

Accelerated Discovery of Materials

Romain Gautier, Linhua Hu, Yuyuan Lin, and Kenneth R. Poeppelmeier

Department of Chemistry, Northwestern University, Evanston, IL 60208

Solid state and materials scientists have often focused on the properties of previously reported compounds, leaving out the numerous unreported compounds that could have potentially interesting properties. Consider, for example, the 18-electron ABX family of compounds, including the half-Heusler subgroup that manifests HgTe-like topological semimetals, thermoelectrics, and superconductors: This family contains 483 potential members, but only 83 have been previously made.

By using first-principles thermodynamics, Alex Zunger, Liping Yu, and Xiuwen Zhang (University of Colorado at Boulder) have examined theoretically the stability of the 400 unreported members, predicting that 54 should be stable. Many of these previously missing and now predicted stable materials have been grown by arc melting and fused silica tube annealing; x-ray studies agreed in all cases with the predicted crystal structure and lattice parameters.

This integrated process—prediction of unreported compounds that are screened theoretically as stable, followed by laboratory synthesis—could be a route to systematic discovery of new, realizable functional materials.

To accelerate our ability to synthesize these new stable materials, we are beginning to use high-energy x-rays with Peter Chupas (Advanced Photon Source, Argonne National Laboratory) to probe the synthesis of materials during the reaction to reveal the critical conditions and intermediate phases that govern the product. We intend to address these difficulties through the application of high-energy x-rays (>60 keV, $\lambda < 0.2$Å) that have opened the possibilities of probing large-scale materials (as thick as one centimeter) under extreme conditions of temperature and pressure. The high intensity of high-energy x-rays can be employed to gain detailed structural insights at a rate of 0.1 s, which allows materials synthesis to be studied on the same scales on which it is carried out in conventional laboratory discovery efforts.

In a synthetic campaign, broad areas of phase space need to be probed by *in situ* methods—a necessary advance over the singular sample state recovered from a conventional offline synthesis—in order to study a large number of predicted stable compounds. Reactions in standard sealed silica ampules (5 mm diameter × 75 mm long) can be probed with high-energy, *in situ* powder diffraction at temperatures up to 1300 K. These studies provide a wealth of information, including beginning temperature of formation, time scale and temperature of complete reaction, and evolution of secondary phases. For example, each ABX synthesis, which originally took approximately two weeks per sample, can be completed in less than an hour. The *in situ* analysis and high throughput methods of high-energy x-rays could reduce the months needed to synthesize novel compounds to mere days, a game-changing improvement that would greatly accelerate our understanding compared to the singular sample state and a conventional *ex situ* evaluation.

For further validation, we will use our new optical floating zone furnaces at Northwestern University and Argonne National Laboratory (John Mitchell), one of the most powerful crystal growth techniques available, to grow bulk crystals. Crystals multiple millimeters in diameter and several centimeters in length are typically obtained, which are suitable for characterization of all of the targeted functionalities of the missing materials.

WK10

Using *In situ* SAXS to Elucidate Phase-separated Morphology and Dynamics in Next-generation Ionomers for Polymer-membrane-based Electrochemical Conversion Devices

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Electrochemical energy conversion devices based on polymer electrolytes have the potential for high system power densities, using relatively inexpensive components, at much higher efficiencies, than can be achieved with heat engines, at their relatively moderate temperature of operation. Devices based on proton exchange membranes (PEMs) are mostly being considered for hydrogen applications because of their realized very high power densities. Here the need is to develop PEMs that operate with less water and at elevated temperatures. In this scenario, devices based on anion exchange membranes (AEMs) have the potential for use with multiple fuels as fuel cells and to electrolyze not only water but also electrochemically reduce a range of substrates. AEMs can be operated with a large variety of anions depending on the application. Here the need is to use water efficiently for anion transport and as a reactant for hydrocarbons or for hydroxide-conducting systems. Next-generation ionomers must be designed for water management and utilization and gas permeation or transport without compromising the mechanical properties of the material through excessive swelling or softening.

In this talk, I will show multiple examples of how *in situ* SAXS can be used to study the phase-separated morphology of state-of-the-art ionomers. For most studies, we use a simple environmental chamber where relative humidity and temperature can be controlled. The chamber has four slots; one is used for a background and the other three for samples, which are mounted on metal sample holders that can be easily removed, enabling high throughput of samples. PEMs include hybrid polymers in which the active group is an inorganic super acid and hydrocarbon materials with novel backbones. Water does not always simply swell the hydrophilic region; if the polymer is hydrophobic enough, the water can escape the fixed pores and swell the entire film. AEMs will be presented with a range of polymer architectures and cations. SAXS has been particularly useful here to help explain how water swells the large organic cations, as well as how it facilitates ionic transport.

WK10

Decoupling Mesoscale Effects in Electrochemical Energy Storage with Hard X-ray Tools

Karena Chapman

Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

The complex coupling of atomic, chemical and electronic transformations across multiple length scales underlies the performance of electrochemical energy storage devices. We have implemented new operando measurement capabilities and combined complementary hard x-ray tools to decouple the complex processes that occur within battery electrodes during cycling. Specifically, by combining pair distribution function (PDF) and small-angle x-ray scattering (SAXS) analysis, we can resolve the coupling of chemistry with atomic- and nanoscale structure in a series of Fe-based conversion electrodes.

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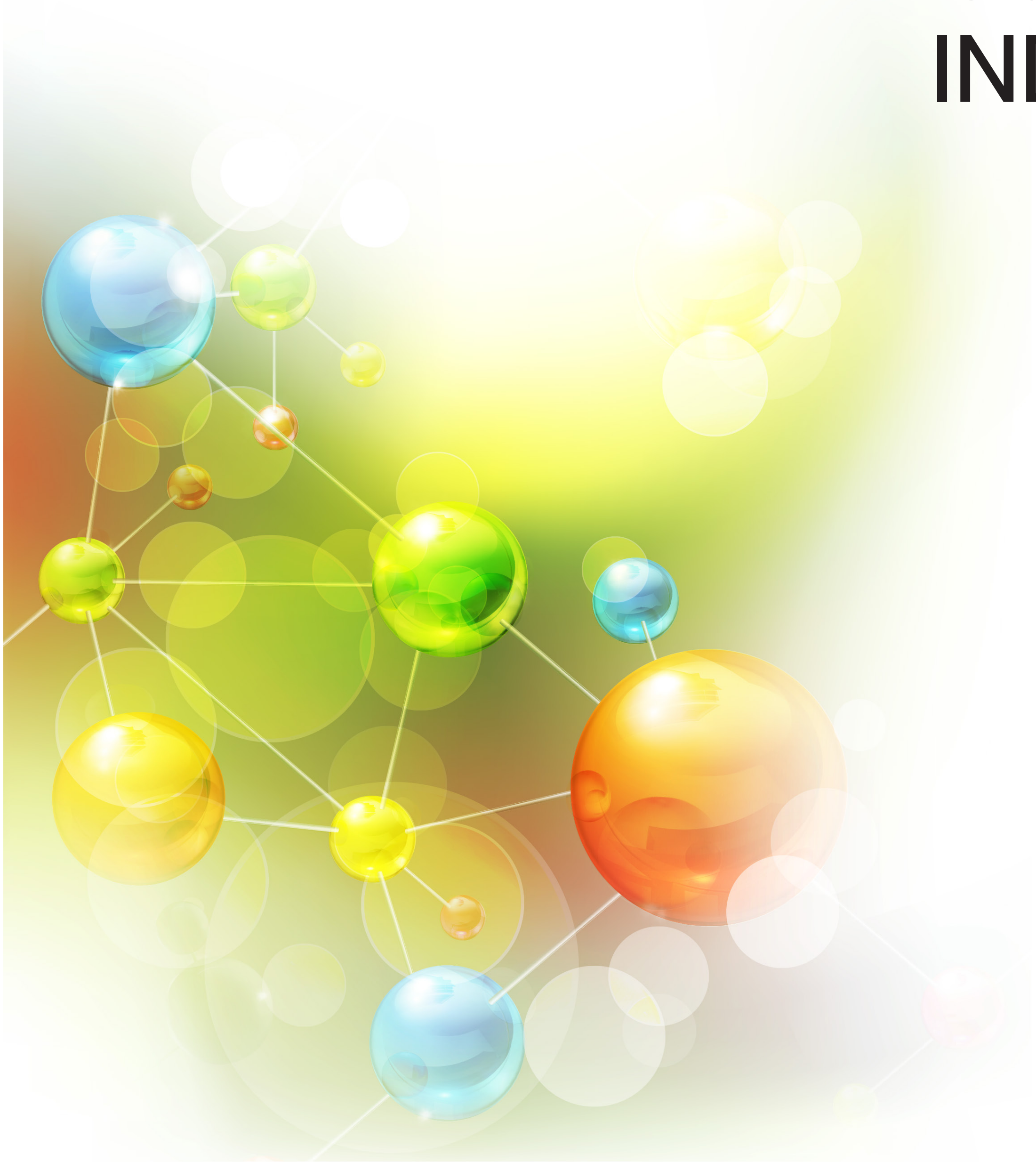

Advanced Photon Source

Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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Center for Nanoscale Materials

Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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Electron Microscopy Center

The electron microscopy was accomplished at the Electron Microscopy Center for Materials Research at Argonne National Laboratory, a U.S. Department of Energy Office of Science Laboratory operated under Contract No. DE-AC02-06CH11357 by UChicago Argonne, LLC.

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NANOSCIENCE AND TECHNOLOGY

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Exemplary Student Research Program

Using the world-class facilities at Argonne's Advanced Photon Source, area high school students and their teachers explore the principles and operation of these tools and conduct research during the school year. Under the guidance of staff scientists, each team develops an achievable project based on the techniques and limitations within a specific research group, prepares and submits a research proposal, sets up the experiment, gathers and analyzes their results, draws conclusions, and prepares a final poster for the Users Meeting.

ESRP-1	Downers Grove North High School	Micro X-ray Fluorescence Mapping of Pb Distribution in *Brassica juncea* Grown in Artificially Stimulated Soils
ESRP-2	Downers Grove South High School	Presence of Metals and Metalloids in Wild Salmon Compared to Farmed Salmon Studied with Hard X-ray Fluorescence Microscopy
ESRP-3	Glenbard East High School	The Effects of Glyphosate on Metal Concentration and Distribution in Transgenic Soybean
ESRP-4	Maplewood Richmond Heights High School	X-ray Crystallography of Co-crystallized Concanavalin-A and IF7
ESRP-5	Nequa Valley High School	The Sustainability of Silver Nanoparticles
ESRP-6	Nequa Valley High School	The Effect of Halogen Ions on Insulin Crystallography
ESRP-7	Oaklawn Community High School	Trace Element Mapping of Fish Otoliths Using Synchrotron Microbeam X-ray Fluorescence as an Indicator of Fish Movement in the Illinois River System

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POSTER ABSTRACTS

Biology

A-1

X-ray Fluorescence Microscopy Analysis of Inclusion Bodies in Adult Neural Stem Cells *in situ*

Brendan Sullivan[1], Gregory Robison[1], Taisiya Zakharova[1], Sherleen Fu[2], Wei Zheng[2], and Yulia Pushkar[1]

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Imaging of *in situ* metal distributions in rodent brains by x-ray fluorescence microscopy (XRF) revealed very concentrated (300 mM) localized (1-µm diameter) Cu deposits in periventricular neural stem cells [1]. Based on their orange-red autofluorescence, high Cu concentrations, and localization in adult stem cells a homology is established between our reported inclusion bodies and previously reported Gömöri-positive inclusion bodies [2]. Whereas traditional techniques for studying metal containing inclusion bodies require sample treatment that alters the physiological metal distribution (e.g. chemical fixation or lysis agents), XRF provides a means to study the transition metal-rich inclusion bodies *in situ* towards elucidating their biological function. It is first shown by micro-cryo-XANES recorded from untreated tissue that Cu is bound as part of a multimetallic Cu-S cluster; imaging at 30-nm resolution reveals a consistent [S]/[Cu] ratio to be 1.66 ± 0.07. Accordingly, it is proposed that metallothionein (MT), a cysteine-rich protein known bind metals with high affinity ([S]/[Cu] = 1.66 ± 0.08 depending on the isoform) as the binding protein. Parallel analysis of MT(1,2) knockout mice reveals that in the absence of MT(1,2), inclusions contain 40% less Cu while no other metals show significant variation anywhere else in the brain. Inclusion bodies in MT(1,2)KO mice are 1/3 as densely packed along the ventricle wall as their WT counterparts. Inclusions in mutants also exhibit indistinguishable XANES spectra and [S]/[Cu] ratios from wild-type controls. Finally, it is shown that inclusion bodies do not reside in lysosomes, implicating them in the ubiquitin-proteasome system (UPS). These results suggest that MT3, a third MT isoform present only in the central nervous system, is capable of fulfilling the role of MT(1,2) in inclusion body formation, which was previously thought to be necessary for inclusion formation [3]. Since the inclusions are handled by the UPS it is proposed that the age-related decline in UPS effectiveness enables accumulation of stem cell inclusions in advanced age [1] and gives rise to diminished neurogenic activity.

[1] Pushkar, Y., et. al. (2013) Aging results in copper accumulations in GFAP-positive cells in the subventricular zone. Aging Cell 823-832.

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A-2

Insight into the Catalytic Mechanism of GABA-producing Enzyme: Glutamate Decarboxylase from *Sphaerobacter thermophilus*

Ruiying Wu[1], Shonda Clancy[1], and Andrzej Joachimiak[1, 2]

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Glutamate decarboxylase (GAD; EC 4.1.1.15) is a pyridoxal 5'-phosphate (PLP)-dependent enzyme, which catalyzes the irreversible a-decarboxylation of L-glutamate to g-aminobutyrate (GABA). This enzyme is widely distributed amongst eukaryotes and prokaryotes. The GAD plays a crucial role in the vertebrate central nervous system where it is responsible for the synthesis of GABA, a major inhibitory neurotransmitter. In the current study, we have determined at atomic resolution several crystal structures of GAD from *Sphaerobacter thermophilus* (*St*GAD), the apo-form, several mutants and in complex with its cofactor PLP, substrate and product. *St*GAD has shown high structure similarity with two isoforms of human GAD67 and GAD65. The enzyme contains a flexible loop near the active site.

This disordered loop of residues 330-340 in wild type *St*GAD becomes a tethered loop covering the active site in three mutant *St*GADs: Y333A, Y333N and Y333Q. Both L-glutamate (substrate) and GABA (product) are found near the PLP-binding domain and the mobile loop respectively, as observed in the Y333A mutant *St*GAD structure. The findings reported herein provide evidence for Y333 as the critical residue responsible for the inherent mobility of the catalytic loop and suggest a key role in the catalytic reaction. The accurate molecular detail of *St*GAD interacting with its substrate, product as well as its PLP cofactor in the atomic structure provides insight into the one-step GABA biosynthesis catalyzed by the glutamate decarboxylase. Detailed information will be presented.

This work was supported by National Institutes of Health Grant GM094585 and by the U.S. Department of Energy, Office of Biological and Environmental Research, under contract DE-AC02-06CH11357.

Chemistry

A-3

Iron Sulfide Particle Size Effects in a Maya Vacuum Resid and an Illinois #6 Argonne Premium Coal

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Coal is, and will remain for the foreseeable future, a major source of energy worldwide. Despite advances in renewable and gas resources, the U.S. Energy Information Administration predicts that coal will provide the majority of fuel for the generation of electricity continuing up to at least 2035. An understanding of sulfur-based mineral behavior in coals is still needed for coal processing and mining.

The FeS_2 polymorph pyrite and marcasite were mixed together with a Maya Vacuum Resid coal model in known ratios, and a scheme was devised to deduce particle size. The behavior of these samples was then tracked with increasing pyrolysis. The results show that marcasite is much less structurally stable if the initial particle size is large. This will result in a sudden generation of H_2S and generation of pyrrhotite, $Fe_{(1-x)}S$, which is a coal gasification catalyst.

A large-particled and a small-particled Illinois #6 coal Argonne Premium Coal was also pyrolized to various degrees. The iron sulfide behavior in this sample showed that there was a difference in transformations from pyrite to pyrrhotite and then to troilite dependent on the particle size. One explanation is the shrinking-core model, in which escaping sulfur gas eventually weakens the particles' outer sulfur-poor matrix, which breaks away, exposing the inner pyrite core.

A-5

Activation-induced Amorphization in a Nanoporous Metal-organic Framework Material

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Over the past decade there has been considerable interest in the development of porous metal organic framework materials (MOFs) capable of storing and/or purifying gases for energy applications (e.g., hydrogen, green house gases). Understanding the nature of the interaction between guest molecules and the host framework is pivotal to the design and development of new MOFs with enhanced gas storage/separation capabilities. However, the crystallinity of these materials is often drastically reduced during industrially relevant processing conditions, such as outgassing routines and pelletization to optimize volumetric storage capacities, which can inhibit traditional diffraction-based structural studies. In many cases MOFs have been observed to transform to amorphous phases, but this is typically ascribed to a lack of stability and pore collapse by the majority of the MOF community, and subsequently few attempts to study these amorphous phases have been reported to date. Here, we probe crystalline-amorphous structural transitions in porous zinc-triazole MOFs, through a combination of *in situ* synchrotron-based powder diffraction and pair distribution function analysis.

A-6

Crystal Structures of Large-volume Commercial Pharmaceuticals

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The crystal structures of a surprising number of the largest dollar volume commercial pharmaceuticals are unpublished. To provide high-quality reference data for the Powder Diffraction File™ database and to determine the crystal structures, synchrotron powder patterns have been collected on many materials at ambient conditions. The new crystal structures to be discussed include (at least): atomoxetine hydrochloride (Strattera™), dutasteride (Avodart™), fingolimod hydrochloride (Gilenya®), levalbuterol hydrochloride (Xopenex®), paliperidone (Invega), norgestimate (progestin, a component of Ortho Tri-Cyclen®), raltegravir potassium (Isentress™), rivastigmine hydrogen tartrate (Exelon®), sitagliptin dihydrogen phosphate monohydrate (Januvia®), ziprasidone hydrochloride monohydrate (Geodon®), and the beta polymorph of 17α-estradiol (which turns out to be a hemihydrate). Density-functional geometry optimizations enable detailed analysis of the bonding in the solid state, particularly the hydrogen bonding. Powder patterns of these materials, as well as nine compounds for which the crystals structures have been reported and 10 amorphous pharmaceuticals will be incorporated in the 2014 release of the Powder Diffraction File™.

A-7

Studying the Structural and Electronic Configurations during Photocatalytic Activation of O_2 at a Diiron(II) Complex

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Several mono and carboxylate-bridged diiron nuclear enzymes are critical in activating dioxygen in various biological processes such as DNA synthesis, hydrocarbon metabolism and cell proliferation(1). Iron-containing enzymes such as cytochrome P450, peroxidases, catalases and methane monooxygenase (MMO) have been shown to activate dioxygen by using two electrons and protons to produce iron (IV) oxo intermediates(2-4). The remarkable efficiency of these enzymes is often attributed to the formation of these iron(IV) cations which serve as active oxidants in enzymatic reactions and are able to attack the C-H bonds of a wide range of hydrocarbon substrates(5). It is widely postulated that ferryl-oxo species are key intermediates in the mechanism of cytochrome P450 and MMO. However due to the complexity of the protein environments in biological iron enzymatic systems(1), monitoring the structural changes occurring during dioxygen activation is a complex undertaking.

This project serves to study the light driven activation of a well characterized artificial analogue of an diiron MMO enzyme, (μ-peroxo) (μ-carboxylato) diiron(III) complex, $[Fe_2(\mu\text{-}O_2)(N\text{-}EtHPTB)(\mu\text{-}PhCO2)]^{2+}$ in a chromophore/diiron complex assembled unit. Such types of assemblies provide new avenues for study of catalytic reaction mechanisms. They are promising examples of artificial molecular systems leading to dioxygen activation as visible light is efficiently absorbed at the chromophore, and light energy is in turn converted into a chemical potential via an electron relay through charge accumulation processes at the iron metal center. Formation of high valent iron peroxo and iron oxo species will be shown by UV-Vis, EPR and Resonance Raman spectroscopy. Planned x-ray spectroscopic analysis together with theoretical calculations will also be discussed to allow for identification of the critical requirements for dioxygen activation by biological mononuclear and dinuclear iron enzymes.

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A-8

Probing X-ray-induced Damage by SHG Microscopy

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Second harmonic generation (SHG) imaging has enabled direct observation of the local electric fields produced from photoelectron – hole separation upon exposure of soft materials to hard x-rays during diffraction analysis under cryogenic conditions. Using the integrated SHG/XRD instrumentation on beamline 23-ID-B strong SHG signal was observed from amorphous vitreous samples following x-ray minibeam exposure, the results of which are qualitatively and quantitatively consistent with electric field-induced SHG (EFISH). Exposing protein crystals to ~1 Å x-rays resulted in increased SHG in the region extending ~3 mm beyond the borders of the x-ray beam. Typical x-ray exposures used for crystal positioning by raster-scanning were sufficient to produce electric fields easily detectable by SHG. The x-ray induced SHG activity was observed with no measurable loss for longer than two weeks while maintained under cryogenic conditions, but disappeared when the sample was annealed to room temperature. Monte-Carlo simulations of x-ray photoelectron trajectories were also used to investigate the EFISH mechanism. The Monte-Carlo simulations suggest the formation of substantial local electric fields in the regions adjacent to those exposed to x-rays, which would be detectable by EFISH. These results provide direct experimental observables capable of validating simulations of x-ray induced damage within soft materials. In addition, x-ray induced SHG provides a convenient method for rapidly identifying regions previously exposed to or affected by x-ray exposure.

A-9

The Retention of Calcium, Barium, and Strontium Ions by a Mollisol Humic Acid: Spectroscopic Investigation

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Humic substances have a major role in controlling the mobility and bioavailability of metallic ions in soils and natural waters. The alkaline earth metals, calcium, barium, and strontium, are broadly abundant in the crust of the earth, and Ca^{2+} ions are known to be important in the formation of structural aggregates in soils. Yet, direct spectroscopic evidence of how Ca, Ba, and Sr ions interact with soil organic matter, is minimal. To develop a deeper understanding of the interaction of the alkaline earth cations in soil, we studied the complexation behavior of strontium, barium and calcium by humic acid (HA) using solid-state ^{13}C CP-MAS NMR, FTIR and extended x-ray absorption fine structure (EXAFS) spectroscopy. A HA sample was extracted from an agricultural mollisol (pH 6, 32.5% clay content, 3.7% organic carbon) located in southwestern Minnesota, USA, by the standard NaOH method. The HA sample was treated with chloride salts of Ca, Sr or Ba, and then freeze-dried prior to spectroscopic measurements. The FTIR spectra, obtained using pressed KBr disks, and the ^{13}C NMR spectra revealed spectral differences, stemming mainly from deprotonation reactions of the carboxylic and phenolic groups of the HA. The association of Ca, Ba, and Sr ions with the HA caused a marked FTIR shift of the carboxylate band, with the Ba shift being the most pronounced (HA 1604.7; HA-Ca 595.1; HA-Sr 1597; HA-Ba 1579.6), which seems to imply that Ba is the strongest bound element. An NMR shift of the carbonyl peak at 171.8 ppm was also observed to 174.5 for Ca, 173.7 for Sr, and 174.4 for Ba confirming that these cations are behaving differently towards soil HA. The EXAFS spectra indicated back scattering from oxygen atoms, in the first shell, for Ca, Sr, and Ba with varied coordination number. Our data prove that (1) the carboxylates and phenolates are the prevailing functional groups involved in the interactions between the extracted HA and alkali metal cations, (2) barium forms the strongest complex compared to strontium and calcium.

A-10

Catalysis Research at the APS

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In the DOE-BES basic research needs "Catalysis for Energy" two grand challenges in catalysis are: 1) Understanding the mechanisms and dynamics of catalytic transformations and 2) Design and controlled synthesis of catalytic structures. An important element to addressing these challenges is the ability to make measurements in reaction environments and x-ray studies can uniquely probe catalytic systems in an *in situ* way. XSD proposes to establish a Catalysis Center at the APS which will be a complete package that will attract catalysis scientists from DOE-supported programs, academic centers and industry. This Center will take advantage of an array of x-ray techniques in scattering, spectroscopy and imaging with the addition of other complementary characterization tools. The base of this center will be found in sectors 9-12 which already have established a presence in catalytic research. DOE EFRC programs such as IACT and industries such as UOP, ExxonMobil, and Chevron are working on these beamlines and are contributing to improving them. A reason to develop this Catalysis center now is that all of the techniques being used and developed will benefit from the APS Upgrade. The MBA lattice technology will provide a small beam with enough x-rays to see very dilute, small nano catalysis. The ability to study a single catalytic particle under reaction conditions would be the ultimate goal of this line of catalysis research. Examples of current catalysis research are presented.

Condensed Matter Physics

A-11

Jamming Transition in Quasi-2D Self-Assembled Nanoparticle Monolayers

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We experimentally probe the structure and interparticle dynamics of iron oxide nanoparticle thin films self-assembled at the liquid-air interface. Upon deposition on a water surface in a Langmuir-Blodgett trough and subsequent lateral compression, iron oxide nanocrystals coated in oleic acid ligands self-assemble into a relatively uniform quasi-2D monolayer. We verified this film structure by X-ray Diffraction in Grazing-Incidence geometry (GIXD). Utilizing X-ray Photon Correlation Spectroscopy (XPCS) at beamline 8-ID-I of the Advanced Photon Source at Argonne National Lab, we have measured the characteristic timescale of in-plane interparticle dynamics. The degree of jamming in the system has been quantified by fitting a stretched exponential model to the autocorrelation functions produced by XPCS measurements. A jamming exponent of 1.5 has been calculated, a value that has previously only been observed in 3D aging soft matter systems. Since the accepted explanation for this exponent is strongly correlated with the number of degrees of freedom [1], this result was unexpected given the reduced dimensionality of our system. Additionally, the q-dependence of the interparticle timescale in the film is supportive of an anomalous diffusion regime, $(x)^2 \alpha t^n$, with $n > 1$. I will present these results and their implications with regards to thin film self-assembly, structure, and rearrangement.

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A-12

Atomistic Computation Model Radiation Damage of Materials Exposed to High-brilliance X-ray Pulses

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We present a combined Monte-Carlo/molecular-dynamics (MC/MD) computational model that is suitable for monitoring the physics of intense, femtosecond XFEL pulses interacting with complex systems of various sizes, from nanometers to micrometers, and matters of various compositions. In this model, the occurrences of x-ray absorption, ionization, relaxation and electron-impact processes are treated by an MC method, and the subsequent dynamics of the all the electrons, ions and atoms are tracked using an MD method. Recently, we have added LAMMPS as the driver of MD dynamics. This is a critical addition as now our code can run on Mira, a new petascale supercomputer with 786K core processors at the Argonne Leadership Computing Facility (ALCF). Also, it can treat both homogeneous and heterogeneous, micron-sized systems with trillions of particles.

A-13

In-situ X-ray Scattering of FeSe Thin Films Grown on SrTiO3(001)

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Recently, a single layer of FeSe film grown on SrTiO3(001) was found to exhibit much enhanced superconductivity (Tc~40 K) compared to its bulk form (Tc~8 K). While it is generally believed that the FeSe/SrTiO3(001) interface, as well as the SrTiO3 substrate, plays an important role in the enhancement of superconductivity, the detailed mechanism is still under debate. Here we employ surface x-ray scattering to probe the structure of FeSe films grown *in situ* by MBE. Various crystal truncation rods (CTRs) are measured to reveal the detailed structures of the film. Resonant x-ray scattering is also performed to investigate the elemental distribution of the films.

A-14

Observation of Internal Energy Transfer in Luminescent Materials by Time-resolved XANES

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Luminescent lanthanide materials have a broad range of both well-established and emerging applications [1-3], including fluorescent lighting, solid-state laser materials, spectrum-converting phosphor coatings for photovoltaic cells, and dyes for biomedical assays. Most applications make use of transitions within the partially filled 4f shells of the trivalent lanthanide ions (which conveniently span the visible spectrum as one moves through the lanthanide series). These transitions are parity-forbidden, and therefore weak, in the bare lanthanide ions. Typically, the lanthanide species in a luminescent material is excited by energy transfer from a "sensitizer," i.e., a strongly absorbing host lattice or ligand [4-6]. The crystal or ligand field can also induce mixing of the lanthanide ion's 4f and 5d orbitals, making 4f-4f transitions weakly parity-allowed and increasing the intensity of the associated emission lines [7-10].

Extensive UV/visible spectroscopy studies [6,11-15] and theoretical calculations [16,17] have mapped most of the process of luminescence in many lanthanide materials. However, there have been no time-resolved optical absorption spectroscopy studies directly targeting the lanthanide ion in these systems, likely due to the forbidden nature of the 4f-4f transitions. In recent work at the APS, we observed a transient Eu L3-edge XANES signal following photoexcitation of several Eu-containing luminescent dyes [18]. The magnitude of this signal correlates well with the efficiency of the internal energy transfer (deduced indirectly from UV/visible spectroscopy). This opens up a novel approach to studies of energy transfer in luminescent materials, complementary to previous optical measurements. In addition, the transient signal shows an unexpected change in 5d electronic structure accompanying the 4f-4f transition, which suggests that the intrashell excitation is associated with a *change* in the degree of mixing of 4f-5d states.

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A-15

Development of Low-temperature Synchrotron X-ray Scanning Tunneling Microscopy (LT-SXSTM)

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Low temperature scanning tunneling microscopy (LT-STM) combined with synchrotron-based x-rays provides a new tool to capture chemical interactions and magnetic spin states on surfaces at high spatial resolution. The technique will drastically increase the spatial resolution, and it measures chemical and magnetic information along with surface topography. Here, we will present the current status of the ongoing development of a LT-SXSTM. The new system features, i.e., 4 degrees of freedom stages for the x-ray beam alignment, in-house developed LabVIEW and MATLAB-based control and analysis software, 6-axis active vibration isolation system and sample and tip cooling down to 4 Kelvin using a liquid Helium flow cryostat.

A-16

Structural Origins of Potential Dependent Hysteresis at the Electrified Graphene/Ionic Liquid Interface

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Electrical double layer capacitors (EDLCs) with room temperature ionic liquid (RTIL) electrolytes and carbon electrodes are promising candidates for energy storage devices with high power density and long cycle life. We studied the potential and time dependent changes in the electric double layer (EDL) structure of an imidazolium-based room temperature ionic liquid (RTIL) electrolyte at an epitaxial graphene (EG) surface. We used *in situ* x-ray reflectivity (XR) to determine the EDL structure at static potentials, during cyclic voltammetry (CV) and potential step measurements. The static potential structures were also investigated with fully atomistic molecular dynamics (MD) simulations. Combined XR and MD results show that the EDL structure has alternating anion/cation layers within the first nanometer of the interface. The dynamical response of the EDL to potential steps has a slow component (>10 s) and the RTIL structure shows hysteresis during CV scans. We propose a conceptual model that connects nanoscale interfacial structure to the macroscopic measurements.

A-17

Thickness-induced Structural Phase Transition of $BiFeO_3$ Thin Films

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Bismuth Ferrite ($BiFeO_3$: BFO) is one of very few materials exhibiting multiferroic properties at room temperature, being both ferroelectric (T_C ~ 1103 K) and G-type antiferromagnetic (T_N ~ 643K) [1]. In its bulk form, it possesses a rhombohedrally distorted quasi-cubic perovskite structure with ferrodistortive displacements along the (111)

direction, giving rise to a spontaneous polarization in the same direction. The structure of epitaxial thin films, however, depends critically on the amount of substrate-induced strain. This effect is accompanied by a significant enhancement of the spontaneous polarization and a series of phase transitions from rhombohedral (R) for small strains to R-like monoclinic (M_A) to T-like monoclinic (M_C) and to tetragonal (T) for larger strains, the latter two of which exhibit a giant c/a ratio.

BFO thin films grown on $SrTiO_3$ (STO) substrates (-1.4% compressive strain) have been shown to exhibit an R-like monoclinic structure (M_A) for films thicker than 26 nm. When deposited on LaAlO3 (LAO) substrates (-4.3% compressive strain), the films (thickness > 20 nm) show the T-like monoclinic structure (M_C) with enhanced c/a ratio (~ 1.25) at room temperature. Interestingly, for this highly strained BFO films, a structural phase transition with (M_C)-(M_A)-(T) sequence is observed as the temperature increases [3].

We have studied thickness-dependence of the film symmetry of the BFO films on both STO and LAO substrates via 3-dimensional reciprocal space map (3D-RSM) measurements. For moderately strained BFO films on STO substrates (grown by molecular beam epitaxy), a clear transition from monoclinic to tetragonal symmetry was observed as the film thickness decreases below 4 nm. The oxygen octahedral tilt pattern from half-order peaks indicates that this transition originates from the corner-connectivity of the perovskite oxygen octahedral network between the film and the substrate [4].

For highly strained films grown on LAO substrates by pulsed laser deposition, the transition temperatures for the temperature-induced (M_C)-(M_A)-(T) sequence decrease as the film thickness decreases, and for 4 nm and 5 nm thick films, (M_A) symmetry can be observed at room temperature. For even thinner film (2.4 nm), a tetragonal symmetry is observed at room temperature, but still maintaining the giant c/a ratio. Unlike a similar transition reported for moderately strained BFO grown on STO [4], there is no significant change in the relative intensity of half-order Bragg peaks at this transition. This indicates that the dominant distortions within the pseudo-perovskite unite cell do not dramatically change at the transition. This suggests that the structural evolution of highly strained BFO films cannot be understood in terms of rigid corner-connected oxygen octahedra, and therefore hints at a different mechanism for film/substrate interaction than what has been postulated for lower-strain BFO.

This work is supported in part by the U.S. Department of Energy (Contract No. DE-FG02-06ER46273, PI: Roy Clarke). Measurements were performed at Sector 13-BM-C, 33-ID-D, and 33-BM-C, Advanced Photon Source, Argonne National Laboratory, USA (The APS is operated under DOE contract No. DE-AC02-06CH11357). C.B., W.S., and H.M.C. were supported by the Materials Sciences and Engineering Division, BES-DOE.

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A-18

Imaging Interface with a Full-field X-ray Diffraction Microscope

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Surface and interface inhomogeneity at the micro- to meso-scale is the key to gain novel properties in many engineered materials, therefore a major interest of various studies. Availability of spatial-resolved and/or time and tempo-resolved structures of such systems would be critical to a better understanding and eventually functional oriented design of new materials. A diffraction based, full-field x-ray microscopy method, the x-ray reflection interface microscopy (XRIM), has been developed to study the structure of the surfaces, buried interfaces, and thin film material systems with the capability to measure the samples *in situ* and in real time.

A-19

Transient Strain and Phase Gratings in $BiFeO_3$ and FeRh Studied by Time-resolved Hard X-ray Nanoprobe

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We have developed a new experimental technique that combines optical transient-grating excitation and time-resolved synchrotron-based hard x-ray nanodiffraction probe at sector 7 of APS.

Transient optical gratings have been widely used to create ultrafast spatially modulated optical excitations. Conventional optical probes rely on optical diffraction from the overall ensemble of the modulation. As a result, local information within the extent of the probe beam cannot be measured, limiting the degree of spatial information that can be recovered and inducing uncertainty in the modeling of experimental results. By using the ultrafast hard x-ray nanoprobe technique developed at sector 7, the structural evolution within the transient grating induced spatial profile can be directly interrogated by focused x-ray pulses, providing insight into the spatiotemporal-dependent dynamics of functional properties such as time-dependent in-plane transport and localized structural phase transitions. In this poster, we show how this technique can be used to study the thermal transport in $BeFeO_3$ and the transient photo-induced phase transition in FeRh down to ~250 nanometers spatial scale and ~80 picoseconds time scale.

Enviromental and Geology

A-20

Synchrotron-based Characterization of the Chemical Characteristics of Carbon in the Subsurface and Root Zones to Improve Earth System Modeling of the Biogeochemical Cycling of Carbon

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Mechanistic understanding of carbon (C) biogeochemical cycling is essential for the development of Earth System Models and predicting the role of root zone and subsurface environments on climate change. Critical for that mechanistic understanding is determination of physical characteristics and chemical speciation of C in subsurface and root zone environments. X-ray absorption spectroscopy investigations of constituents of subsurface and root zone materials can provide critical insights into the chemical nature of C in these materials. Although soft x-ray scanning transmission x-ray microscopy (STXM) can provide spatially resolved chemical information about C in samples, the thickness and hydration state of environmental samples often preclude the utility of soft x-rays. This limitation can be overcome with the x-ray Raman technique, which enables measurement of C 1s x-ray absorption (XAS) spectra using high energy x-rays. We are using x-ray Raman approaches (Sector 20) to develop a mechanistic understanding of C cycling.

Our x-ray Raman investigations of C speciation in a variety of standards, microbial biomass, and soil constituents from peats, humic materials, Alaskan permafrost (Mishra, et al., 2013) and Spruce Site soils showed that x-ray Raman measurements can distinguish important C moieties like aromatic-C, amide-C, phenol-C, carbonyl-C, and carboxyl-C. Additionally, we have shown that x-ray Raman can enable quantitative determination of the relative percentage composition of these moieties. Comparisons of results determined with x-ray Raman to those determined with nuclear magnetic resonance (NMR) measurements indicate agreement and complementarity of the two approaches.

A-21

Reduction of Hg^{II} by Mn^{II}

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The reduction of Hg^{II} to Hg^0 can occur via both abiotic and microbially mediated processes; therefore, in addition to direct microbial reduction, abiotic reduction is a key component of global Hg biogeochemical cycling. Reduction of Hg by Fe^{II} (mixed $Fe^{II/III}$ mineral phases, Fe^{II} sorbed to minerals, and aqueous Fe^{II}) has gained significant attention in the past few years.

Manganese (Mn) is Earth's second most abundant transition metal next to Fe and resembles iron in several aspects of its geochemistry. Oxidation of Mn^{II} to Mn^{III} and Mn^{IV} is largely driven by microorganisms. In addition, recent studies have shown the importance of mineral surface-catalyzed Mn^{II} oxidation, which can influence Hg^{II} reduction. Reduction of Hg^{II} to Hg^0 coupled with oxidation of Mn^{II} to $Mn^{III/IV}$ is thermodynamically favorable at pH 7 and above. However Mn^{II} has never been documented to reduce Hg^{II} to Hg^0.

Here, we evaluated the potential of Mn^{II} to reduce aqueous Hg^{II} by characterizing the solid-phase Hg and Mn species with synchrotron x-ray absorption spectroscopy (XANES and EXAFS). Solution phase activity of Hg and Mn was monitored using ICP-AES. We find that the redox reactivity, the reaction pathways, and the resulting Hg speciation strongly depend on pH, presence of complexing ligands, and surface area of minerals.

At pH 7.5, the majority of Hg^{II} was reduced to Hg^0 within hours. Hg^{II} reduction was coupled with oxidation of soluble Mn^{II} to highly insoluble Mn^{IV} oxide. Formation of a Mn^{IV} oxide mineral auto-catalyzes the reaction for first few hours, followed by significantly slower rates of reaction concomitant with changes in Mn^{IV} mineral phase. The presence of redox inactive mineral surfaces (e.g. Al_2O_3 and TiO_2) inhibited the rate of Hg^{II} reduction. Hg^{II} reduction by Mn^{II} results in the formation of meta-stable Hg^I species in the presence of complexing ions such as sulphate, which slowly transforms to Hg^0 over an extended period of time. Since Mn^{II} can exist at up to millimolar concentrations in natural waters, Mn could have important implications on the overall mobility and bioavailability of Hg. Mn oxides, which are strong oxidants, likely re-oxidizes Hg^0; with Mn playing a dual role of reductant as well as oxidant of Hg in natural systems.

A-22

Update on the Factors Controlling U(IV) Speciation during (Bio)Reduction of Aqueous and Solid-Phase U(VI): Effects of Phosphate and Ti(IV)

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Uranium is a radionuclide contaminant of significant concern at DOE nuclear material production facilities such as Oak Ridge, TN, Rifle, CO, and Hanford, WA. Reductive remediation approaches, whereby soluble U(VI) is reduced to U(IV), have been studied extensively because of their potential to decrease U concentrations below the drinking water standard (<30 mg/L) through the precipitation of uraninite (UO_2). However, experiments at the Rifle, CO, site show that reduced U(IV) is not present as uraninite in the solid phase (Bargar et al., PNAS 2013, p.4506), and the analysis of reduced sediments from the Oak Ridge field site during the 2009 Emulsified Vegetable Oil (EVO) biostimulation campaign shows that U(VI) is reduced to a non-uraninite U(IV) form (Boyanov et al., in prep.). Despite these observations, the factors controlling the molecular speciation of U(IV) following U(VI) reduction and the stability of non-uraninite U(IV) remain poorly understood. Improved knowledge is essential for advancement of the current predictive models and in the design of nuclear fuel repositories.

As part of understanding uranium transformations and speciation in field-site sediments, we are continuing to study the biological and abiotic reduction of U(VI) in laboratory systems of increasing complexity. Here we show that Ti(IV) impurities inhibit uraninite formation during the abiotic reduction of aqueous U(VI) by magnetite and by other Fe^{II}-containing phases. Ti(IV) is commonly incorporated in natural magnetite and is also found in the magnetic sediment fraction at the Hanford nuclear site. Titanium-doped magnetite of varying Ti content ($Fe_{3-x}Ti_xO_4$, $0<x<0.5$) was reacted with aqueous U(VI). Analysis of the solids by U L_{III} edge XANES and EXAFS spectroscopy indicates that Ti incorporation in magnetite does not affect its ability to reduce U(VI) to U(IV). Reactions with Ti-doped magnetite resulted in a non-uraninite U(IV) phase, whereas reactions with pure magnetite resulted in nanoparticulate uraninite. Analysis of the EXAFS data indicates that the non-uraninite U(IV) is stabilized abiotically by the formation of a previously unobserved corner-sharing complex between Ti and U(IV), with a U(IV)-Ti distance of 3.43 Å.

We are also continuing to study the biomolecular mechanisms of U(VI) reduction by metal-reducing bacteria. Here we show that *Shewanella*, *Anaeromyxobacter*, and *Geobacter* spp. are able to slowly reduce U(VI) added in the form of hydrogen uranyl phosphate solids (HUP). Comparisons between bioreduction experiments that either favored or inhibited HUP dissolution suggest that these bacteria reduce predominantly the dissolved U(VI) fraction, despite their known capabilities to inject electrons into solid-phase Fe(III) oxidants. Analysis of the reduced U(IV) species in the solid-phase indicate the formation of a non-uraninite, edge-sharing U(IV)-phosphate complex, with a U(IV)-P distance of 3.40 Å. A similar form of U(IV) was observed in U(VI) reduction by the field-site isolate *Anaeromyxobacter* strain FRC-R5.

The stabilization of diverse non-uraninite U(IV) species by trace phosphate or Ti(IV) suggests that the U(IV) geochemistry relevant to subsurface systems may be more complex than just the formation of the least soluble form of U(IV), uraninite. Further studies are needed to elucidate the formation/stability of U(IV) species and to obtain the necessary information for their incorporation in computational field-scale models.

High Pressure

A-23

Nuclear Resonant Scattering at High Pressure and Low Temperature

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We present new capabilities of nuclear resonant scattering at high pressure using diamond anvil cell (DAC) at low temperature. Nuclear resonant scattering (NRS) includes nuclear forward scattering (NFS) and nuclear resonant inelastic x-ray scattering (NRIXS). NRS techniques are powerful tools for understanding lattice dynamics, thermodynamics, and electronic and magnetic properties of materials containing the resonant isotopes (Fe, Sn, Eu, Dy, and Kr). NRS experiment under high pressure and ambient temperature is routine at sector 3 of the APS. Due to technical difficulties, no capability of NRIXS under high pressure in a DAC and at cryogenic temperatures is available at any synchrotron radiation facility around the world. At sector 3, we are developing NRIXS technique at high pressure and low temperature. The new capability can be used in studies of pressure and temperature induced magnetic, superconducting and metal-insulator transitions. Fe partial phonon density of states and magnetic hyperfine field upon the pressure-induced magnetic and superconducting transitions in $EuFe_2As_2$ are shown as an example.

A-24

Time-resolved Studies of Phase Transition Dynamics

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Studies of the dynamics of pressure-induced phase transitions are a frontier scientific challenge that requires progress beyond traditional equilibrium understandings of states of matter. New diagnostic instrumentation and experimental platforms are enabling increased levels of detail and sophistication beyond simply identifying a transition pressure and the crystal structure of the phases. Time-resolved x-ray scattering measurements of transitions provide unique microscopic insights into the dynamics of pressure-induced phase transitions; including nucleation, growth and the observations of intermediate and/or metastable phases. In addition, tunability of the pressure drive permits evaluations of the influence of compression rate. In this presentation we will discuss our use of the dynamic diamond anvil cell (dDAC) to study the dynamics of phase transitions under various compression rates in simple metals.

Portions of this work were performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344 and funded by the LLNL LDRD program under project tracking code 11-ERD-046. Portions of this research were carried out at Petra-III at DESY, a member of the Helmholtz Association (HGF). We thank the experimental support team lead by H.-P. Liermann for assistance in using the Extreme Conditions Beamline (ECB) P02.2. Portions of this work were performed at HPCAT (Sector 16), Advanced Photon Source (APS), Argonne National Laboratory. HPCAT operations are supported by DOE-NNSA under Award No. DE-NA0001974 with partial instrumentation funding by NSF. APS is supported by DOE-BES, under Contract No. DE-AC02-06CH11357.

A-25

Electronic Structure of Gadolinium and Terbium at Extreme Pressure

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The 4*f* electrons in heavy lanthanides are atomic-like at ambient pressure. Their exchange interaction with the conduction electrons sets up an indirect, long-range RKKY interaction between the lanthanide cations leading to magnetic order below a critical temperature. Upon increased pressure, the reduced volume is expected to broaden the 4*f* states and bring them closer to the Fermi level, leading to a plethora of possible novel ground states. In particular, the high-pressure volume collapse observed in many lanthanides may signal the onset of 4*f*-conduction electron hybridization and/or direct 4*f*-4*f* interactions [1-3].

We investigated the effect of pressure on the 4*f* electrons of gadolinium and terbium. Through a combination of x-ray spectroscopy and transport measurements on the pure lanthanide metals and their dilute magnetic alloys with Y, we conclude that the volume collapse in Gd is unrelated to 4*f* electron interactions, whereas that in Tb seems to be due to increased hybridization (covalent mixing) between 4*f* and conduction electrons as manifested by the apparent onset of Kondo effect phenomena [4]. Furthermore, preliminary studies on the high-pressure magnetic order of these lanthanides and Dy will be discussed.

[1] B. Johansson, *Philosophical Magazine* **30**, 469 (1974).
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[3] A. K. McMahan et al., *Journal of Computer-Aided Materials Design* **5**, 131-162 (1998).
[4] G. Fabbris *et al., Physical Review B* **88**, 245103 (2013).

A-26

Multichannel Collimator for Structural Investigation of Amorphous Materials, Liquids, and Melts at Extreme Conditions

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One of the central aspects for obtaining high quality structural information of disordered materials by x-ray diffraction is perfect background subtraction. This is particularly difficult when employing high-pressure vessels, such as diamond anvil cells (DAC) and Paris-Edinburgh large volume presses (PEP). Their background contribution is very high compared to the low diffuse scattering signal of the sample, especially at high diffraction angles, and furthermore the background is changing during compression and decompression.

In order to overcome this challenge we have successfully installed a multichannel collimator (MCC) for the DAC setup at the GSECARS 13-ID-D beamline, APS, and the installation for the PEP at 13-IDC is in progress. The MCC is similar to the one used for the PEP at ID-27, ESRF [1]. The MCC is made of two concentric sets of 75 slits located 50 mm and 200 mm away from the sample, with slit sizes of 50 mm and 200 mm, respectively. The slits are separated by an angle of 0.8° from each other covering a total angle of 60°. The MCC leads to a significant increase in signal to background ratio and the background remains constant during compression. In order to show the capability of the new setup we will present preliminary results on Mg_2SiO_4 glass under high pressure.

[1] Morard, G., Mezouar, M., Bauchau, S., Álvarez-Murga, M., Hodeau, J.-L., Garbarino, G., 2011. High efficiency multichannel collimator for structural studies of liquids and low-Z materials at high pressures and temperatures. Rev. Sci. Instrum. 82, 023904. doi:10.1063/1.3551988

A-27

Pressure-Tuning Ferromagnetic State in Sr_2FeOsO_6 Double-Perovskite

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The newly synthesized iron-osmium-based double-perovskites Sr_2FeOsO_6 and Ca_2FeOsO_6 have attracted significant attention due to their exotic magnetic, electronic and crystallographic properties. Sr_2FeOsO_6 is an antiferromagnetic (AFM) semiconductor and crystallizes in the tetragonal space group I4/m, where the Fe-O-Os angles are collinear along the c axis. The chemically compressed Ca_2FeOsO_6 compound shows ferrimagnetism (FiM) and a primitive monoclinic structure with substantial distortions in the connectivity of OsO6 octahedra. X-ray magnetic dichroism (XMCD) measurements at the Os L2 edge were performed at high pressure and low temperature on the Sr_2FeOsO_6 AFM sample in order to check if hydrostatic pressure is capable of inducing FiM ordering in this compound in analogy with what is observed with Ca substitution (chemical pressure). Magnetization reversal curves taken with XMCD at 30 GPa and T=15 K show that a significant FM component has developed under pressure, with a coercivity not far from that observed for Ca_2FeOsO_6 at ambient pressure. The XMCD signal, although increased 4-fold at 40 GPa relative to ambient pressure, is still four times smaller than the signal obtained in the Ca compound at ambient pressure indicating that the sample did not fully convert into the FiM state of the Ca compound. High-pressure x-ray powder diffraction measurements on the Sr_2FeOsO_6 compound did not show evidence of a structural phase transition under pressure from tetragonal to monoclinic phase as observed with chemical pressure. This indicates that emergence of FiM can take place in the presence of local OsO_6 octahedral distortions (and their connectivity) without the need for a reduction in macroscopic symmetry.

A-28

Partnership for Extreme Crystallography (PX^2): New Facility for Advanced High-pressure Crystallography at 13-BM-C

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In situ high-pressure crystallography has been one of the principal analytical tools of mineral physics research and has significantly contributed to the development of this very fertile field. The concepts of comparative crystal chemistry, isostructural surfaces in the pressure – temperature - composition space, crystal chemical trends have all been coined and developed largely based on high-pressure single-crystal studies. Recent technological developments, such as novel detectors, focusing optics, gas loading systems, as well as developments in synchrotron-based high-pressure crystallographic techniques have opened new opportunities to explore the behavior of crystals with much smaller sizes (down to below 1 micrometer) to significantly higher pressures (well above 100 GPa) while retaining the main advantages of single-crystal techniques.

This presentation will offer an overview of the new joint project of the University of Hawaii, COMPRES and GSECARS located at APS experimental station 13BMC. Recent upgrade of the monochromator and focusing optics in that station allows us to extend the experimental capabilities offered at 13BMC to include powder and single crystal diffraction experiments in diamond anvil cell. Unique design combining Newport 6-circle diffractometer with laser spectroscopy optics, currently under commissioning, will enable crystal x-ray diffraction measurements at combined high pressure and high temperature. The PX^2 instrument currently offers 30 keV incident energy beam, focused to 25 × 12 mm size, with supplementary imaging system, which allows accurate sample monitoring and positioning. Several successful commissioning measurements of microcrystal samples in the air, solid inclusions in natural kimberlitic diamonds, as well as crystal inside diamond-anvil cell have been performed and will be reviewed.

Instrumentation

A-29

Creating a Fluorescence Probe for X-ray Beam Characterization

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Using the nano-fabrication facilities at Argonne National Laboratory's Center for Nanoscale Materials, a gold-fluorescence probe was constructed for use in measuring x-ray beam widths of energies above ~12ke . Optimized to measure a narrow vertical line focus beam, the probe consists of a series of vertical and horizontal lines ranging from 20mm-500nm width, with a gold-wall thickness of ~500nm. To avoid difficult alignment issues that result when using edge-on nanometer thick probes, this device has been designed to intercept the x-ray beam parallel to the height of the gold wall. This creates what a user would consider a gold-wire scan and reduces alignment requirements to a single degree of freedom. Internal calibration points have been included to assist in correcting for vertical or horizontal angular offsets. Multi-line series were patterned on the substrate to use the tool for both horizontal and vertical probing as well as make multiple measurements of each x-ray beam profile. Spacing between gold lines was varied to accommodate normal horizontal beam sizes (up to 100mm full-width half-maximum) as well as the narrow horizontal width of the vertical line focus beam, which may dip below 1mm. Vertical line focus beam heights are anticipated to be 50-100mm tall as a general rule, so the gold lines used to measure vertical beam profiles within any given series are spaced slightly farther apart. Examples will be given to show how the device works for circular mini-beam sizes in the range of 5-20mm (FWHM).

This work was supported by the U.S. Department of Energy, Office of Biological and Environmental Research, under contract DE-AC02-06CH11357. Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

A-30

Hybrid Pixel Detectors for the APS Upgrade

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To accommodate the higher brightness of an upgraded APS implementing an MBA Lattice, the Upgrade is exploring the possibility of developing fast pixelated area detectors with an integrating readout. The proposal includes two detectors:

FASPAX: The Fermi-Argonne Semiconductor Pixel Array X-ray detector (FASPAX) will provide an MHz burst image matched to the bunch rate of the proposed APS timing mode. FASPAX will record high resolution movies for time-resolved applications.

CDI Detector: A high dynamic range integrating detector with small pixels (50-60 mm) for coherence based science.

Both detectors implement a novel passive integrator for wide dynamic range, with logic to self-select the gain on a pixel-by-pixel basis. Interposer technology will be used to construct wafer-sized sensors without coverage gaps.

This poster will present technical details for the detectors, and provide an overview of R&D plans.

A-31

APS Modular Deposition System

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The "Modular Multilayer Deposition System" will be a custom thin-film deposition and ion milling machine with the capability to be modified in the future to suit APS mission needs as they arise. The deposition system is based around a precision in-vacuum linear motor, which translates substrates or mirrors at well-defined velocities and positions to various devices within the vacuum system for film deposition, ion milling, or measurements. The machine will be approximately 22 feet long, with four cryopumps, and multiple sputtering sources. One bank of sources utilizes 75mm diameter targets for fast target changes to satisfy simple coating requirements. A second bank of sources will have well matched magnetic packs and utilize 90mm wide × 250mm tall cathodes for the most demanding multilayer requirements. Upon delivery and after commissioning, the machine will be able to deposit single films, periodic multilayers, laterally graded and/or depth-graded multilayers, as well as multilayer Laue lens. The "base machine" is designed to have the ability to accommodate ion mills, *in situ* metrology such as Fizeau interferometry, dynamic apertures for true 3-D film thickness gradients, and other deposition sources such as cylindrical cathodes or ion-beam assisted deposition. The design also allows for an add-on device where the substrate cart can be automatically removed from the chamber for precision *ex situ* metrology, if such a need is required in the future.

This work was supported by the DOE office of Science, Office of Basic Energy Sciences, under contract No. DE-AC02-06CH11357.

A-32

Synchrotron X-ray Scanning Tunneling Microscopy (SXSTM) at the Advanced Photon Source

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The synchrotron x-ray scanning tunneling microscope (SXSTM) is a new *in situ*, high-resolution microscope technique, being developed at the Advanced Photon Source. The microscope images nanoscale materials at the surface with chemical, electronic, and magnetic contrast, taking full advantage of the chemical, electronic and magnetic sensitivities that synchrotron radiation offers, and combines these radiological sensitivities with the sub-nanometer spatial resolution that scanning tunneling microscopes attain [1].

Successful nanometer-scale, elemental contrast has been demonstrated with SXSTM instrumentation. The elemental sensitivity, demonstrated by this technique, was accomplished by placing a chopper system upstream of the SXSTM instrument. The chopper system modulates the incoming monochromatic beam of radiation, on and off, at a frequency of 3 kHz. By inserting an electronic lock-in amplifier and a topographic low-pass filter downstream, a modulated current signal, generated at the tip of the scanning tunneling microscope, can be de-convoluted into its component parts: (i) the chemical signal and (ii) the topographic signal [2]. These latest developments in the SXSTM instrumentation will prove powerful in surface characterization and will enhance our understanding of nanoscale physical phenomena at the surface.

This work was funded by the Office of Science Early Career Research Program through the Division of Scientific User Facilities, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant SC70705. Work at the Advanced Photon Source, the Center for Nanoscale Materials, and *the Electron Microscopy Center was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357.*

[1] http://www.aps.anl.gov/Xray_Science_Division/Sxspm/

[2] U.S. Patent Application 13/791,157

A-33

Developments in the X-ray Fluorescence Capabilities at 8-BM

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New hardware developments that enable focused, mission-driven science have been made over the past year at beamline 8BMB. These developments at have included new double multilayer monochromator (DMM) multilayers that have increased brightness (9-18keV) by 10-fold. Further, adding in new KB-mirror optics produces total of 100-fold flux increase. Two new mirror sets added include KB mirrors on generous loan by GSE-CARS, which provides 30um resolution at our large area instrument (LAI). In collaboration with the Optics group, we have also developed and installed a dedicated KB mirror set that provides 1 micron focus for our microprobe. We have used our beamline at 8BM in applied science. In one example, a collaborative project that examined the root nodules of plants, we reported on how to use x-ray analysis to map a path to increasing the amount of nitrogen that legumes deposit into the soil. This work will help sustainable agriculture practices and further diminish the environmental damage from overuse of nitrogen fertilizers. Since the average rate of energy capture by photosynthesis globally is approximately 130 terawatts, which is six times larger than the current power consumption of human civilization, this research is a significant finding towards our efficient capture of energy.

A-34

High Brightness Beam for Microcrystallography at GM/CA@APS

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GM/CA is a world leader in the development of microcrystallography capabilities for biological macromolecules. The combination of the GM/CA-developed quad-mini-beam collimator and advanced rastering and vector collect software tools has revolutionized microcrystallography. Recently, beamline 23-ID-B was reconfigured by shifting the focusing optics 3.8 m downstream. This significantly increased the source demagnification and led to a 4-fold increase in the 5- and 10-micron beam intensity.

Beamline 23ID-D is also being upgraded. A Pilatus3-6M with a 1.0 mm thick X-ray sensor was commissioned in January 2014 allowing shutterless data collection with high S/N. The detector specifications include 100 Hz frame rate, 10 MHz/pixel count rate, and high x-ray efficiency. The beamline optics and endstation are also being upgraded to provide a high intensity beam whose size can be variable rapidly in the range of 1-20 micron, a new air bearing goniometer with a sphere-of-confusion (SOC) of ~100 nm, a miniature sample XYZ stage that allows centering and scanning of a micron-sized crystal, and a new on-axis-visualization system that provides high resolution optical images of sample crystals.

The proposed Multi-Bend Achromat lattice upgrade of the APS will dramatically increase the source brightness and intensity into a micron sized spot. Both beamlines will be significantly improved by the source upgrade. Moreover the new microfocusing optics for 23ID-D will fully exploit the new source and could deliver a 500 nm (FWHM) beam with >2e13 photons/sec. This unprecedented flux density will provide new opportunities and challenges, and allow the study some of the most important problems in biology. Details of these developments will be presented.

A-35

SIXNS: Software Institute for X-ray and Neutron Scattering

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Over the past four decades, enormous advances in computing and in scattering have occurred independently, but today there are exciting opportunities to combine them to facilitate scientific discovery. Computational scattering science aims to do just this, but the full potential of this field has not been realized because appropriate computational tools and resources are not yet in the hands of scattering scientists.

Diverse experiments are performed with x-rays and neutrons at the scattering facilities in the U.S. No single software package can provide advanced data analysis for all users. A set of modular computational workflows would be more appropriate for discovery in scattering science, with a way to adapt these workflows to new types of experiments. The central engines in these workflows would be tools from computational materials science that are in broad use for predicting the structure and dynamics of materials.

We are in the conceptualization phase of an NSF program to plan a Scientific Software Innovation Institute (S2I2), a center for software infrastructure and technologies to serve the scattering community. SIXNS is focused on the subfield of materials physics, with workflows that would include, among other components, electronic ground state calculations by density functional theory and molecular dynamics, and electronic excited state calculations for x-ray spectroscopy. With modest coordination, other groups could be added to cover other fields of scattering research.

A-36

HD Colors and 3D: Watching Samples with XRF Tomography at the APS Microprobe at 2-ID-E

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After the first proof-of-principle x-ray fluorescence tomography experiment at the XRF scanning microprobe 2-ID-E at APS [M. de Jonge and S. Vogt, 2010] it was clear that this technique had great potential. However, the instrumentation needed extensive improvements prior to further applications, especially in terms of ease of use for both user and beamline scientist. Thus, we replaced the previous tomography setup with a new, robust stack of rotation and linear stages and implemented it permanently to a redesigned sample box. Now we are offering XRF tomography as a standard technique to our users and have unique results in geological, biological and environmental applications. Instrumentation development as well as data analysis will be presented and discussed based on results from a variety of user applications.

A-37

Current Capabilities of the 20-ID Micro-spectroscopy Station

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During the past few years the micro-spectroscopy station at 20-ID has seen continued improvements in capabilities. This poster summarizes the current capabilities and shows some example data. The station is a KB mirror based microprobe providing a focus in the range of 2-8 microns with flux approaching 5x10^{12} for the larger spot sizes. The available energy range is 4.4 to >35 keV. Some recent improvements include quick (fly) scanning in both ROI and full spectrum mode, confocal capabilities (25, 5, and 2 micron depth resolutions) using polycapillary or microchannel [1] optics, and a range of high resolution detection options, including a variety of miniXES spectrometers [2], microspec based WDX, bent Laue analyzers, and a polycapillary based flat crystal spectrometer. There is also the possibility for micro-XEOL measurements that will be described in another poster. We continue to support standard detectors such as four and single element vortex and 13-element Ge. A 100K Pilatus is available for microdiffraction and miniXES. [MAR165 area detectors can be requested for more-detailed micro-XRD studies. Low temperature (80K) capabilities are available for radiation sensitive samples, as well as a variety of sample mounts for anaerobic or radioactive samples. This combination of capabilities results in a versatile station that can be used for XRF mapping, valence sensitive mapping, microXANES and EXAFS, resonant and non-resonant emission spectroscopy on a wide variety of samples.

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A-38

USAXS/SAXS/WAXS Instrument for Materials Research

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Practical engineering materials typically exhibit complex microstructures spanning many decades in size. These are often responsible for the in-service properties. Advances and developments for new or improved materials require a detailed understanding of these microstructures over their entire operative size range. Complete characterization over the size range is usually complicated by the need to combine multiple techniques such as SAXS, SANS, electron or optical microscopy, tomography, etc. In this context, the Bonse-Hart type USAXS instrument at APS [Ilavsky et al., 2009] with its wide range of length scales characterized during one measurement was already a unique tool for the quantitative, statistically representative, characterization of material microstructures relevant to a wide range of scientific applications.

To address the needs of the user community, we have recently upgraded the USAXS instrument through increases in the measurable ranges of both scattering vector (q) and scattering intensity [Ilavsky et al., 2013]. At large q values, the combination with He-filled pinhole SAXS (pinSAXS) and in-air WAXS cameras improves the data quality by increasing sampling statistics and signal-to-noise sensitivity. More importantly, it extends the contiguous scattering vector q range coverage up to 6 Å^{-1} (energy dependent).

The need for environmental chambers to simulate *in-operando* measurements requires higher energy x-rays that minimize window absorption and reduce the exit angles. To reach x-ray energies between 20 keV and 30 keV, the USAXS instrument uses higher order Si(440) instead of Si(220) optics. The narrower Si(440) rocking curves also reduce $qmin$ to $\approx 3 \times 10^{-5}$ A^{-1}.

Currently, the combined USAXS/SAXS/WAXS instrument at the ChemMatCARS facility at APS, comprising USAXS with Si(440) crystals, pinSAXS, and WAXS, can span about five decades in q, characterizing structures from ≈ 30 micrometers down to ≈ 1 angstrom during one measurement of typically less than 8 minutes. The talk will present the technical design and capabilities of this instrument, as well as scientific examples taking advantage of this unique instrumentation.

ChemMatCARS Sector 15 is principally supported by the National Science Foundation/Department of Energy under grant number NSF/CHE-0822838. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science.

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A-39

Optics Testing Updates at the Optics and Detector Testing Beamline 1-BM of the Advanced Photon Source

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The bending magnet beamline 1-BM was recently reconfigured, in part, for optics testing. The beamline has water-cooled silicon double crystal monochromator with energy ranges from 6 keV to 28 keV. It has three stations A, B, and C. Experiments are performed in stations B and C, and can be operated in either monochromatic or white beam mode with beam size of horizontal of up to 80 mm and vertical of up to 2 mm is available. The 1-BM beamline optics testing capabilities agenda includes: 1) white beam topography, 2) monochromatic beam topography, 3) crystal studies, 4)testing the performance of the microfocusing mirrors and Lens. Here we present the beamline layout, experimental setup, and results of white beam and mono beam topography.

This work is supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.

A-40

X-ray Characterization of a Multichannel Smart-pixel Array Detector

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The Voxtel VX-798 is a prototype x-ray detector featuring a NIU-fabricated silicon sensor photodiode array of 48 × 48 pixels, each 130 um × 130 um × 500 um thick. Here we present the first synchrotron x-ray characterization of this detector and demonstrate its ability to sort individual x-rays by arrival time and energy. In our first trial run, the detector achieved a 30 ns time resolution and a < 1 keV energy resolution in agreement with design parameters. Notably, the "smart-pixel" technology allows energy and time resolution to be set and optimized *in software*. We found that the detector linearity follows an isolated deadtime model, implying that MHz count rates should be possible in each pixel. Measurement of the point spread function showed negligible spatial blurring. We also demonstrated that the detector could perform routine picosecond time-resolved x-ray diffraction and near edge fluorescence spectroscopy measurements with acquisition times considerably faster than currently available multichannel detectors. Finally, we explored the scientific impact of this new technology by detecting non-thermal diffuse scattering from sub-picosecond lifetime acoustic phonons, a measurement previously not feasible at the APS.

A-41

Status of Superconducting Energy Dispersive Detector Development at APS

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We present the current status of R&D efforts at the APS to develop the next generation of high-resolution (i.e., single-eV resolution) energy dispersive detectors using low-temperature microcalorimeters. Currently, we are focusing on developing a superconducting technology called microwave kinetic inductance detectors (MKIDs), which is a resonator-based technology. The currently available microcalorimeter technologies are all affected by the difficulty of multiplexing large numbers of pixels (>1000). Microwave kinetic inductance detectors, on the other hand, are intrinsically highly multiplexible. We have recently shown that it is possible to use a superconducting resonator as a thermometer for a microcalorimeter (TKID) enabling simplified multiplexing of low temperature microcalorimeters for x-ray spectroscopy.

A-42

The APS Detector Pool

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The APS Detector Pool provides Users with access to many different types of X-ray detectors and related equipment. The most popular devices include: Area Detectors (Pilatus 100K, Mar 165 CCD), Microscopy Cameras (Andor Neo, CoolSNAP, Prosilica), SAXS (Scint-X), Spectroscopic Detectors (Vortex SiDD, Oxford Ge, Amptek CZT), Point Detectors (Oxford Cyberstar, Mythen silicon strip, PIN Diodes), and Temperature Control Stages (Linkam). It also coordinates equipment loans from vendors for beamlines to test new and exciting products like the EIGER and the PiXirad. Additionally, the Detector Pool is doing detector and scintillator characterization at 1-BM.

A-43

Statistical X-ray Spectral Diffraction Imaging with Enhanced Linear Dynamic Range and Pulse Pileup Correction

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Photon counting type x-ray array detectors have several advantages compared to signal integrating type detectors (i.e. the elimination of readout noise), though most of the potential advantage of these detectors is untapped. These detectors uniquely provide access to the distribution of observed photon energies, which inherently contains much more information than the simple measurement of the number of photons that struck the detector. In the work here, a mathematical model was developed to model the observed energy distribution, and is exploited to acquire additional information about the detected photons and the detector. First, the model was used to mathematically calibrate the response of each pixel in the detector for its gain, variance, charge sharing. Second, the signal decay time at each pixel was measured and modeled, and provided a mathematical calibration for detector pulse pileup effects. Third, the model was used to perform a spectroscopic measurement from a broadband x-ray source by mathematically separating the contributions of each photon energy. Finally, the model was used to enhance the linear dynamic range of the detector.

A-44

The Possible Use of Photon Beam-Induced Thermoacoustic Waves in an Ultrafast Photon Beam Position Monitor System

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In this poster we discuss how existing phenomena can be exploited as a new photon beam position sensing modality. Pulsed laser sources interact with matter resulting in thermal expansion-induced acoustic wave propagation. This so-called thermo-elastic wave or thermo-acoustic wave is due to the elastic deformation resulting from localized temperature rise in a short time. This phenomenon can be used to detect the interaction of a pulsed photon beam with material. We demonstrate a thermoacoustic technique that allows us to characterize the elastic wave traveling in matter. We present experimental and Finite Element Analysis of mechanical wave propagation in matter launched by a focused ultrafast laser onto a sample. In the experiment, a laser Doppler vibrometer was used to measure the acoustic wave propagation in Silicon caused by a 10 ns, 140 mW drive laser pulse. This concept can be readily applied at the APS to monitor beam position in mirrors and monochromators, to detect the spallation-wave-propagation characteristics in materials, and to monitor structural health.

A-45

Exploring 3-dimensional Reciprocal Space: A Powerful Tool to Answer Basic and Applied Materials Science Questions

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The efficient exploration of large volumes of reciprocal space, made possible by the advent of high frame rate and low noise x-ray area detectors, allows for rapid characterization of a sample's structure and morphology, as all of its crystalline phases and their orientations can be determined simultaneously. The method is particularly powerful if not all the constituent phases (and the corresponding locations of their diffraction signals) are known, and aids in the discovery of unexpected phenomena or crystal structures. Additionally, the mapping of diffuse scattering yields information on local disorder or phonon modes present in the sample.

The authors present the latest developments in making reciprocal space mapping a readily accessible user technique at the APS. Large data volumes, collected with a few scans, can be processed to yield 3-dimensional reciprocal space maps, high-quality q-2q theta scans, or pole figure measurements which simultaneously span a continuous range of a few degrees in 2q. Data collection of an entire pole figure currently requires between 20 and 60 minutes for samples with reasonably strong diffraction signals using a Pilatus 100K detector at a bending magnet beamline. Local reciprocal space maps can be obtained in minutes, while the mapping of larger reciprocal space volumes may take several hours. The capabilities of this technique are highlighted using two topical research projects, namely the determination of the domain structure of ultra-thin multiferroic $BiFeO_3$ films via 3D reciprocal space mapping, and the characterization of the heteroepitaxial relationship of hematite (Fe_2O_3) films grown on indium tin oxide planar buffer layers and epitaxial nanowires used for photoelectrochemical water splitting through multi-phase pole figure measurements.

A-46

Second Harmonic Generation Microscopy Enables X-ray Diffraction at PPM Limits of Detection

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An integrated non-linear optical (NLO), synchrotron x-ray diffraction (XRD) instrument has been constructed at the Advanced Photon Source at Argonne National Laboratory. NLO microscopy, in particular second harmonic generation (SHG), is rapidly emerging as a sensitive technique for the detection of chiral crystals. Dilute physical mixtures of active pharmaceutical ingredients (APIs) within amorphous excipients were imaged on the combined instrument. With rapid sample characterization made possible by SHG, the combined instrument allows the guiding of "mini-beam" XRD experiments to be performed only in areas where trace crystallinity has been detected via SHG. In addition to negating the need for slow x-ray raster scanning, this instrument allows high signal to noise XRD experiments to be performed with overall crystallinity in the low ppm range. Enabling both NLO and XRD measurements, this instrument adds chemical information to an ultra-sensitive measurement of trace crystallinity, and lowers the limit of detection of synchrotron XRD.

A-47

A Comparison of Synchrotron-based and Laboratory-based XES and XANES

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Synchrotron x-ray facilities provide a gold standard in technical capability, instrumental diversity, and user support. That being said, many problems of high scientific or industrial importance have a poor fit with the necessary access model at synchrotron facilities, i.e., infrequent, short beamruns requiring travel and extensive, often blind, preparation of samples. With this in mind, and further motivated by the increased constraints on XAFS beamtime caused by the looming shut-down of NSLS-1, we are investigating whether the synchrotron radiation facilities for x-ray absorption near edge structure (XANES) studies and x-ray emission spectroscopy (XES) can be productively augmented by laboratory-based instruments that use only conventional x-ray tubes.

We will report the development of two lab-based x-ray spectrometers and compare and contrast their demonstrated or expected performance with spectra taken at the APS. First, we have constructed and commissioned an inexpensive, versatile modern lab XES/XANES instrument that uses only a tiny, 0.01 kW bremsstrahlung source. For XES studies, this simple, prototype system achieves impressive detection count rates that are intermediate between those expected at monochromatized ID and BM beamlines at the APS. Second, we are constructing a higher-powered XANES spectrometer that will reach monochromatized incident fluxes of approximately 107/sec with 1 eV or better energy resolution from 5 keV to 10 keV. This instrument will be part of a new user facility in the University of Washington Clean Energy Institute (CEI) where we anticipate strong impact on long-term programs in electrical energy storage science and technology.

This work has been supported by the U.S. Department of Energy, Basic Energy Sciences, by Grant No. DE-FG02-09ER16106 and by the University of Washington Clean Energy Institute. PNC/XSD facilities at the Advanced Photon Source, and research at these facilities, are supported by the U.S. Department of Energy - Basic Energy Sciences, the Canadian Light Source and its funding partners, the University of Washington, and the Advanced Photon Source. Use of the Advanced Photon Source is provided by ANL under support by DOE Contract No. DE-AC02-06CH11357.

A-48
Photon-integrating Pixel Array Detectors for Time-resolved and High Dynamic Range Experiments

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We present an overview of x-ray detector development activity at Cornell University. Photon-integrating pixel array detectors (PADs) are being developed to meet the needs of synchrotron users and to enable challenging experiments. Due to the photon-integrating pixel front-end, these detectors can tolerate instantaneous hit rates exceeding those of photon-counting PADs. Two detectors in an advanced stage of development will be described in detail. The Mixed-Mode PAD (MM-PAD) uses mixed analog and digital readout to achieve a pixel well depth of 4x10^{7} 8 keV photons while maintaining single-photon sensitivity. The detector frames at up to 1 kHz and can tolerate an instantaneous hit rate of 10^{12} photons/pixel/s and a sustained hit rate of 10^{8} photons/pixel/s. A tiled unit with 256x384 pixels has been used in several user experiments, including coherent diffractive imaging experiments at the APS and PETRA III, and time-resolved experiments at the Cornell High Energy Synchrotron Source (CHESS). The Keck PAD uses in-pixel frame storage to achieve time resolution down to 150 ns (compatible with single-bunch imaging at the APS). The Keck PAD has not yet been used at the APS, but data from high frame rate diffraction experiments at CHESS will be presented to demonstrate the detector capabilities.

A-49
The New APS Profile Deposition System

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The new APS Profile Deposition System is intended for fabrication of aspherically figured mirrors using the conventional profile-coating technique as well as differential deposition. With two vertically-oriented cathodes, fast arc-surpressing power supplies, a low-drift capacitance manometer, accurate gas flow delivery subsystems and modern control software, this machine will serve the APS user community for many years to come. A key new feature with this machine is the ability to translate the substrate through an arbitrarily defined velocity/position profile. Encoder feedback indicates that the stage maintains position placement with less than 4 microns of error during velocity trajectories. This capability allows film thickness gradients to be controlled by the stage, instead of masking which is a new capability at the APS. When the technique is matured, this can be used not only for aspherically figured mirror deposition, but also for laterally-graded multilayers. When used for conventional profile coating, the system can deposit on mirrors up to 120 mm long at a useful aperture length of 110 mm. When used in the horizontal configuration for differential deposition, the machine can accommodate useful aperture lengths of 150 mm. XRR measurements of a 500 bilayer WSi$_2$/Si reactively sputtered multilayer with a d-spacing of 1.8 nm deposited in early February suggest that the substrate transport, power supplies, gas delivery subsystem, and controls are operating properly. While parameter optimization will be a continuous process, this deposition system is "ready for business."

This work supported by the DOE office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357 and under Contract No. DE-AC-02-98CH10886.

A-50

Mechanical Design of Multidimensional Flexure Stages for X-ray K-B Mirror Focusing at Sub-50-nanometer Scale

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The Kirkpatrick-Baez (K-B) mirrors are sophisticated x-ray micro- and nano-focusing tools for synchrotron radiation applications. Hard x-ray K-B mirror focusing at sub-50-nanometer scale is required for future hard x-ray nanoprobe beamlines planned as part of the APS Upgrade project [1-4]. To meet the demanding mechanical specifications for such special K-B mirror mounting and manipulating system for the x-ray nanofocusing optics, a prototype of multidimensional flexure stage system has been developed for APS sector 34 x-ray microdiffraction station [5].

The design specifications, as well as the detailed mechanical designs for the individual flexure stages are presented in this paper.

Work supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.

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A-51

High-contrast Sub-millivolt Inelastic X-ray Scattering for Nano- and Meso-Scale Science

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Photon and neutron inelastic scattering spectrometers are microscopes for imaging condensed matter dynamics on very small length and time scales. Inelastic x-ray scattering (IXS) permitted the first quantitative studies of picosecond nanoscale dynamics in disordered systems almost 20 years ago. However, the nature of the liquid-glass transition remains one of the great, unsolved problems in condensed matter physics. It calls for studies at hitherto inaccessible time and length scales, and therefore for substantial improvements in the spectral and momentum resolution of the IXS spectrometers along with a major enhancement in spectral contrast. Here we demonstrate a conceptually new IXS spectrometer featuring a spectral resolution function with steep, almost Gaussian tails and sub-meV (~620 meV) bandwidth. A novel x-ray crystal optic - an atomic-scale diffraction grating - combined with a special collimating device is shown to produce unprecedented performance. The spectrometer opens up uncharted space on the dynamics landscape, precisely the space of vital importance for the science of disordered systems.

We report new results on the dynamics of liquid glycerol, in the regime that has become accessible with the novel IXS spectrometer.

A-52

First Test of a Real-time Charge Sharing Analysis Software for the GOTTHARD Detector with Micrometer Resolution

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GOTTHARD stands for 'Gain Optimizing microsTrip sysTem witH Analog ReaDout'. It is a 1D detector system based on the principle of charge integration with automatic gain switching capability. The detector is mainly intended for applications at XFELs, where it has to sustain the instantaneous deposition of many photons and retain the same data quality as a single photon counting detector. The standard GOTTHARD module has 1280 channels at 50-mm pitch (different pitch values are possible). Due to the high frame rate of 40 kHz (or even 200 kHz for a region of 256 channels) the GOTTHARD detector is also very interesting for synchrotron applications. One example is the application of the GOTTHARD to high-resolution imaging experiments by analyzing charge sharing between adjacent strips in order to obtain a sub-pitch spatial resolution. It is envisioned that this method will enable sub micrometer resolution. Another application would be the use of a GOTTHARD module to improve the energy resolution of IXS and RIXS spectrometers. The main disadvantage of the charge sharing analysis is the complicated data analysis. So far, large amounts of data have to be stored at a data rate of 100 MB/s and analyzed offline after the experiment. To overcome this, we developed a real-time analysis program that allows visualization of the data during the measurement. We will present results of first measurements performed at 1-BM, where we used the GOTTHARD for the characterization of a new focusing mirror.

A-53

Development of *in situ* X-ray Diffraction Capabilities using Modulation Techniques at NSLS-II

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An x-ray powder diffraction (XPD) beamline is being commissioned at the new synchrotron light source (NSLS-II) at Brookhaven National Laboratory, with an expected user operation start date of summer 2015. XPD is designed to be a multi-instrument facility with the ability to collect diffraction data at high monochromatic x-ray energies (30keV-70keV), offering rapid acquisition as well as high angular resolution capabilities. XPD is to combine high Q-space diffraction and real-space pair-distribution function measurements. Highly demanded technological materials are usually quite complex, nanostructured and heterogeneous. Understanding of their properties and structure is challenged by obtaining robust and quantitative (micro)structural information at several length scales and under varying temperature, pressure, magnetic or electric field and stress applications. By forcing the external stimulus in periodic oscillations, the structural part involved in the process may also change periodically (and reversibly) with time. Therefore, the frequency analysis of the diffraction signal provides selective access to those partial contributions, which are otherwise hardly detectable by static diffraction. The demodulated diffraction data contain only the signal from the active structural phase or from the active atoms involved in the periodic oscillations. These so-called phase-sensitive detection (PSD) and modulated enhanced Diffraction (MED) techniques [1] will be implemented at XPD and will be applied to a wide range of time dependent measurements. We will show preliminary data collected at NSLS and APS on oxidation/reduction studies of various metal oxide catalysts.

[1] Chernyshov, D. et al. Acta Cryst. 2011, A67, 327.

A-54

New Triple Detector System for Simultaneous Data Collection at Multiple Length Scales at DND-CAT

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The DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT), sector 5 of APS, has acquired and installed a new triple detector system for broad q-range SAXS data collection. It consists three, high speed (10 to 100 frames per second), CCD fiber-optic/phosphor coupled, area detectors produced by ©Rayonix L.L.C. The small-angle detector (0.017° to > 0.97° 2q), mounted at least 7.5 m from the sample, receives scattering mainly from above and inboard of the direct beam. The medium angle detector (0.87° to > 4.8° 2q), mounted 1m from the sample, receives scattering mainly from below and outboard of the direct beam; and the wide-angle detector (4.4° to 31° 2q) again above and inboard of the direct beam. Each detector receives an azimuth range of better than 120° including both the meridian and equator. The custom build vacuum chamber allows for windowless data collection or a small air path for a wide variety of sample environments. With the ability to collect data over three decades of q-space simultaneously at a high frame rate and over a large azimuthal angle, this system is ideal for a wide variety of static and dynamic experiments with isotropic or oriented samples.

A-55

1K Frame Store CCD Detector Collaboration between ANL and LBNL (Status and Preliminary Measurements)

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This poster will describe the status of the ongoing 1K Frame Store Fast CCD (1kFSCCD) detector collaboration between the Advanced Photon Source (APS) at Argonne National Laboratory (ANL) and the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL).

The 1kFSCCD detector uses a custom LBNL-designed CCD and readout IC. The CCD consists of 960 × 1920 pixels in full mode, or 960 × 60 in frame store mode. All modes use the 192 outputs for a nearly column parallel readout, enabling a fast readout. The detector is currently being used at 8-ID for x-ray photon correlation spectroscopy experiments. One of 8-id's common modes of operation is in the 960 × 92 pixel mode at 1000 frames per second. In order to enable long acquisition sequences from the 1kFSCCD, the ANL data acquisition software uses parallel programming with the Message Passing Interface (MPI) to perform real time image processing. The MPI software continuously performs, image descrambling, dark subtraction, and compress on the raw 200MB/s coming from the detector.

The poster will present the detector status and preliminary measurements along with future plans for the detector and future CCD devices.

Work supported by U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

A-56

Exploring Catalysis and Energy Storage at APS Beamline 9-BM

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As a beamline dedicated to the x-ray absorption spectroscopy, 9-BM is capable of covering a very wide energy range of 2145.5 eV (P-K edge) to 24350 eV (Pd-K edge). Along with routine XAFS measurements, this beamline is well-known for its capability to perform XANES measurements at the P-K and S-K edges, and has been popular for users in the research areas of environmental, geological, and earth sciences. In recent years more effort has been spent on the fields of catalysis and energy storage, focusing on catalysis for efficient conversion of energy resources into usable forms, and storage of such energy in high-performance and safe batteries or other energy capacitors. To understand and predict how catalysts and/or energy storage materials function, it's very important to characterize the materials under actual reaction conditions (*in situ* or *operando*). 9-BM has upgraded its capabilities to support the advanced needs for research.

At 9-BM, multiple sample cells and reactors, for operando catalysis and/or cycling battery experiments, have been developed for evaluating liquid-phase and gas-solid reactions that can be inserted into the beamline for studying materials under reaction conditions. The experimental stations are equipped with ventilation systems and gas manifold systems to accommodate a wide variety of reaction feed compositions including hazardous gases. A remote-accessed mass flow controller and an on-line analytical system with a mass spectrometer are available for measuring reaction conversion and selectivity.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is a valuable tool for understanding surface species and reaction intermediates of catalytic reactions. In 2012, an environmental reaction cell was customized to perform concurrent *in situ* DRIFTS and XAS at 9-BM. This is a unique capability at the APS that allows us to probe simultaneously the structural and local coordination environment of metal center(s) in catalytic materials using XAS and the nature of organic moieties coordinated to the metal center(s) using DRIFTS. This capability was used successfully in research on a La-Al_2O_3 supported Pd catalyst, illuminating why the turnover frequency (TOF) was improved with a Lanthanum-modified alumina support.

A-57

Double-crystal Monochromator Stabilization of Micro-collimated Beams Using Phase-sensitive Intensity Feedback

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One of the primary sources of intensity loss over long time scales is the slow drift of the Double Crystal Monochromator (DCM) 2nd crystal off of the Bragg peak. While PID type intensity feedback holding the DCM 2nd crystal on the edge of the Bragg peak can compensate the slow drift, this configuration increases the 2nd crystal susceptibility to vibrations. Pure software based feedback suffers similar problems since it requires moving the 2nd crystal substantially off of the Bragg peak to discriminate its location. Such detuning degrades intensity stability through micro-collimators, where an unstable DCM 2nd crystal can walk the beam along the collimating aperture defining the beam size. Here, we demonstrate phase sensitive intensity feedback (PSIF) [1, 2, 3, 4, 5] of the DCM 2nd crystal can stabilize the intensity of micron sized beams down to 0.42% RMS, close to the top up limit of 0.27% RMS. In this technique, the x-ray intensity out of the DCM is modulated by dithering the DCM 2nd crystal. Using a lock-in amplifier (LIA), we detect the x-ray modulation projection onto the dithering sinusoid and feed the resultant signal back into the DCM 2nd crystal's Piezo actuator. As the signal out of the LIA is proportional to the slope of the Bragg peak, this setup locks DCM 2nd crystal onto the Bragg peak maximum. We find that using the LIA's internal low pass filter, as opposed to an external integration stage, removes undesired low frequency oscillations and reduces settling times to the order of seconds. The high SNR inherent in phase sensitive LIA detection allows for 2nd Si (111) crystal to be dithered with amplitudes below 40 nanoradians, providing negligible spatial broadening of the beam.

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Materials Science

A-58

X-ray Studies of Intercalated Epitaxial Graphene on SiC(0001)

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Atomic-layer 2D materials have unique properties that are strongly influence by the underlying substrate. For epitaxial graphene on silicon carbide (EG/SiC), strong covalent interaction between Si and C at the EG/SiC interface leads to the formation of an electronically inactive graphene-like layer. This interfacial layer is known to strongly influence the behavior of the overlaying graphene, resulting in *n*-type doping and drastically reduced electronic properties. However, the electronic properties and structure of the interface layer can be altered by intercalating other elements into the interface layer. We examine the structure of H-intercalated and Ge-intercalated interfaces with x-ray reflectivity to produce an electron density profile for the intercalated interface and graphene layers along the SiC(0001) direction.

A-59

Investigating Silicon Solar Cell Impurities and Oxygen Catalyst Cation Distributions using Hard X-rays

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Materials are the energy conversion devices in renewable energy and energy storage technologies, and understanding the performance impact – good or bad – of material inhomogeneities is critical. In silicon photovoltaics, the conversion efficiency is generally limited by defects scattered throughout the bulk crystal, even when concentrations are at or below *parts per billion*. Using a focused x-ray beam with less than 50-nm spot size at the APS Beamline

26-ID Hard X-ray Nanoprobe, we determine that the recombination activity of dislocations in multicrystalline silicon is strongly correlated with the presence of metal nanoprecipitates. By coupling large-area (100s μm^2), 200-nm resolution x-ray fluorescence elemental mapping at APS beamline 2-ID-D with defect kinetics simulation, we optimize the time-temperature profile for metal impurity removal during silicon solar cell processing.

Similarly, for oxygen catalysis, activity is exquisitely sensitive to surface and near-surface chemistry. Using Coherent Bragg Rod Analysis (COBRA) of thin film surface diffraction data collected at APS beamline 33-ID-D, we successfully determine the near-surface distribution and segregation of cation species in highly active oxygen reduction and oxygen evolution catalysts. Synchrotron-based hard x-ray characterization of the nanoscale elemental variations in these renewable energy and energy storage materials provides valuable insight for their further development and optimization.

A portion of research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

A-60

Measuring Strains *In Operando* in Inverse Opal Si and Ni-Sn Alloying Anodes for Lithium-ion Batteries using X-ray Diffraction

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Lithium-ion batteries must have higher volumetric and gravimetric energy densities to be successfully deployed into many emerging applications, such as transportation. Alloy-based anode materials such as Si and NiSn are promising candidates for increasing the capacity and energy density of lithium-ion batteries (up to 10x the capacity of currently utilized graphite) but suffer from dramatic volume changes during (de)lithiation (up to 300%), which limit their lifetime. Nanostructured anodes represent one possible route for reversibly accommodating large volume changes, but their design is hindered by a lack of experimentally measured, quantitative strain data for NiSn anodes and few measurements of nanostructured Si anodes. The amorphous nature of lithiation in Si anodes and unclear lithiation mechanism in nanostructured NiSn anodes has greatly hindered *in operando* strain measurement to date. Using synchrotron-based x-ray diffraction techniques at the Advanced Photon Source, lattice strains in Si and NiSn coated nanostructured inverse opal nickel scaffolds were measured *in operando* in order to deduce the mismatch stresses and strains evolution during charging and discharging in the deposited anode material thin film (Si and NiSn) and the nickel scaffold. Since both anode films form strong bonds with the inverse opal nickel scaffold, the elastic strains measured in the nickel are similar to those present in the anode material, and thus the stress and strain state in the Si or NiSn can be indirectly measured. These inverse opal anodes were cycled with different voltage windows and (dis)charge rates in order to explore the sensitivity of strain evolution to changes in the electrochemical conditions associated with cycling. Strains measured in the nickel scaffold were directly correlated with the electrochemical cycling of the anode. These strains are discussed in terms of elasto-plastic deformation of the scaffold, cracking of the active material and other potential stress relief mechanisms.

A-61

Electrostatics-driven Assembly of Catanionic Membranes: *In situ* X-ray Scattering Studies

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Electrostatic interactions between positively and negatively charged groups induce the organization of biomolecules into highly complex structures. Mixtures of cationic and anionic amphiphiles represent an important model system for the self-assembly of molecules consisting of polar and hydrophobic groups. In particular, cationic and anionic molecules can spontaneously co-assemble into faceted vesicles resembling viral and bacterial shells. The focus of this work is to gain insight into two fundamental questions. 1) How is the global morphology of these self-assembled structures related to the packing of the constituent molecules? 2) Can we tune the inter-particle interactions to produce structures with diverse molecular packing and consequently diverse morphological shapes? To answer these questions, we studied the assembly of binary mixtures of cationic amphiphiles C_{16}-K_3^{3+} or C_n-K_2^{2+} (K = lysine) and anionic amphiphiles C_{15}-COO^- or $C_{n-1}COO^-$ as a function of pH, which tunes the electrostatic interactions between the lipid headgroups and lipid tail length (n = 14-22), which controls the inter-molecular van der Waals' interactions. We used a combined approach of *in situ* small- and wide-angle x-ray scattering (SAXS and WAXS), cryo-transmission electron microscopy (cryo-TEM) and molecular dynamics (MD) simulations.

In situ SAXS reveals that in all cases the assembled structures comprise of crystalline lipid bilayers, with thicknesses strongly dependent on the pH. For the case of intermediate tail length (C_{16}-C_{20}), WAXS reveals re-entrant structural phase transitions in lipid tail packing (hexagonal (hex)- centered rectangular (rect-C)- primitive-rectangular (rect-P)-rect-C-hex) as a function of pH [1]. Overall, combined x-ray scattering and cryo-TEM shows that closed-faceted vesicles are observed only for cases where the lipid tails pack in a hexagonal lattice. Otherwise, the assembly consists of planar bilayer ribbons [2]. Molecular dynamics simulations provide an explanation for this correlation between the membrane morphology and molecular packing, as well as the variation in the bilayer structure as a function of pH.

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A-62

Chemical and Structural Quasi-reversibility of Fe(III)/Fe(IV) Redox in $NaFeO_2$ for Sodium-ion Batteries

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There have been extensive efforts to efficiently use iron-based materials as cathodes for lithium-ion batteries, since iron is the most abundant transition metal on the earth crust. While there are a few examples that utilize Fe(II)/Fe(III) redox such as $LiFePO_4$, the reversible operation of Fe(III)/Fe(IV) redox, which will provide higher operating potential and subsequently higher specific energy, has not been successful in lithium-ion cells. However, recently renewed interests on sodium-ion batteries have identified that the quasi-reversible operation of Fe(III)/Fe(IV) redox is possible in iron-based layered oxide materials for sodium-ion batteries. The sodium-ion batteries employing cathodes based on earth abundant sodium and iron will be ideal for large-scale electrical energy storage system, for which the cost factor is of primary importance. However, these iron based layered oxide materials still show low cycle performance and the redox of the unusual Fe(III)/Fe(IV) couple needs to be better understood.

In this study, we have examined the quasi-reversibility of layered $NaFeO_2$ materials in sodium-ion cells. The chemical instability of Fe(IV) state in charged cell is revealed by *ex*-Mössbauer spectroscopy. The *in situ* synchrotron x-ray diffraction further observed the inequilibrium phase transition pathway during charge-discharge cycle. These findings explain the quasi-reversibility of $NaFeO_2$ in sodium cell, and provide guidance for the future development of iron based cathode materials for sodium-ion batteries.

A-63

Ab initio Molecular Dynamic Simulations of Reactions in Batteries

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We will present the results of *ab initio* molecular dynamics simulations for reactions in Li-ion and Li-air batteries. The blue moon ensemble was used to simulate the dissolution of Li from the surface of $LiMn_2O_4$ into the aqueous phase. Metadynamics was used to simulate the decomposition of Lithium Bis(oxalate)borate in the electrolyte di(ethylene glycol)-substituted trimethylsilane. These calculations provide estimates of the free energies and reaction barriers for the fundamental mechanism of these reactions.

A-64

Probing Large-wave vector Phonons in Silicon and Silicon-Germanium Nanomembranes via X-ray Thermal Diffuse Scattering

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Phonons, the quantized modes of lattice vibration influence the electrical, thermal, mechanical and optical properties of bulk and nanoscale systems. In silicon nanoelectronics, large-wavevector phonons dominate the thermal conductivity and impact electron mobility through the intervalley scattering of electrons. In nanoscale thermoelectrics such as Si-Ge a strategy for improving the thermoelectric figure of merit, ZT, is to reduce the lattice thermal conductivity. The phonon dispersion plays an important role in determining the phonon group velocity, mass-disorder, and boundary scattering rates, and the phonon heat capacity, all of which contribute to the lattice thermal conductivity. A deeper fundamental understanding of vibrational phenomena in nanoscale systems enables precise and controllable engineering of these phenomena.

Synchrotron thermal diffuse x-ray scattering (TDS) probes thermally populated phonon modes in nanoscale systems with wave vectors spanning the full Brillouin zone. TDS measurements were performed at the nanoprobe facility at sector 26-ID-C of the APS, using suspended silicon and silicon-germanium nanomembranes fabricated in collaboration with the CNM. In these experiments, the Brillouin zone of 97-nm-thick and 21-nm-thick silicon nanomembranes was mapped by taking multiple slices through reciprocal space and extracting information about the phonon population. Profiles extracted along the high symmetry directions of the 21-nm-thick silicon nanomembrane data show regions of excess intensity compared to their bulk counterparts in directions with an out-of-plane component but not in directions with solely in-plane components. Experiments carried out on a 60 nm-thick

Si-SiGe-Si trilayer membrane show regions of excess TDS intensity compared to bulk silicon. The magnitude of the excess intensity is greater than what is expected from solely the effects of alloying, suggesting an additional contribution arising from the spatial confinement.

A-65

Novel Approach to *In situ* XAS Study of Bi-functional Catalyst Systems

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In situ x-ray absorption spectroscopy (XAS) with reaction control can enable detailed investigation of the reaction mechanisms for variety of heterogeneous and electro- catalysts. Bi-metallic catalysts in form of alloys and mixes are widely used as they provide combination of catalytic mechanisms. Previous XAS experiments (along with other spectroscopic techniques) have attempted to understand these mechanisms using primarily bulk alloys. Inconclusiveness and discrepancies in the results comes from the fact that a XAS signal is collected from the surface and the bulk of the catalyst, where the oxidation reaction takes place at the surface.

We have developed a novel approach to study bi-functional catalysts by using sub-monolyer depositions of one metal onto the solid nanoparticles of another metal. The results presented are for a model anode Ru@Pt catalyst for methanol electro-oxidation in Direct Methanol Fuel Cells (DMFCs). By the use of an original electrodeposition technique, ca. 0.3 monolayer of Ru was deposited on the surface of unsupported Pt nanoparticles (Ru@Pt). The presence of Ru atoms only at the surface of nanoparticles turns a bulk-sensitive XAS technique into a surface methodology which permits correlation of the x-ray absorption fine structure at the Ru K-edge to the role of Ru atoms in the methanol oxidation process.

Our study uniquely tracked the role Ru plays in methanol oxidation by deposition of a 30% monolayer of Ru on the surface of Pt nanoparticles (Ru@Pt) and using *in situ* XAS, specifically x-ray adsorption near edge structure (XANES) spectroscopy and extended x-ray adsorption fine structure (EXAFS) spectroscopy at the Ru K-edge. Measurements at various potentials allowed correlation of both the electronic and atomic environment around surface Ru as a function of applied potential to methanol oxidation. This novel technique of deposition and subsequent direct observation of surface mechanisms can be expanded to other Pt alloyed systems such as Sn, Ph, Rh, etc.

A-66

Interfacial Evolution in Four Dimensions: Dendritic Solidification and the Effects of Highly Anisotropic Microstructures

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In industrial casting processes, solidification of metallic alloys often involves the formation of solid dendrites or platelets. The ability to observe and quantify the interfaces of such morphologically and topologically complex structures provides unprecedented insights into microstructural evolution. However, the growth and dissolution of these complex interfacial morphologies remains poorly understood due to the lack of 4D (i.e., time and space resolved) studies. Recent advances in the temporal resolution (0.25 s) and spatial resolution (1 mm) in synchrotron-based 4D x-ray microtomography (SR-CT) experiments, along with developments in data processing, computing power, and software, allow us to investigate the real-time interfacial dynamics of the solidification process. Examples of the 4D SR-CT results in the Al-Cu and Al-Si systems will be presented and discussed.

A-67

UO_2 Melt Structure and Properties: First X-ray Scattering Measurements of UO_2 up to 3300K

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Uranium dioxide (UO_2) is the major fuel component for most nuclear power reactors in use today (even mixed oxide fuel is typically ~90% UO_2). A key safety concern in nuclear accidents is the melting and subsequent leakage of radioactive UO_2 as it burns through its containment. The very high melting temperature (3140K), however, has also severely limited study of the liquid phase. High-temperature solid UO_2 is also interesting from a fundamental point of view as it exhibits a pre-melting super-ionic lambda transition at 2670K. Approaching this transition there is a rapid rise in specific heat capacity above 1800K, and a corresponding upturn in the thermal conductivity. In this work we report high-energy x-ray pair distribution function measurements of solid and liquid UO_2 from room temperature up to 3300K. These measurements are used to validate and refine high temperature MD models of UO_2 from which accurate liquid properties including thermal expansion, heat capacity, and isothermal compressibility are obtained.

A-68

An Exploration of Anode Materials for Sodium-ion Batteries

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Large-scale implementation of energy from renewable sources will require equally extensive local storage capabilities to regulate their inherently variable output. Energy storage in sodium-ion based electrochemical systems has recently emerged as a complementary technology to well-established lithium-ion analogues. Both are capable of high-power operation and, while Na-ion chemistries possess lower energy densities, they are not plagued by resource availability concerns associated with Li-ion batteries, making them prime candidates for large-scale stationary storage applications. We have investigated several classes of candidate active materials for Na-ion battery electrodes using a variety of synthesis and advanced characterization techniques. The goal of these studies was to gain detailed knowledge of the material structures and electrochemical reactions underlying charge storage. Anode materials investigated include hard carbons and the alloying-type materials Sn and Sb which were studied using techniques including inelastic x-ray scattering and *operando* HEXRD. Half cell and full cell Na-ion results were finally compared to analogous Li-ion systems to gain a deeper understanding of the promise of this new technology.

A-69

Tethered Nanoparticle Polymer Composites: Structure, Dynamics and Rheology

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Polymer nanocomposites are ubiquitous in the modern world and find application in many diverse areas. However, limited control of the nanoparticle dispersion in the polymeric host offered by the current technologies limits our ability to fine tune the nanocomposite bulk properties and extend their utility.

In this poster, we will explore the possibility of employing nanoparticle tethered with polymers chains to overcome the strong van der Waals attraction forces among the nanoparticles and limit their aggregation tendencies. Model nanocomposites comprising of silica nanoparticles grafted with polyethylene glycol (PEG) chains and dispersed in PEG matrix were characterized using a variety of experimental techniques, including small-angle x-ray scattering (SAXS), x-ray correlation spectroscopy (XPCS), electron microscopy and mechanical rheology. SAXS results were found to be instrumental in determination of the phase behavior of these nanocomposites, and a comparison with contemporary studies is presented. The synthesis platform was found to provide a fine control over the bulk properties of well-dispersed nanocomposites with an ability to facilely vary their flow properties over a large range through small increments in particle loadings. Further, SAXS results revealed an anomalous structural pattern wherein particle correlation was found to decrease with increasing loading. This structural anomaly was followed a dynamic anomaly as indicated by XPCS measurements, the nanoparticle motion was found to get faster with increasing loading. We conclude by elucidating the possible origins of this anomalous behavior and its connections to the bulk flow properties in these materials.

A-70

Nanoscale Quantized Fluorescence Tomography Reconstructions

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Nanoscale x-ray computed tomography (nCT) reconstructions offer a unique means to view structure and structural changes of solid objects on the nanoscale. The use of both x-ray absorption spectroscopy and x-ray fluorescence microscopy techniques have been used to extend nCT work to included elemental and chemical contrast. The goal of this work is to generate a three dimensional reconstruction of the object which is not only a contrast mechanism but also accurately quantifies element concentration and chemical states. To achieve this goal we have developed a method where the nCT reconstructions are used to develop 3D model elemental maps. The model is then used to compute the theoretical x-ray fluorescence microscopy map, which is then iteratively fit to the experimental x-ray fluorescence microscopy data. The end result is a three dimensional reconstruction with a quantifiable elemental concentration per voxel.

A-71

Effect of Polar Discontinuity on the Growth of Epitaxial $LaNiO_3$ Ultrathin Films

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We have conducted a detailed microscopic study of epitaxial $LaNiO_3$ ultrathin films grown on (001) $SrTiO_3$ as a function of thickness by using oxide molecular beam epitaxy with *in situ* surface x-ray diffraction and soft x-ray absorption spectroscopy at the Advanced Photon Source to explore the influence of polar mismatch on the resulting structural and electronic properties. Our data demonstrate that the initial layers on the nonpolar $SrTiO_3$ surface exhibit a smaller than expected out-of-plane lattice-spacing with a Ni valence of 2+. As the film becomes thicker, the lattice constant expands to its elastic limit, and the Ni valence approaches 3+. We will also discuss the energetics for vacancy formation during the initial growth as determined by density functional theory calculations.

Work at the APS, Argonne is supported by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

A-72

Impact of Synthesis and Doping on the Microstructure of High-k Dielectric Materials

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High k dielectrics play a critical role as gate dielectrics not only in conventional semiconductor devices, but also in power electronic devices based on gallium nitride and silicon carbide. Typically synthesized using atomic layer deposition, achieving stable microstructures of these oxides is crucial in order to achieve long-term reliability as well as delay the onset of dielectric breakdown. Therefore, strategies such as the insertion of dopants to frustrate their crystallinity as well as the design of nanolaminate materials combining group 4 oxides such as TiO_2 or HfO_2 with other materials such as Al_2O_3 and SiO_2 have been pursued in the literature. One of the challenges of these materials is their amorphous nature. This complicates the characterization of the microstructure of the material beyond confirmation of their lack of crystallinity using techniques such as XRD or TEM, and limits our ability to understand the impact of synthesis on the microstructure of the films.

The goal of this work is to establish a link between synthesis and microstructure of high-k dielectrics based on group-4 oxides, using a combination of *in situ* and *ex situ* characterization of both the synthesis process and the materials. The core of our approach is the use of x-ray fine structure (XAFS) to understand the impact of synthesis and doping on the coordination environment of Hf in pure and doped HfO_2 films synthesized by ALD. These measurements have been taken at 9-BM, as part of a broader project aimed at developing *in situ* ALD capabilities at the Advanced Photon Source. From a fundamental point of view, one of the key advantages of HfO_2 is the existence of three crystalline phases of increasing symmetry. This allows us to rationalize the impact of increasing disorder on the fine structure, and evaluate the ability of the Debye-Waller factors to account for the presence of increasing disorder on the oxide materials.

A-73

Chromium Redox on the Charging of Li-air Batteries

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Global warming due to greenhouse gas emission from large and rather inefficient usage of hydrocarbon fuel for energy production and transportation is an undeniable grand challenge of the century. Steps to electrify transportation can both provide efficiency boost in usage of traditional fossil fuels and allow flexibility in energy sources from coal to natural gas to renewables. Li-air (Li-O_2) batteries promise to provide energy densities upwards of three times that of current state of the Li-ion batteries utilized in emission-free electric vehicles (EV). Reducing the energy loss associated with Li_2O_2 electrochemical oxidation is paramount toward the development of efficient rechargeable lithium-oxygen (Li-O_2) batteries for practical use. While $LaCrO_3$ is inactive for oxygen evolution upon water oxidation in alkaline solution, it is found to have excellent catalytic effect towards Li_2O_2 oxidation. Further exploring Cr-based catalysts showed that Cr nanoparticles (Cr NP) with an average particle size of 40 nm, having oxidized surfaces, had comparable surface area activities to $LaCrO_3$ and mass activities comparable to noble metals Pt and Ru. Unlike Pt/C and Ru/C that promote electrolyte oxidation in addition to Li_2O_2 oxidation, no evidence of enhanced electrolyte oxidation was found having Cr NP relative to Vulcan carbon. X-ray absorption spectroscopy at the O K and Cr L edge revealed a redox process of Cr^{3+} « Cr^{6+} on the surface of Cr NP upon Li_2O_2 oxidation, which might be responsible for the enhanced oxidation kinetics of Li_2O_2 and the reduced charging voltages of Li-O_2 batteries. This catalytic process is much unlike the traditional surface physisorption route encountered for oxygen evolution in aqueous media.

A-110

Trends on X-ray Optics for synchrotron Beamlines: large, nested, flat, curved, one or two dimensional, monolayer, multilayer or stripe multilayer

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In our contribution we will be giving an overview on one- and two-dimensional multilayer optics for synchrotron Beamlines. We will be showing our current developments in coating of large X-ray optics up to 150 cm, multi-stripe multilayer optics for tomography beamlines and Montel-Optics for synchrotrons.

Total-reflection X-ray mirrors are required at beamlines for beam guidance and beam alignment. These optics are used at grazing incidence angles, therefore, more and more optics with lengths of 100 cm and longer are needed. A sputtering system for substrates up to 150 cm has been installed at the Helmholtz-Zentrum Geesthacht. The variation in film thickness over the whole length has been investigated by X-ray reflectometry. Good uniformity (< 2%) and low roughness (< 0.5nm) were achieved.

We also will show first results of a 50 cm laterally graded multilayer optic, developed for a special mini-synchrotrons. The deviation of the desired shape is less than 0.3 %. A new special coating unit for long multilayer coatings was installed last year.

At imaging beamlines multilayer optics are often used as double crystal multilayer monochromators (DCMM). For instance, in tomography a homogeneous and stable beam profile is required, in order to achieve optimal background corrections. Due to the high coherence of radiation the optical components need to be designed with particular care in order to avoid a reduction in beam quality.

We will also be showing a multi-stripe multilayer optic with an optimized coating for different beam energies in the range of 10 to 45 keV which is used at the TomCat beamline at SLS. Multilayer coatings with up to 5 stripes were produced with films homogeneities < 0.2% as well as gradients.

At least we will be showing the first Montel Optics especially designed as an analyzer system for inelastic scattering. Laterally graded multilayers were optimized for energy of about 9.1 keV. The first Montel optics have already been delivered to DLC and NSLS. With our new technology we are able to minimize the diagonal dimension to 15 mm.

Keywords: Multilayer, X-Ray optics, incoatec, synchrotron, DCMM, Montel, nested

For more information, please contact Frank Hertlein Hertlein@incoatec.de

Nanoscience and Nanotechnology

A-74

Characterizing the Local Structure of Nanoclusters of $Au_{98}Ag_{46}(SR)_{60}$ by X-ray Absorption Fine Structure Spectroscopy

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The synthesis and characterization of nanostructures should go hand in hand with the continuous development of techniques. Also, the synthesis of nanoclusters is complex and still not fully controllable. Synchrotron techniques such as x-ray absorption fine structure spectroscopy (XAFS) are the tools of choice for the characterization of nanostructures. However, since there are no references (i.e., inorganic compounds) with known structures close to the structures under investigation the usually used fingerprint method is not applicable. Other techniques include EXAFS fitting and *ab initio* calculations, e.g., using the FEFF code. We face several difficulties in the characterization process using these techniques. The nanoclusters of the desired structure do not comprise 100% of the synthesized sample; there is a size distribution, a distribution of different structures (core-shell and random), and remaining precursors [1]. To help determine the structure of the synthesized sample without a long time analysis process we have started generating a catalog of extended x-ray absorption fine structure (EXAFS) model spectra and x-ray absorption near edge structure (XANES) model spectra of Au-Ag nanoclusters using FEFF [2].

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A-75

Studying Supported Nanoparticle Coalescence using Grazing Transmission Small-angle X-ray Scattering

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Supported nanoparticles are researched for application in catalysis [1], fuel cells [2] and sensors [2]. To this end, it has been shown that the overall performance of the particles is a function: size, shape, assembly and stability over time [3]. In recent years, many exciting methods to achieve control over these factors have been reported. Generally, one can divide these efforts into either a bottom-up or top-down approach, depending on whether the before mentioned parameters are manipulated during or after synthesis, respectively. Here, electrodeposition from a deep eutectic solvent is used as a simple method whereby metal ions are reduced on an electrode surface, electrochemically.

Nanoparticle electrodeposition has been extensively studied in many aqueous systems. Specifically, the mechanisms of particle nucleation and growth have been extensively researched in an effort to control the resulting particle morphology. Specifically, the idea of particle coalescence has, to this point, remained elusive [4] because it is difficult to observe how the particle morphology changes *in situ* over a very short period of time (ms). However, this may not necessarily be true in DESs, as these solutions contain very high concentrations of ions that impede transport significantly compared with aqueous solutions [5]. Using a grazing transmission geometry, we are able to observe a slow progression of Ag particle coalescence just after nanoparticles are formed on a glassy carbon surface. Therefore, we offer experimental observation of particle mobility and coalescence, as it is observed in two different DES solutions. From these results, we aim to understand and manipulate particle assembly by tailoring the solution from which the particles are deposited.

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A-76

Exploring the ALD Overcoat Catalysts using Small-angle X-ray Scattering

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Overcoated catalyst prepared through atomic layer deposition (ALD) is a rapidly developing field because the prepared catalyst is both coking- and sintering-resistant. It is believed that nano-sized pore (1–5 nm) formed during the calcination leads to the inhibiting of the coking and sintering of catalyst, while maintaining the high catalytic activity. However, the pore formation has not yet been conclusively understood due to the limited characterization. We investigate the mechanism of pore formation during the calcination using *in situ* time-resolved small-/wide-angle x-ray scattering, high-resolution x-ray diffraction as well as grazing incidence small-/wide-angle x-ray scattering technique, to understand how the ramping rate, heating condition, nature of supports and overcoated materials, size of metal catalyst, and overcoated layer, and composition of metal catalyst, affect the formation of the pore.

A-77

Stepwise and Epitaxial Growth of DNA-Programmable Nanoparticle Superlattices

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Many researchers are interested in developing methods for rationally assembling nanoparticle building blocks into periodic lattices. These superlattices could in principle be used to create designer materials with unique properties, useful in optics, biomedicine, energy, and catalysis. DNA is a particularly attractive ligand for the programmable assembly of nanoparticles, as synthetically tunable variations in nucleotide sequence allow for precise engineering of the nanoparticle hydrodynamic radius and hybridization properties. These factors, in turn, dictate the crystallographic symmetry and lattice parameter of the assembly. Although superlattices with diverse geometries can be assembled in solution, the incorporation of specific bonding interactions between particle building blocks and a substrate would significantly enhance control over the crystal growth process. Herein, we use a stepwise growth process to systematically study and control the evolution of a bcc crystalline thin-film comprised of DNA-functionalized nanoparticle building blocks on a complementary DNA substrate. We examine crystal growth as a function of temperature, number of layers, and substrate-particle bonding interactions. Importantly, the judicious choice of DNA interconnects allows one to tune the interfacial energy between various crystal planes and the substrate, and thereby control crystal orientation and size in a stepwise fashion using chemically programmable attractive forces. We further demonstrate that such assemblies can be grown epitaxially on lithographically patterned templates, eliminating grain boundaries and enabling fine control over orientation and size of assemblies up to thousands of square micrometers. The effects of drying on the superlattice structure are examined; surprisingly, this allows for a reversible contraction and expansion of the colloidal crystal with a greater than 60% decrease in the volume of the lattice. Ultimately, this work will be important for the development of on-chip material platforms that take advantage of the periodicity and/or controlled density of the inorganic core, such as optical metamaterials, photonic crystals and heterogeneous catalysts.

A-78

Understanding *Operando* Battery Nanomechanics: Lensless Strain Mapping via *in situ* Coherent X-ray Diffractive Imaging

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Lithium ion batteries are ubiquitous in mobile devices, increasingly used in transportation, and promising candidates for renewable energy integration into the electrical grid. To fulfill their powerful promise, electrodes with increased capacity, faster charge rates, and minimal capacity fade must be developed. Understanding the nanomechanics at the individual particle level is a crucial step in achieving these ambitious goals. Here we reveal three-dimensional strain evolution of a single $LiNi_{0.5}Mn_{1.5}O_{4-d}$ nanoparticle in a coin cell battery under operando conditions during charge/discharge cycles with *in situ* coherent x-ray diffractive imaging. We report the first direct *operando* observation of both stripe morphologies and coherency strain. Our results suggest the critical size for phase separation is 50 nm. We directly measure the elastic energetics of the phase transformation. Surprisingly, the characteristics of the femtojoule energy barrier depend on charge versus discharge. This approach opens a powerful new avenue for studying battery nanomechanics, phase transformations, and capacity fade under *operando* conditions in a wide range of electrochemical energy storage systems.

Other

A-79

Optics for APS Operations and MBA Upgrade

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The APS relies on high quality x-ray optics to deliver the x-ray beam to the sample under study, and in many cases to collect the relevant signal from the experiment (such as with crystal analyzers). As one of the world's largest hard x-ray synchrotron radiation facilities, the APS has invested early in optics fabrication and characterization infrastructure. This supports the APS scientific mission by developing and providing state-of-the-art optics and related services efficiently and at low cost. Over the years, the APS has developed expertise and know-how in many key optics areas including crystals, mirrors, multilayers, and zone plates. To support APS mission, 1-BM Optics and Detectors Test Beamline has been established with capabilities including Monochromatic topography, White beam topography, Talbot grating interferometry, K-B mirrors testing, and zone plate and MLL testing.

As the APS is embarking on the MBA upgrade, the APS Optics group has a set of strategies to develop optics that meet future needs. This includes:

- Improve crystal optics fabrication techniques
- Develop advanced thin film optics capabilities
- Develop advance simulation tools for optics' design and beamline optimization
- Push focusing optics' performance to nano-scale resolution
- Enhance ex-situ and beamline optics evaluation tools and techniques
- Continue working with other DOE facilities, industry, and other institutions to supplement in-house capabilities.

A-80

Distribution of Macro-Ions at Air-Water Interfaces

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Studies of ion distributions at air-liquid interfaces are leading to a fundamental understanding of interfacial phenomena in myriad physical, chemical, atmospheric, and biological processes. Prior to the last 2 decades, the depletion of ions from the air-water interfacial region was believed to explain the increase of macroscopic interfacial tension with increasing bulk ionic-concentrations. But with advancements in non-linear optics, x-ray scattering, and molecular dynamics simulations in the last 2-3 decades, this simplistic picture has changed. Contemporary research demonstrates that anions can populate the interface depending on their size, charge, and polarizablity. But this new picture is not universally accepted because of shortcomings and limitations of experimental measurements. For instance, although the non-linear optical methods, like Second Harmonic Generation or Sum Frequency Generation, are truly interface sensitive, the interpretation of the data does not provide a direct window on the interfacial structure. Moreover, the small sizes of ions compared to the interfacial roughness of liquid surfaces diminish the resolution of ion-distributions obtained by use of interfacial x-ray scattering measurements. We will demonstrate that this limitation can be overcome by selecting ions that are large, in the form of polyoxometalates (POM)s, compared to the interfacial roughness. POMs are very well known inorganic metal-oxo clusters with a wide range of well-defined charges, shapes, and sizes, and that are easily soluble in water. We probed both in-plane and out-of-plane distributions of Keggin POM ions, with 3e- charge and 1 nm diameter, near air-water interfaces by using x-ray reflectivity and Grazing Incidence Diffraction measurements. The results show the formation of a monolayer of the POMs just beneath the air-water interface and the in-plane separation between the POMs in the monolayer is found to be much shorter than the bulk separations measured by small-angle x-ray scattering measurements. Though there is no theoretical understanding yet for this novel aggregation behavior of charged macro-ions beneath the interface, our findings can help in predicting the behaviors of macro-ions like proteins, viruses, etc., near interfaces.

A-81

X-ray Emission Analysis of the S-state Intermediates of the Photosystem II Protein Complex

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Large-scale implementation of man-made systems based on artificial photosynthesis to harvest solar energy could lead to an abundant chemical storage of solar power in the form of hydrogen.

The process of splitting water ($2H_2O \rightarrow O_2 + 4e^- + 4H^+$) during photosynthesis requires a catalyst, the oxygen-evolving complex, or Mn_4Ca cluster, located within the trans-membrane metalloprotein complex photosystem II. Characterization of sub-millisecond reactive intermediates in this system is central to understanding the catalysis involved in water splitting.

X-ray emission spectroscopy techniques provide information on the electronic structure of these states.

Following the progression of x-ray induced damage, we demonstrate the feasibility of collecting room temperature Mn Kb x-ray emission data on the dark stable S_1 state of photosystem II in two different beam modes: continuous monochromatic beam, and pulsed pink beam. The dosage/damage relation for continuous beam measurements matches preliminary room temperature models well. Additionally, the determined damage thresholds, likely representative of other metalloproteins, are sufficient for the analysis of electron dynamics and the catalytic mechanism. Computational modeling of protein damage kinetics in monochromatic mode is extrapolated to higher dose deposition rates. The results support the theory of 'detection before destruction' both for pulsed pink beam and free electron laser sources.

In order to learn more about the water-splitting step in particular, time-resolved Kb emission laser pump (to advance the catalytic cycle), x-ray probe experiments were conducted in pulsed pink beam mode. For the first time ever, emission data are presented for the S_3 ® S_0 transition.

Room temperature data are shown for all S-states. Analysis of the lower states agrees well with limited published results. For the water splitting transition, we observe immediate Mn reduction, within 50 ms from the final flash. This likely eliminates two of the five currently supported mechanisms of water oxidation, with radical coupling mechanisms or an OH- nucleophilic attack left as the strong candidates.

A-82

Alignment of Low-dose X-ray Fluorescence Tomography

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X-ray fluorescence microscopy (XFM) allows one to quantifiably image various trace metals simultaneously with no need for staining. XFM has relatively deep penetration depths, which allow us to perform tomography on many-micrometer-thick cells or tissues. Many people have started to be interested in XFM tomography because of these benefits. However, the sample has to be exposed to x-rays significantly longer since approximately 60 projections or more are required for tomography. In order to reduce x-ray dose to the sample, the idea of dose fraction is discussed but it is yet to be applied as it is harder to align projections to common rotation axis. In this poster, we suggest what we could do better for low-dose projections.

A-83

U.S. Forest Service Research at the APS

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Approximately 400 million acres of public and private forest land in the United States need restoration. Typically, restoration means removing excess forest biomass. The estimated cost for one round of forest restoration is $69 billion, which is overwhelming compared to the $0.3 billion the U.S. Forest Service is funded annually for restoration efforts. However, inaction is not an option. The accumulation of excess forest biomass fuels catastrophic wildfires. In addition to the devastating loss in lives and property, the U.S. Forest Service typically spends over $3 billion annually fighting wildfires and costs continue to rise. Faced with this staggering challenge, the U.S. Forest Service is pursuing advanced materials research in an effort to find market-based outlets for the excess forest biomass removed during restoration. The aim is to recoup some or all of the restoration costs and accelerate forest restoration without having to rely upon additional funding.

One avenue to increase the use of forest biomass is to improve the durability of forest products. Durability issues include fungal decay, fastener corrosion, and dimensional instability. A commonality between these durability issues is moisture. Decay and corrosion only occur in moist environments, and moisture-induced swelling and shrinking cause dimensional instability. U.S. Forest Service researchers have recently begun to utilize the APS to help address these challenging durability issues. X-ray fluorescence microscopy (XFM) at beamline 2-ID-E is a new tool for forest products research. XFM has the sensitivity and spatial resolution to map out adhesive infiltration into wood cell walls. Using a custom-built humidity chamber, XFM was also used to identify moisture thresholds for chemical transport through wood cell walls, and to quantify diffusion coefficients of chemicals transporting through different wood cell wall layers. Chemical transport through wood cell walls is believed to be the onset mechanism for decay and fastener corrosion, and if the mechanism can be better elucidated improved protective treatments could be more effectively developed. Diffusion coefficients are also needed to optimize biorefinery processes for the production of fuels, chemicals, and nanomaterials. XFM is used to study fungal decay processes as well. X-ray computed tomography (XCT) at beamline 2-BM-B has also been used to investigate the effect of adhesive molecular weight distribution on the flow of adhesive into wood cellular structure. Current XFM and XCT results will be presented.

A-84

Identification of Dopaminergic Neurons of the Substantia Nigra Compacta as a Target of Manganese Accumulation

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Manganese (Mn) is a trace metal important for proper body development and function. It serves as a cofactor to a variety of proteins, including mitochondrial super-oxide dismutase and glutamate-synthetase. Overexposure to Mn can result in a neurological condition known as *manganism,* which resembles Parkinson's disease (PD). Although the mechanism(s) by which manganese overexposure results in neurological disruption is not known, bulk measurement techniques (e.g., ICP-MS) have identified the globus pallidus and thalamus as targets of Mn accumulation in the brain. Unfortunately, smaller structures cannot be analyzed by these techniques. Here x-ray fluorescence microscopy was used to measure the metal content and distribution of the substantia nigra (SN) in thin (10-30 µm thick), unfixed tissue sections from the rodent brain at tissue level resolution (~20×20 µm^2). Additionally, *in vivo* labeling of dopaminergic cells of the SN pars compacta (SNC) was achieved using a retrograde tracer administered during survival surgery which subsequently allowed for XRF imaging of cells *in situ* at subcellular resolution (~0.5×0.5 µm^2).

Tissue level images revealed that chronic Mn exposure resulted in a significant increase in Mn content in Mn treated groups as compared to saline injected control animals in both the SNr (>163%) and SNc (>170%). No other metal concentrations (i.e. Fe, Cu, and Zn) were significantly changed as observed at the tissue level due to Mn treatment. An increased Mn concentration was observed in the SNc as compared to the SNr within a given experimental group, with the difference between the two structures about 10%.

At the cellular level, Mn is heterogeneously distributed with the highest content observed in the cytoplasm, possibly adjacent to the nucleus. Average Mn concentrations range between 40-200 µM depending on the experimental group. Concentrations of 100 µM have been observed to cause cell death in culture [2] although the half inhibitory maximal concentration is at least 300 µM [3]. Decreased tyrosine hydroxylase staining further supports that chronic Mn exposure decreases dopaminergic neuron density in treated rodents. Direct observation of Mn accumulation in the SNc could establish a biological basis for movement disorders associated with manganism, specifically that insult to the SNc may decrease dopaminergic signaling in the basal ganglia resulting in motor dysfunction. Additionally, Mn accumulation in the SNc may help clarify the relation between Mn exposure and the predisposition to the early onset of PD.

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A-85

Performance Simulation of Two Beamlines with the APS MBA Upgrade

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The APS MBA upgrade will open up new scientific opportunities as well as technical challenges. Many beamlines will benefit from the two orders of magnitude increase in brightness and coherent flux enabled by the MBA lattice. The beamline design and optics requirements will be also significantly impacted, and therefore need to be revisited to profit from the new source. We recently developed a new fast tool for beamline simulation based on a hybrid method combining ray tracing and wavefront propagation [1]. In this presentation, expected performances of two APS upgrade beamlines, the resonant inelastic x-ray scattering (RIXS) beamline and the *in situ* nanoprobe (ISN) beamline [2], are calculated with the new MBA lattice and compared to those calculated with the current APS source. The possible optimization of the beamline layouts and the corresponding optics requirements (e.g., mirror figure errors and stability of monochromators) are evaluated in order to take full advantage of the MBA upgrade.

[1] X. Shi, R. Reininger, M. Sanchez del Rio, and L. Assoufid, J. Synchrotron Rad. (2014) Accepted.

[2] J. Maser, B. Lai, T. Buonassisi, Z. Cai, S. Chen, L. Finney, S.-C. Gleber, C. Jacobsen, C. Preissner, C. Roehrig, V. Rose, D. Shu, D. Vine, and S. Vogt, Met. Mater. Trans. A 45, 85 (2014).

Technique

A-86

Coherence Conversion for X-ray Spectroscopy at Few-femtosecond Resolution at the Advanced Photon Source

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A proof-of-principle experiment was conducted for a recently proposed method [1] to obtain a few-femtosecond time resolution in x-ray spectroscopy and diffraction at the APS, i.e., more than a factor 1000 better than the bunch duration. The underlying idea is that the spatial and temporal resolution in an optical measurement are given by the number of electromagnetic-field modes contributing to a data point (the fewer, the better). In most cases, the spatial/momentum and temporal/energy dimensions of phase space are considered separately.

However, by applying a proper projection out of phase space, a high resolution in space/momentum from the transverse coherence of x-rays can be put to use to improve the time resolution in experiments that preserve the transverse coherence of the synchrotron beam.

Currently, the APS has one transverse mode in tens of microns in the vertical direction, and several ten thousand longitudinal modes at eV energy resolution. The latter corresponds to about 100 ps in time resolution when applied directly without coherence conversion.

The method is best understood for the case of x-ray, near-edge absorption spectroscopy in transmission through a thin-film sample with transversely coherent x-rays incident along the surface normal. A femtosecond laser pulse hitting the sample at an angle of tens of degrees from the surface normal induces fs-scale changes in an x-ray absorption edge. A line defined by the intersection of the laser pulse with the film travels across the sample at superluminal velocity and trails behind it the time history of the photoexcitation in a map of time to a spatial dimension. Direct resolution of this time history would require a fs-resolving imaging detector, which does not exist. However, by going into the far field of the x-ray diffraction pattern from this structure, the lateral motion is no longer evident, and information on correlations internal to the time history is contained in the angles of the diffraction pattern. It is then possible to reconstruct the time history by computational inversion of the diffraction. Direct far-field detection would require an impractical working distance of hundreds of meters, but the angular resolution can alternatively be obtained from an analyzer crystal in Bragg reflection. The method is background-free and self-synchronizing: As long as the fs laser pulse hits the sample at any time that x-rays are incident on the sample, a diffraction pattern is produced, and all other x-rays remain in the original transverse mode. Likewise, a small change in x-ray absorption only leads to a reduction of the diffracted intensity, but no background on the signal.

A proof-of-principle experiment was done to study the effect of photoexcitation on the bond charge in GaAs, and the results will be presented. The experiment was done in diffraction instead of transmission, using 30-fs pulses from a Ti:Sapphire oscillator to photoexcite GaAs oriented to the (222) reflection. X-rays in the APS 324-bunch mode were tuned to just below the As K edge for a high sensitivity to the Ga-As bond charge. There is a clear signature of an instantaneous, i.e., not average-thermal effect of the laser on the diffraction pattern.

[1] B.W. Adams, presentation at the **APS-U MBA Lattice Workshop, October 2013.**

A-87

The X-ray Streak Camera at the APS, Recent Results

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Sector 7 of the APS is operating an x-ray streak camera with a time resolution of 2 ps to do x-ray absorption spectroscopy and x-ray diffraction of processes that are faster than the 50 to 150 ps duration of the APS. Recent results obtained with the streak camera will be presented, including near-edge absorption spectroscopy of iron in photoexcited potassium iron hexacyanoferrate, and diffraction from satellite peaks due to acoustic phonons in germanium.

A-88

Probing Microelectronic Devices for Single Event Effects Using Focused X-ray Pulses

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Integrated circuits (ICs) scheduled for use in satellite systems need to withstand the harsh radiation environment of space [1]. Energetic particle strikes on an integrated circuit can generate a charge carrier track along their trajectory that results in current or voltage transients which can disrupt the IC's normal operation, and potentially degrade the performance or disable the operation of systems in which they reside. It is critical that all ICs under consideration or scheduled for on-orbit deployment are tested beforehand so that their susceptibilities to these single event effects (SEEs) are documented, characterized, and if possible mitigated [2].

In order to fully understand SEE susceptibilities, it is important to develop methods that can simulate the effect of charged particle strikes – i.e., a method that can deposit charge in a highly localized area around individual circuit elements such as transistors, and measure the IC's response to the impulsive charge deposition. In principle, using a beam of energetic particles with low flux, such that a single particle would be incident on a transistor at any given time, would be the ideal method. Although focused ion microbeams have been used to locate nodes in ICs that are sensitive to SEE, the ion flux in such systems is relatively high and the location of the ion strike is still uncertain by ~ 5mm. No existing energetic ion beam sources allow for the regular placement of incident ions with high enough spatial resolution and accuracy to probe SEE in modern ICs. Lasers can be used to generate charge carriers and inject current into a circuit, but most wavelengths are too long and cannot be focused to a spot size corresponding to the sensitive node of an individual circuit element in sub-100 nm fabrication technologies.

Furthermore, lasers will not penetrate metallization layers, which can cover virtually all of the functional area on newer ICs. In contrast to heavy ion or pulsed laser techniques, x-rays have properties that are advantageous for characterizing individual circuit elements on microelectronic circuits – they can be focused to extremely small spots and can penetrate metallization. We have previously used the Advanced Photon Source to show that focused x-ray pulses can generate charge transients in localized positions on microelectronic devices. These measurements were highly successful, and a paper on the technique has been recently published [3]. We will present data from our recent APS measurement campaigns that compare x-ray induced transients with those produced by both lasers and heavy ions. We will show that having the capability of focusing high energy radiation provided by synchrotrons like the APS on localized positions on microelectronic circuits is of high value for SEE susceptibility testing. We will also discuss the how the upgrade of the APS will benefit SEE testing using ultrashort x-ray pulses.

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[2] R. A. Reed, et al., "Single-event effects ground testing and on-orbit rate prediction methods: the past, present, and future," IEEE Trans. Nucl. Sci., vol. 50, pp. 622-634, 2003.

[3] D. Cardoza, et al., "Single Event Transients Induced by Picosecond Pulsed X-Ray Absorption in III-V Heterojunction Transistors," IEEE Trans. Nucl. Sci., vol. 59, pp. 2729-2738, 2012.

A-89

Combined Cryogenic Ptychography and X-ray Fluorescence Microscopy of Biological Samples

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X-ray fluorescence microscopy (XFM) offers high sensitivity for quantitative mapping of elements in biological samples. However, a majority of biological structures are not easily visualized in XFM since XFM is relatively blind to the light elements (such as H, C, N, O) which are the main constituents of biological materials. Ptychography, a more recent method of coherent diffraction imaging (CDI) that delivers quantitative phase contrast and high spatial resolution, provides a good solution to visualize biological ultrastructure. While the spatial resolution of ptychography can in theory reach the wavelength limit, radiation damage to biological samples affects the obtainable resolution. A good solution towards this problem is to work with frozen-hydrated biological specimens under cryogenic conditions. Therefore, the combination of cryogenic ptychography and x-ray fluorescence microscopy will provide us with simultaneous views of ultrastructure and elemental compositions of specimens at high resolution. The Bionanoprobe at the Advanced Photon Source (APS) is a first-of-its-kind instrument for x-ray fluorescence studies of trace elements within whole cells and tissue sections. It offers a high spatial resolution, cryogenic conditions, and 3D tomographic imaging capabilities, providing us with good opportunities to integrate cryogenic ptychography seamlessly alongside the existing fluorescence imaging capability.

A-90

Time-resolved XEOL Capability at the Sector 20

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We have implemented a time-resolved x-ray excited optical luminescence (TR-XEOL) detection system at sector 20 of the Advanced Photon Source (APS). This system can be used to track x-ray excited optical luminescence in both the energy (wavelength) and the time domain. The standard XEOL setup uses an Avantes spectrometer with 2048 pixel CCD detector. It can detect photons over a range of 200 – 1100-nm with 2.4 nm resolution. The TR-XEOL uses a HORIBA Micro-HR scanning monochromator with a Hamamatsu R928 photomultiplier tube (PMT). The scanning monochromator equips with an interchangeable dual grating turret, our current choice of gratings are: 600 and 150 gr/mm. The best achievable resolution is about 0.6 nm. The PMT has a spectral response from 185 – 900 nm, and a rise time of 2.2 ns (anode pulse rise time). We can measure standard XEOL spectra and optical excited XAFS and XANES. We can also do Micro-XEOL mapping in conjunction with micro-XRF mapping and resonant x-ray emission (RIXS/RXES) simultaneously with TR-XEOL. All setups are available at ambient condition and low temperature (80K). The whole setup is portable and can be used on both the 20BM and 20ID lines. It is available to general users.

PNC/XSD facilities at the Advanced Photon Source, and research at these facilities, are supported by the U.S. Department of Energy - Basic Energy Sciences, the Canadian Light Source and its funding partners, the University of Washington, and the Advanced Photon Source. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. Research at University of Western Ontario is supported by NSERC, CRC, CFI, OIT and the University of Western Ontario.

A-91

X-ray Scattering from Optically Trapped Nanoparticles

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Nanoparticles cover the intermediate length scale between bulk materials and atoms and molecules. Studying their interaction with radiation, such as optical photons and x-rays, can provide insight into how collective properties of materials emerge from their atomic building blocks. A major barrier to applying x-ray scattering to freestanding micro- and nano- scale objects is their tendency to freely move within the intense beam from synchrotron source. Typically such objects must be securely bonded to a substrate, which can alter their internal structures. While the forces moving such particles are not completely understood, we believe optical tweezers may be a solution.

Optical tweezers provide a unique method to control small particles, ranging from several microns to tens of nanometers. Using optical techniques, these laser trapped particles can be manipulated and forces on the objects in the trap can be measured. Combined with phase modulation techniques, optical traps with different geometries and polarization can be generated, resulting in an accurate orientation of anisotropic particles [1,2].

We have built an apparatus of dynamic holographic optical tweezers which is compatible with x-ray diffraction imaging at beamline-34 of APS. We are going to test the x-ray diffraction from optically trapped micro- and nano-particles of both materials and biological sample origin with the goal of eliminating the barrier to studies of free standing objects due to uncontrolled sample drifts. By observing the Bragg peaks, we can determine and optimize the

stability of trapped particles. Then we will use coherent x-ray diffraction imaging [3] to image a free floating sample explicitly selected and trapped by the user for the first time.

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[2] Zijie Yan, Justin Jureller, Julian Sweet, Mason Guffey, Matthew Pelton, Norbert F. Scherer, 2012. "Three-Dimensional Optical Trapping and Manipulation of Single Silver Nanowires," Nano Letters, 12 (10), 5155-5161.

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A-92

In situ Coherent Diffraction Imaging at APS

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One of the great promises of coherent x-ray diffraction imaging (CXDI) is the ability to image structure in three dimensions at the nanoscale from *in situ* environmental cells. This capability arises from the fact that the ultimate spatial resolution of the imaging method does not rely on x-ray optics with potentially limited working distance.

At the APS there are efforts to image samples in several environments and conditions. These include high temperature with and without corrosive gases, high pressure within diamond anvil cells, cryogenic temperatures to access low-lying phase transitions and to mitigate sample radiation damage, in the presence of electric or magnetic fields and ultrafast laser pump/x-ray probe measurements. This poster will present highlights of these efforts.

A-93

Recent Advances and Current Capabilities of Polishing Activities at the Advanced Photon Source

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The mission of the Polishing Laboratory in the Optics Group at the Advanced Photon Source (APS) is to support beamlines by in-house fabrication of x-ray optics and advise scientists on vendors and procurement of substrates. To meet the requirements of future APS MBA lattice source, there is a need for higher-quality crystal optics and mirrors. Most fabricated optical components are custom made, yet, the manufacturing process must be robust enough to reliably reproduce the results.

For example, the process of fabricating fixed geometry KB mirrors using metal thin film deposition [1] strongly relies on the ability to produce substrates with excellent surface quality. Surface finish of 1Å RMS roughness and strict control of surface figure irregularity are necessary requirements. Additionally, the strain-free state of the crystal surface is very important for performance of all crystal optics.

Currently, the Optics Group is on the research path to develop a reliable and repetitive polishing process to achieve 1Å RMS surface roughness on flat silicon substrates with slope error below sub-microradian. Frequent intermediate surface metrology provides best feedback on the progress of process development. The choice of polishing equipment, specifically the size and stability of polishing machines, will also be discussed.

We will present recent surface finish results achieved with optical pitch continuous polishing process, as well as polished crystal's x-ray topography at 1-BM Optics and Detector testing beamline.

This work is supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.

[1] Profile coating of KB mirrors at the Advanced Photon Source, C. Liu, et. al., Proc. SPIE 4782, X-Ray Mirrors, Crystals, and Multilayers II, 104 (December 1, 2002).

A-94

Recent Advances in Fluid Dynamics Measurements at the 7-BM Beamline

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The 7-BM beamline at the APS was commissioned in October 2012 for time-resolved studies of turbulent and multiphase fluid flowfields. The past 18 months has seen a significant expansion in the user community and the measurements that have been performed. Several examples of recent measurements will be outlined, including two-fluid mixing with signal trapping corrections, combined radiography and time-resolved fluorescence to separately measure gas and liquid density in multiphase flows, and droplet statistics measured with highly time-resolved radiography. Recent and upcoming upgrades to the beamline, including a wider energy range, higher flux, and a greater scope for imaging will also be discussed.

A-95

Measurement of Strain Profile Evolution using Time-resolved X-ray Diffraction

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Using time-resolved x-ray diffraction techniques, we measured the photo-induced strain in a thin film BiFeO3 sample [1]. The x-ray intensity along the crystal truncation rod near the 002 Bragg peak was measured for a 35-nm thick film. This is effectively a 1D coherent diffraction imaging and allowed us to extract the layer-by-layer strain profile as a function of time. The retrieval of the strain profile takes our knowledge about the film thickness as a support to the retrieval algorithm, with added fitting parameters on the surface roughness. The phase is first retrieved using the Gerchberg–Saxton algorithm [2], followed by a six-point spline algorithm fitting the phase and the layer-by-layer occupancy of BFO unit cells [3]. The strain profile directly reflects the piezoelectric response of the unit cells. We show that, in combination with optical measurement and DFT simulation, the measured strain profile is consistent with applying a time dependent uniform electric field along the film normal. This gives so far the most direct evidence for unraveling the mechanisms driving the photovoltaic effects in ferroelectric materials [4].

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A-96

Profile Etching for Monolithic KB Mirror Applications

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Previously we have invented and succeeded a profile coating technique to make monolithic elliptical Kirkpatrick-Baez (KB) mirrors using flat Si substrates. A pair of these KB's was successfully used at sector 34-ID for over two years under normal operation. However, under extreme x-ray irradiation with slit fully open and continuous operation of several days, these KB's underwent plastic deformation due to possible film stress relaxation of thick coatings [1]. Later, we have been using spherical substrates so that less coating is needed. When a spherical substrate is used, however, one can only use its centerline for focus since only the centerline is converted to an elliptical profile. Here we present a profile etching technique to pre-figure a flat substrate to an elliptical surface to achieve a much thinner corrective profile coating with freedom to translate the mirror to a new position whenever the mirror performance is deteriorated. One can also use two such mirrors with identical elliptical surfaces to fabricate nested KB mirrors by polishing the side edge of one mirror and align the polished side to the middle of the other mirror [2].

Profile etching is done by using a Kaufman KDC100 broad beam ion source and a graphite mask, with the substrate moving over the mask. The contour of the mask was calculated using the ion beam intensity map and the required elliptical profile, similar to the method used in profile coating. To obtain the ion beam intensity map, a 5-inch-diameter Si wafer with painted parallel graphite strips was etched. After etching, the graphite was removed by solvents, leaving un-etched strips on the wafer. The step-height map of un-etched strips represents the ion beam intensity distribution. Parameters targeted for Sector 8BM nested KB mirrors were used for profile etching tests, with a source-to-mirror distance of 5.7975m, mirror-to-focus distance of 0.2025m, and mirror glancing angle of 3 mrad. Flat super-polished Si substrates with dimensions of 100mm × 12mm × 7mm were used for etching. An etching depth of 11μ is needed over a 100mm mirror length. After more than 60 etching tests using different ion source optics and various etching conditions, we were able to achieve the targeted profile within 48nm rms figure error and 2Å rms roughness using only one profile etching and 600V beam voltage. The etching involved 10 runs of 10 moving loops at 2.6-mm/sec speed, with one hour break between each run for things to cool down, for a total of ~12h. The tests demonstrate that by using profile etching, the coating thickness of a follow-up corrective profile coating can be drastically reduced.

The biggest challenge for profile etching is the particulate contamination on the mirror. Particles are generated and scattered in vacuum wherever energetic Ar ions hit a surface. Some of them may contaminate the mirror surface. In this poster, details of the profile etching technique and efforts to eliminate particulate contamination will be presented.

This work is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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A-97

Properties of Multilayer Laue Lenses Measured at Beamline 1-BM

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Multilayer Laue lenses (MLL) are linear zone plates made with thin film deposition techniques. MLLs can focus hard x-rays to well below 10 nm with very high efficiency. We studied MLLs fabricated with the BNL deposition system using reactive sputtering with nitrogen, and we measured their diffraction properties at the Optics Test Beamline at 1 BM. A prototype MLL microscope was used to position the MLLs [1]. The transmitted wavefront was recorded while rocking an MLL through the Bragg condition. The diffraction patterns were recorded with a Pilatus 100k placed roughly 1 m downstream from the lenses, and the extinction patterns in the transmitted beam were recorded with a CCD-based high-resolution x-ray camera. We tested a novel tilted MLL having WSi2/Al bilayers, flat interfaces, and a growth thickness of 100 microns at a photon energy of 12 keV. The 100-micron aperture is sufficient to accept the full lateral coherence lengths at typical APS beamlines. We also studied a novel wedged MLL at energies ranging from 12 keV to 18 keV. For comparison purposes, we additionally measured the diffraction properties of a tilted, non-wedged, MLL with a 43-micron growth thickness having WSi2/Si bilayer. This MLL had been used for focusing experiments previously [2]. Results from the measurements indicate that many individual layers in the wedged MLL comply with their respective Bragg angle at the same rocking angle and that thus the slanting angles of the individual zones are matched with the theoretical growth model.

We acknowledge sectioning work at BNL by Juan Zhou and Nathalie Bouet.

This work was supported by the DOE office of Science, Office of Basic Energy Sciences, under contract No. DE-AC02-06CH11357 and the European Union and the Free State of Saxony via ESF project 100087859, ENano.

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A-98

X-ray Photon Correlation Spectroscopy at the APS with the Dectris EIGER Detector

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We have evaluated the suitability and performance of the Dectris EIGER detector for x-ray photon correlation spectroscopy (XPCS) as performed at beamline 8-ID-I at the APS. The EIGER detector is a newly released photon counting bump-bonded area detector with 1,030 × 1,065 75-mm pixels that currently runs at a maximum sustained frame rate of 800 frames per second (fps) with 3,000 fps promised in the near future. With respect to other detectors currently used for XPCS at 8-ID-I, the EIGER promises high efficiency photon counting operation and, most significantly, considerably higher data rates than have previously been available (~ 3 gigapixels per second versus 0.1 gigapixels per second). Using the EIGER, we measured the ensemble-averaged small angle scattering from various reference samples and made a detailed comparison to measurements made using other detectors. We also measured the x-ray speckle contrast with and without focusing optics from static reference samples and found that the speckle contrast was easily observable even within beamline 8-ID-I’s current layout that is not optimized for the larger pixels (75 mm versus 14, 20, or 30 mm) of the EIGER. Time correlation functions from dynamic reference samples were also obtained and agree well with previous work. In addition to the reference samples, we measured time correlation functions from flowing colloidal suspensions—measurements that have proven hard to obtain with other detectors. Lastly, we describe successful initial efforts to incorporate the high data rates from the EIGER detector into the XPCS high-performance computing data pipeline at 8-ID.

Performance and measurements described in this abstract and data that will be presented on the poster were made with a detector on loan from Dectris. The object on loan is a prototype of the EIGER 1M detector system with limited functionality and performance as compared to the eventual production model. We acknowledge the support of the APS Detector Group in both securing the detector loan and in deploying the detector at 8-ID-I.

Work supported by U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357

A-99

DTXRD – Software for Evaluation of Single Crystals using X-ray Diffraction

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A specialized software package DTXRD includes several utilities for evaluation of single crystals using methods of x-ray diffraction. It provides calculations of x-ray rocking curve topographs based on a sequence of x-ray diffraction images collected along a rocking curve of a single crystal under examination [1]. The collected data are sorted for each pixel thus allowing analysis of local rocking curves and mapping of their parameters (e.g., full width at half maximum, peak position, etc.) over the crystal. This characterization method is particularly sensitive to intrinsic and extrinsic (e.g., mounting-induced) crystal strain that should be evaluated and minimized for applications of single crystals in x-ray optics. Additional utilities based on the dynamical theory of x-ray diffraction provide calculations of reflectivity/transmissivity and rocking curves for several single crystals commonly used in x-ray optics as well as data handling and evaluation. The new software [2] is python-based and now available for use on Red Hat Linux computers at the Advanced Photon Source. The software has been utilized in several publications [3-5].

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A-100

The Limit in Detecting Trace Elements Using Synchrotron-based X-ray Fluorescence

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Nanoprobe instruments push for ever better spatial resolution, and new detector technology becomes available that permits high count rates and large solid angles. The question as to what the ideal sample-detector geometry for trace element mapping is remains and is sample and geometry dependent. We have developed a model for simulating the x-ray fluorescence (XRF) spectrum including background signals from elastic and Compton scattering. We used the model under different instrument geometries, and applied it to test samples similar to those used at a synchrotron beamline. We compare the best signal-to-noise ratios that can obtain under each geometry. We are hoping to have a better understanding of the physical limits in detecting trace elements in a sample, so as to make full use of the instruments currently available, and boost the detection ability of synchrotron based XRF techniques. This will not only augment present-day experiments, but also aid utilization of the significantly increased beam brightness provided by the planned APS Upgrade.

A-101

Polarization-dependent DANES on Vertically-aligned ZnO Nanorods

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We developed a polarization-dependent diffraction anomalous near edge structure (DANES), which can describe the orientation-dependent structural and chemical properties of a selected element in a crystal. The local structural properties of vertically-aligned ZnO nanorods were examined by using DANES measurements at Zn K edge with incident x-ray electric field parallel and perpendicular to the x-ray momentum transfer direction from *c*-oriented ZnO nanorods. The DANES obviously demonstrated orientation-dependent local structures around Zn atoms in wurtzite-phased ZnO nanorods. Unlike other techniques, polarization-dependent DANES can uniquely describe the orientation-dependent local structural properties and the local density of states of a selected element in a selected phased crystal of compounds or mixed-phased structures.

A-102

In Operando X-ray Absorption Near-edge Structure of All Vanadium Redox Flow Battery

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Vanadium redox flow battery (VRB) is one of the most suitable energy storage systems for large-scale intermittently renewable energy storage systems [1-2]. In the VRB, positive and negative electrolytes play important roles to store the energy [3-4]. Consequently, in order to develop new electrolyte solutions for the VRBs with higher energy and power density, as well as longer cycling life and better safety characteristics, the in-depth understanding of the relationship between the oxidation state /local structure changes of the electrolytes and electrochemical performance is critically important. Synchrotron-radiation-based x-ray adsorption fine structure (XAFS) could be very informative when applied to probe the environment around atoms of all states of matter. Also the x-ray absorption near-edge structure (XANES) could be especially powerful to determine the average oxidation state and local symmetry of the elements in all phases. With these considerations in mind, we carried out *in operando* XANES measurements during cycling of an all vanadium redox flow battery (VRB). In the positive half-cell, the K-edge of the vanadium continuously shifts toward the higher binding energy. This shift indicates an increase in the average valence state of vanadium in the electrolyte, while the K-edge of vanadium shifts back to the lower binding energy, indicating a decrease in the average valence state of vanadium in the electrolyte. In summary, a new *in operando* XANES technique has been demonstrated to study the average oxidation state of the electrolytes in the all vanadium redox flow battery under realistic cycling conditions.

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A-103

Experimentation and Simulation of Acoustically Levitating Liquid Droplets

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An acoustic levitator has been successfully employed at the Advanced Photon Source for *in-situ* high-energy x-ray diffraction measurements via particles suspended in an acoustic field. It is demonstrated that acoustic levitation can be utilized to mimic the spray drying amorphization process under controlled conditions. It is important to understand the physics behind levitation and the flow field around levitating liquid droplet to enhance the drying process of pharmaceuticals and food products. This paper presents experimental results to map the flow field in an acoustic field using Particle Imaging Velocimetry and high-speed infrared imaging. Finite element analysis is also employed to simulate the required experimental conditions. The finite element results of acoustically levitated droplets from an ultrasonic wave operating at 22 KHz are compared and presented. The simulation results are in good agreement with the experiment.

A-104

Ptychographic Overlap Constraint Errors and the Limits of their Numerical Recovery Using Conjugate Gradient Descent Methods

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Ptychographic coherent x-ray diffractive imaging is a form of scanning microscopy that does not require optics to image a sample. A series of scanned coherent diffraction patterns recorded from multiple overlapping illuminated regions on the sample are inverted numerically to retrieve its image. The technique recovers the phase lost by detecting the diffraction patterns by using experimentally known constraints; in this case the measured diffraction intensities and the assumed scan positions on the sample. The spatial resolution of the recovered image of the sample is limited by the angular extent over which the diffraction patterns are recorded and how well these constraints are known. Here, we explore how reconstruction quality degrades with uncertainties in the scan positions. We show experimentally that large errors in the assumed scan positions on the sample can be numerically determined and corrected using conjugate gradient descent methods. We also explore in simulations the limits, based on the signal to noise of the diffraction patterns and amount of overlap between adjacent scan positions, of just how large these errors can be and still be rendered tractable by this method.

APS Ugrade

A-105

Hybrid Pixel Detectors for the APS Upgrade

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To accommodate the higher brightness of an upgraded APS implementing an MBA Lattice, the Upgrade is exploring the possibility of developing fast pixelated area detectors with an integrating readout. The proposal includes two detectors:

1. FASPAX: The Fermi-Argonne Semiconductor Pixel Array X-ray detector (FASPAX) will provide a MHz burst image matched to the bunch rate of the proposed APS timing mode. FASPAX will record high-resolution movies for time-resolved applications.
2. CDI Detctor: A high-dynamic-range-integrating detector with small pixels (50-60 mm) for coherence based science.

Both detectors implement a novel passive integrator for wide dynamic range, with logic to self-select the gain on a pixel-by-pixel basis. Interposer technology will be used to construct wafer-sized sensors without coverage gaps.

This poster will present technical details for the detectors, and provide an overview of R&D plans.

A-106

APS-Upgrade: The Next-generation Synchrotron Source

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The upgrade of the APS will usher in the fourth generation of storage ring sources and set the brightness standard for several decades to come. The incorporation of a multi-bend achromat (MBA) lattice will provide three key improvements over today's APS:

- The ability to focus all of the x-rays down to nanometer-size spots,
- 100 to 1,000x increase in coherent flux to open up new experimental capabilities, and
- 100 to 1,000x increase in brightness per pulse for time-resolved experiments.

These improvements will create an unparalleled x-ray microscope to open new research phase spaces and address global grand challenges. The high brightness and high energy provided by an MBA lattice at the APS will significantly enhance x-ray studies under extreme conditions and in real operating environments. This will transform our ability to observe nano- and meso-scale structures evolve *in situ* during synthesis and *in operando*, enabling the highest possible spatial resolution over a broad temporal range. This also will provide x-ray sensitivity to atomic structure and strain, elemental composition and chemical states, and electronic and magnetic structures.

A-107

Multi-bend Achromat – A Brilliant New Source for the APS

APS-U Design Team

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The multi-bend achromat upgrade to the APS will provide more than two orders of magnitude increase in brightness for ID sources over a wide range of hard x-ray energies and at least a factor of two increase in hard x-ray flux (BM and ID). Support will be maintained for canted insertion device beamlines, and a flexible range of fill patterns from 48 to 324 uniformly spaced bunches. Performance comparison of the present and future APS is presented, along with descriptions of lattice design algorithms, gradient-dipole magnets, and on-axis injection.

A-108

Zone Plate Development for the Advanced Photon Source

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Today, nanoprobe experiments are typically all limited in their performance by the achievable focused flux. This situation will dramatically change with the MBA upgrade of the APS. The upgrade will provide a 200x brighter source, and revolutionize high-resolution x-ray microscopy in the hard x-ray range. We are developing zone plate based optics and methods to improve both spatial resolution and focusing efficiency in the hard x-ray range, to make full use of the outstanding properties of the MBA upgrade.

X-ray zone plates are focusing optics similar to circular diffraction gratings but with changing period as a function of radius. Zone plate optical performance is determined largely by the outermost zone width for focus spot size and zone height for focusing efficiency. In order to achieve 20-nm focused spot size, outer most zone width of 16 nm is required; achieving peak focusing efficiency will require zone plate thicknesses ~100 times the zone width, and zone plate optics with these properties do not currently exist. We are working to achieve 20 nm focused spot size and peak efficiency for 25 keV x-rays. Results from several techniques being developed, stacking multiple zone plates and zone doubling zone plates, will be presented. We also will present foundations for future work on zone plate development as well as how zone plates fit into optics development for the APS-U.

Use of the Advanced Photon Source and the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357

A-109

Advanced X-ray Beam Position Monitor System Development

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APS-U front ends will have extensive x-ray diagnostic capabilities. The high-heatload front end (HHLFE) will include a grazing-incidence insertion device x-ray beam position monitor (GRID-XBPM) utilizing Cu K-edge XRF from a pair of GlidCop absorbers capable of withstanding 17 kW power from two inline Undulator A devices. A second XBPM located outside of the accelerator enclosure monitors fluorescence footprint from the front end exit mask, a critical beamline-defining aperture. An beam intensity monitor measures the x-ray fluorescence signal from the photon shutter, while a second intensity monitor is located immediately downstream of the exit mask, utilizing the Compton-scattered photons from the Be window.

Chemistry

C-1

Photocatalysis with Hybrid Nanomaterials

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HMS (Hybrid metal-semiconductor) nanorod clusters with one Au nanocrystal connected with multiple CdSe nanorods were synthesized through the welding of the Au-tipped CdSe nanorods (i.e., Au nanocrystal with only one CdSe nanorod) at the Au sites. The as-synthesized HMS clusters show a huge performance boost towards the photocatalytic MER (multiple-electron reduction), with the MB (methylene blue) molecules as the redox indicator at room temperature and in the water solution without the application of inert atmosphere. The results presented in this poster could shed light on the rational design of efficient photocatalysts for MER reactions.

This work was performed at the Center for NanoscaleMaterials, U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences User Facility under Contract No. DE-AC02-06CH11357. We thank Dr. Shengye Jin and Dr. Peng Wang for help with characterizations of spectroscopy and photocatalysis.

C-2

Layer-by-layer Fabrication of Oriented Porous Thin Films Based on Porphyrin-containing Metal-organic Framework

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Given that energy migration in natural photosynthesis is generated by highlyordered porphyrin pigments (chlorophylls), equally highly ordered porphyrin-based metal–organic frameworks (MOFs) might exhibit similar behavior. Ideally a MOF-based strategy could facilitate antenna-like light-harvesting and position such materials for solar energy conversion. Previously, we reported that in a metalloporphyrin-based, pillared paddlewheel type MOF, DA-MOF, a photo-generated exciton can migrate up to 45 porphyrin struts within its lifetime and with a high anisotropy along a preferred direction. However, incorporating single crystals of DA-MOF into films, a structure relevant to solar energy conversion devices, is a significant challenge. Herein, we report the synthesis and characterization of two thin films (DA-MOF and L2-MOF) of porphyrinbased MOFs on functionalized surfaces using a layer-by-layer (LbL) approach. Profilometry measurements confirm that the film thickness increases systematically with number of growth cycles. Polarization excitation and fluorescence measurements indicate that the porphyrin units are preferentially oriented, while x-ray reflectivity scans point to periodic ordering. Ellipsometry measurements show that the films are highly porous. Since there are currently few methods capable of yielding microporous MOFs containing accessible free-base porphyrins, it is noteworthy that the LbL growth permits direct MOF incorporation of unmetalated porphyrins. Long-range energy transfer is demonstrated for both MOF films. The findings offer useful insights for subsequent fabrication of MOF-based solar-energy-conversion devices.

Condensed Matter Physics

C-3

Efficiency Determination of Optical Third Harmonic Generation in Cuprous Oxide

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Cuprous oxide (Cu_2O) is a centroysmmetric material used in excitonics, photovoltaics, and photocatalysis. The efficiency of third harmonic generation in cuprous oxide was measured. Intensities followed a non-cubic power law which indicates nonperturbative behavior

$$I_{3\omega} = (4.41 \pm 0.08) \cdot 10^{-28} I_{\omega}^{2.32 \pm 0.06} \times \left(\cos^2(2\phi) + 3.6 \pm 0.2\right) \text{ Watts/m}^2$$

for a pump Iω in Watts/m2 propagating along [100]. Polarization (*j* measured between elecric field and [010]) anisotropy of the harmonic generation was demonstrated and related to the third order susceptibility tensor *c*(3) by the polarization-independent fraction

$$\frac{2\left(3\chi^{(3)}_{1212}\right)^2}{2\left(3\chi^{(3)}_{1212}\right)^2 + \left(A_0 \frac{g_{3b}}{N} \frac{\chi^{(3)}_{1111} - 3\chi^{(3)}_{1212}}{4}\right)^2} = 0.78 \pm 0.01$$

The results will influence the understanding of harmonic generation in centrosym-metric materials and are potentially relevant to device design and the interpretation of exciton behavior.

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C-4

Development of Force Field for Reactive Interfaces from First Principles

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The atomic interactions at reactive interfaces and the associated chemistry play a pivotal role in energy applications such as catalysis, capture, storage and conversion. Previous spectroscopic and computational works on energy-related materials provide remarkable insights into the structural and transport characteristics of such interfaces. Yet, a fundamental understanding of the atomic scale dynamical processes that occur across reactive interfaces is lacking; such knowledge is crucial for the design of novel functional materials for energy applications with superior performance (e.g., battery capacity, battery lifetime, efficiency). Molecular dynamics simulations based on classical force fields (FFs) provide an ideal route to unravel these atomic-scale mechanisms. The accuracy of this technique is, however, severely limited by the description of atomic interactions by force fields currently available in the literature. The deficiencies of these FFs are primarily related to the use of pre-defined functional forms (often decided by intuition) and the overemphasis of near-equilibrium structures in the fitting procedure. In this work, we circumvent the problems with traditional FFs by defining the potential as a superposition of linearly independent functions (e.g., cosines, powers, gaussians, bessel functions etc.), which precludes the reliance on intuition for functional forms of FFs. The expansion coefficients are obtained by fitting against an extensive set of dataset of forces and energies from density functional calculations on numerous structures (both near and far-away from equilibrium). Furthermore, the fitting is performed using sparse regression techniques (e.g., compressive sensing) since the potential is an over-complete basis set and is expected to result in a sparse matrix of expansion coefficients (i.e., most are zeroes). The conceptual framework of this path-breaking methodology will be discussed by using our results on gold nanoclusters as an example..

Materials Science

C-5

Growth of Ti-doped Half-metallic Fe_3O_4 Thin Films Deposited on $SrTiO_3$, Al_2O_3, Si, and Float Glass Substrates

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We investigate the effects of Ti doping on the structural and transport properties of half metallic Fe_3O_4 films grown on varying substrates [$SrTiO_3$ (100), Si (111), Al_2O_3 (0001), and Float Glass (FG)] by pulsed-laser deposition technique (PLD). X-ray diffraction (XRD) pattern infers that parent and Ti doped magnetites have cubic spinel structure. The first order phase transformations at the Verwey transition *T*v for Fe_3O_4 thin films are 123 K ($SrTiO_3$), 120 K (Si), 123 K (Al_2O_3), and 121 K (Float Glass). No first order phase transition was observed for Ti doped films. Raman spectra infer the formation of magnetite phase for $Fe_{3-}x$ TixO_4 (x = 0 and 0.0206) and changes in Raman spectra as a function of doping show that the changes are gradual for Ti doped films on different substrates. Magnetoresistance (MR) curves show linear magnetic field dependence for the parent films, while an increase in MR and departure from linear field dependence is observed for Ti-doped films. The Magnetoresistance (MR) curves display highest change in MR for doped and undoped films grown on Al_2O_3 (0001) substrate. For parent Fe_3O_4 films MR is of -0.48% at room temperature which increases below the Verwey transition up to -1.12% at 100 K, while in Ti doped films MR is of -1.56% at room temperature which increases up to -3 %.

PACS No.: 74.25.Fy, 67.80.dk, 61.05.Qr, 61.05.cp, 71.30.+h

C-6

Direct Growth of Graphene on Diamond at Wafer in Seconds and Device Fabrication

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Owing to its high carrier mobility, high Young's modulus, and high thermal conductivity, graphene has been a center of attraction for researchers around the world particularly for understanding the fundamental physics of electronic transport in 2D materials [1]. However, the fact that the one atom thick graphene membrane strongly affected by the substrate interactions puts limit on exploiting excellent intrinsic properties of graphene for various applications. Diamond offers multiple distinctive properties, such as high phonon energy, low trap density, and high thermal conductivity, which make it an ideal substrate for fabricating graphene devices on diamond. Our research in this direction has been initiated earlier [2] demonstrating fabrication of grapheme-based devices on diamond and their unique properties for the first time. However, the graphene was transferred onto the diamond surface using mechanical exfoliation process limiting the applicability of this process to the industrial scale. In present studies, we demonstrate a novel process to grow large area single and few layer graphene on the diamond thin film deposited on the silicon wafer. The fact that single and few layer graphene can be grown on diamond thin films on wafer scale (100 mm diameter) at relatively lower temperatures (~800˚C) than other existing high temperature methods (such as on SiC) without any transfer process makes this approach unique and offers new opportunities for developing graphene based nanoelectronic devices on diamond. We discuss growth process and characterization of graphene in detail as well as fabrication and performance of top-gate graphene devices on diamond.

Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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C-7

First Principles Investigations of Reactions Mechanisms of Li_xMO_4 (M=Fe, Mn, Co) Electrodes/Electrocatalysts for Hybrid Li-ion/Li-O_2 Cells

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Electrochemical experiments with Li_5FeO_4, which has a defect antifluorite-type structure, have demonstrated a substantially smaller voltage polarization during charge and discharge and hence higher energy efficiency compared to standard reactions between lithium and oxygen to form Li_2O_2. Other materials in this class include Li_6MO_4 (M=Mn, Co) that offer a theoretical capacity of ~1000 mAh/g at ~3 V. The mechanisms by which these materials delithiate and lose oxygen, however, is not well understood. The results of first principles density functional theory (DFT) calculations to establish the thermodynamic conditions for the extraction of Li/Li+O from Li_5FeO_4 and Li_6MO_4 compounds will be presented. A step-by-step, history-dependent, removal process is followed; the stability of Li and Li+O deficient samples is investigated on the basis of the extraction reaction energies. Various stages of Li/Li+O removal are identified. Structural changes and electronic structure evolution, as well as computed characterizations of the reactions will also be reported.

C-8

Mechanistic Studies of Lithium-oxygen Reactions using Rotating Ring Disk Electrode

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Non-aqueous lithium–air batteries have been estimated to deliver gravimetric energy three to four times that of conventional lithium-ion batteries at comparable gravimetric power [1, 2]. Fundamentally understanding reaction mechanisms and associated intermediates during lithium-O_2 cell operation is critical for implementing practical lithium-air batteries with high reversibility and long cycle life. In particular, the superoxide reaction intermediate generated during oxygen reduction is known to be potentially chemically unstable against the electrolyte solvent [3], reaction surface [4] and cell components [5], leading to high overpotentials during charge, and short cycle life. We use the rotating ring disk electrode (RRDE) technique to probe the influence of different electrolyte solvents on the stability of the superoxide intermediate generated on planar glassy carbon and Au electrodes in several organic electrolytes. Superoxide stability was found to exhibit a solvent-invariant potential dependence on carbon and Au. These results yield insights into potential criteria for highly reversible lithium-oxygen cell configurations, and have implications for the growth mechanisms and surface chemistries of the Li_2O_2 discharge product.

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C-9

Carbon Nanotube Electrodes for Rechargeable Na-O_2 Batteries

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The progressive depletion of fossil fuels and their non-renewable and pollutant nature, is leading to ever increasing interest in developing high-energy storage devices. Metal-air batteries are considered promising for electric vehicle applications due to their high energy density, made possible by the use of readily available oxygen as one of the reactants, reducing the weight and freeing up space for other battery components [1]. Lithium-oxygen batteries have attracted a great deal of interest in recent years; however, it is uncertain that lithium reserves are capable of fulfilling the ever-increasing lithium demand. In this context, nonaqueous Na-O_2 batteries are receiving growing attention as they combine the broader availability of Na and O_2 with similarities to the widely studied Li-battery technology and the highly reversible formation of NaO_2 as the discharge product, supplying energy efficiencies during the first cycle greater than 90% [2-5].

In this study we report the reversible formation of NaO_2 in Na-O_2 cells with vertically aligned carbon nanotube (VACNTs) oxygen electrodes. The use of VACNTs also facilitated an exploration of the influence of NaO_2 morphology on oxygen reduction and evolution reaction kinetics across a wider range of electrochemically relevant current densities than would be feasible using lower specific surface area electrodes such as carbon paper. Effects of discharge current density on product crystal structure and chemistry will also be discussed, including possible consequences for nucleation and growth mechanisms of NaO_2.

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C-10

Complex Oxide Nanomembranes: A Route to Multifunctional Devices

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The structural phase, ionic/electrical conduction, ferroelectric domain structure, and catalytic activity of epitaxial perovskite-based oxide heterostructures can be controlled with strain and interface engineering. This wide range of materials properties makes oxide heterostructures attractive for use in multifunctional devices: devices that, for instance, utilize electrical conductivity, piezoelectricity, and ferroelectricity simultaneously. To realize such devices, materials with different crystalline structures, lattice constants, and thermal expansion coefficients must be combined to optimize the overall functionality of each integrated system (e.g., oxide heterostructures on silicon). Materials integration through epitaxy, however, restricts the types of materials that can be grown on one another; in general, the crystal structure and lattice constants need to be nearly matched to maintain good crystalline quality. We show here that we can manipulate strain in oxide thin films and combine dissimilar materials with oxide nanomembrane (NM) synthesis through the release of single-crystalline oxide thin films from the original growth substrate. The freestanding oxide NMs are very thin (40-200nm) with large aspect ratios (length:thickness ≥ ~10^4). NMs readily bond to most surfaces because they are flexible and can conform to a new host substrate.

We demonstrate the fabrication of elastically relaxed $SrRuO_3$ (SRO) nanomembranes. Epitaxial SRO has been grown on $SrTiO_3$ (STO) substrates. The lateral size and shape of the SRO thin films are defined with a selective epitaxy process. The SRO NMs are released from the original STO growth substrates via selective etching. During the release process any epitaxial strain in the SRO is elastically relaxed. The research presented here provides the basis for NM synthesis of oxide heterostructures. Going forward, we will be able to strain engineer oxide heterostructures based on elastic strain sharing and probe fundamental materials properties such as piezoelectricity and ferroelectricity in freestanding oxide NMs.

C-11

Insight into the Structural Evolution of a High-voltage Spinel for Lithium-ion Batteries

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With high operating voltage and three-dimensional lithium ion diffusion pathway, $Li_xNi_{0.5}Mn1_{.5}O_4$ (high voltage spinel) is considered promising high energy and high power density cathode material for lithium-ion batteries. Here we investigate the crucially structural dependence of spinel cathode on the stoichiometry of cation/anion ration, especially with an unprecedented over-stoichiometric Li intercalation. This material undergoes well-known cubic phase transition with one lithium insertion from fully delithiated state. The further over-stoichiometric Li intercalation results into a cubic to a tetragonal phase transition when x reaches 3. When x is electrochemically pushed to x ~4, the co-existence of a rock-salt structure with a layered component is observed. The parent spinel structure is reformed upon complete deintercalation. This reversibility underscores the fact that the HV spinel has a distinct memory of its original form. The resultant phases and morphologies are identified by x-ray diffraction (XRD) and microscopy methods.

C-12

Control of Magnetic Domain Behavior in Coupled Ferromagnetic/Antiferromagnetic Multilayer Discs

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Here we report on the control of magnetic domain behavior in patterned discs consisting of ferromagnetic (NiFe) and antiferromagnetic (IrMn) heterostructures by modifying their energy landscape. The magnetization reversal mechanism was identified as a combination of magnetization rotation in the pinned layer and localized vortex nucleation in the free layer through direct visualization. The influence of localized exchange bias pinning on vortex core motion was determined using *in-situ* Lorentz transmission electron microscopy. Quantitative estimates of the energy scale calculated from experimental data for the local pinning sites, combined with micromagnetic simulations helped corroborate the novel reversal mechanism. The work presented here provides new opportunities for macroscopic control of the energy landscape of magnetic heterostructures for functional applications.

Nanoscience and Nanotechnology

C-13

Influence of Doping on Crumpled Graphene Wettability

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Graphene is a wonder material having many outstanding characteristics including rich surface physiochemical properties. Surface wettability of graphene has direct influence on many of its application areas including sensing, energy storage, biomedicine, thermal management, etc. Two key factors controlling wettability are surface topography and surface functionality. Surface topography of graphene can be changed by crumpling in a controlled manner. Intrinsic wrinkles formed in an uncontrolled manner during graphene sample fabrication are insufficient to influence surface wettability. One of the ways to obtain controlled crumpling of graphene is to utilize the surface adhesion between graphene and elastomer structures. Graphene transferred on a prestreched elastomer structure can be crumpled during relaxation of the elastomer. Based on the amount of stretching of the elastomer, the crumpling or surface topography of graphene is controlled. Crumpled graphene made in this way has been shown to reach superhydrophobic behavior in a reversible way [1]. On the other hand, surface functionality of graphene has been found to be closely related to the electrical doping of graphene [2]. Electrical doping of graphene can be modulated by the application of external stimuli e.g. chemical or electrical perturbation. We have fabricated crumpled graphene structures and studied the impact of electrical doping on wettability of a CVD-grown crumpled graphene film by modulating the carrier density of a crumpled graphene transistor structure by electrical means and observing the water-graphene interaction. We believe that our investigations on possible tunable wetting property of crumpled graphene will provide ways to better understand the potential of graphene as next-generation tunable surface adhesion and sensing devices.

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C-14

Electrochemical Response of Graphene Ribbon to Europium (III)

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One of the most important pieces of information after a release of nuclear material is identifying the presence of uranium and/or plutonium. This work seeks to develop a new hand-held analytical instrument that characteristically identifies a radioactive material and its isotopes in a liquid. Europium nitrate solution is used as a surrogate compound and is prepared by dissolving 0.025 g of europium nitrate pentahydrate in 5 mL of distilled water. We report the electrochemical response to europium nitrate of graphene. Measurements are performed in a four electrode configuration; two gate electrodes are used to drive europium ions towards the graphene ribbon and the other pair, to drive the ion-modulated electrical current through graphene. Graphene samples were grown by thermal CVD on copper foil; a 3 × 3 cm2 sample was transferred to an oxide wafer (3.6 × 3.6 cm2) by using PMMA as a carrier. This fabrication approach is novel. Specifically, the CVD graphene was patterned by selective plasma etching at low power (20 W) and the fluidic device was patterned by laser writing. We employ acetone instead of a typical optical resist remover and find out that acetone preserves better the graphene adhesion to the silicon dioxide substrate. We also cover the contact electrodes (drain and source) with photoresist in order to isolate them from the europium solution and thus avoiding any direct leakage between fluid and contact electrodes. We propose a fluidic reservoir made of optical resist as a practical alternative to test graphene response in fluidic media. The optical transparency of the resist contributes to the correct patterning of the graphene ribbon on metal electrodes and the patterning of the fluidic reservoir on the graphene ribbon. All patterning is performed by direct write optical lithography and liftoff.

Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

C-15

Near-field Optical Characterization of Nanomechanical Resonators

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A novel plasmonic near-field optical microscopy (p-NSOM) technique is developed to detect flexural vibration in doubly clamped nanostructure with sub-wavelength lateral spatial resolution and exquisite temporal resolution. The detecting technique is based on conversion of propagating surface Plasmon polaritons (SPPs) to localized surface plasmons (LSPs) at the apex of a metal coated scanning probe. The intensity of scattered light is strongly dependent on the separated distance between tip and resonator, thus allowing for sensitive detection of vibration of resonator with a minimum detectable displacement of 0.4 pm. During the experiment, a heterodyne demodulation approach is utilized in the steady measurement of harmonic vibrations of a nanoresonator, and laser excitation is used to measure the transient response of the resonator due to a pulsed source in both time and space. This technique, which offers local sensitivity to optical and mechanical properties, offers a platform for dynamic characterization of nanostructures with high spatial and temporal resolution.

C-16

Controlling the Length of Self-assembled Cu-Si Nanowires by Electric Field

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Self-assembled metal silicide nanowires are considered prospective basic building blocks for future nanoscale devices [1]. A self-assembly method, which is a bottom-up approach, generally can produce a large volume of nanowires in a short amount of time with relatively simple procedures. Hence, self-assembly methods are very attractive especially in a large scale operation. As compared to top down methods such as the electron-beam lithography, fabrication of a nanowire can take up to several hours. Although, there are many self-assembly methods, our focus is on electron-beam evaporation of copper (Cu) on thermally heated silicon (Si) in ultrahigh vacuum (UHV) [2], which directly self-assemble planar copper-silicide (Cu-Si) nanowires on the substrate. As with most self-assembly methods, despite having many benefits, the e-beam evaporation method has several drawbacks. One of the main issues is the inability to directly control the fabrication process, which results in self-assembled Cu-Si nanowires of varying shapes, diameters, and lengths. Wide variations in geometries and sizes are not practical for a large-scale production because manufacturers cannot produce repeatable nanoscale devices. Therefore, our aim of this study is to control one aspect of the fabrication process, which is the length of the self-assembled Cu-Si nanowires. Roos et al. in [3] proposed that the growth mechanics of self-assembled silver (Ag) nanowires on Si(001) is by step bunching method. Since Cu-Si can self-assemble into nanowires on Si(001) using the same approach as Roos et al., we assume Cu-Si nanowires also step bunch along vicinal Si. Therefore, we hypothesize that if the Si vicinal steps are long and straight, then the self-assembled Cu-Si nanowires will be long and straight as well. Several studies such as in Refs. [4-6] have indicated that Si atoms under an electric field can electromigrate on the Si wafer surface, which then can transform the length of vicinal steps. In our experiments, we used only Si(110) substrates because there is only one Si<110> direction on the substrate surface. Since Cu-Si tend to self-assemble along Si<110> direction [7], the fabricated nanowires will only be along a single direction. Hence, by changing the direction of the electric field on Si(110) during the e-beam evaporation process, the length of the self-assembled Cu-Si nanowires can be observed and verified. The results strongly suggest that, on average, self-assembled Cu-Si nanowires will be the longest when the electric field is perpendicular to Si<110> and shortest when the electric field is parallel to Si<110>. Therefore, our experiments have shown that self-assembled Cu-Si nanowires can be controlled by the electric field.

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C-17

Three-dimensional Transfer of Graphene

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Graphene has been widely investigated for its potential applications such as ultrafast photodetectors and transistors, and bioelectronic interfaces, owing to its exceptionally high carrier mobility, transparency, and mechanical stability/flexibility. Furthermore, a large elastic deformation is achievable for graphene without perturbation/degradation of the electrical properties, providing a promising platform material to realize flexible and 3-dimensional (3D) optoelectronics and bio-electronics. In this work, we report a novel 3D transfer method of graphene that can lead to a 3D structure of graphene for various potential applications. To carry out nonplanar 3D transfer of graphene, 3D polydimethylsiloxane (PDMS) structures were fabricated. To provide ductility that is critical for the conformal transfer/interfacing of graphene with underlying 3D substrates, a thin Au layer was used as a transfer/sacrificial material for the solution transfer process. O_2 plasma treatment of the PDMS was implemented before the transfer to facilitate the 3D conformal graphene transfer without suspensions. Vapor-phase etching of Au layer was performed in a sealed chamber to prevent the delamination of graphene during the etching process, which is challenging for the conventional wet-etching process. Raman characterization and scanning electron microscope (SEM) imaging demonstrated the graphene was successfully transferred over a broad area without significant suspensions/damages. The proposed integration procedure of free-standing graphene onto nonplanar structures will pave the way for the graphene-based 3D optoelectronics and bioelectronics in the future.

C-18

Effect of Hydrogen During Cooling-Phase to Achieve Continuous Growth of Bilayer Graphene on Copper

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Graphene has attracted attention due to its high electron mobility, optical transparency and mechanical strength. Because of these exceptional properties, graphene is a promising candidate material for transparent conducting electrodes, mechanical resonators, and for electronic interconnects. To achieve large-area graphene synthesis, chemical vapor deposition (CVD) has been studied extensively. However, achieving continuous bilayer graphene on copper foil over large area is still a problem. Bilayer graphene in particular is interesting for band gap engineering in presence of external bias. It is therefore pertinent to develop better understanding of the growth mechanism that dictate the formation of single or bilayer graphene growth, and to achieve uniform bilayer graphene films over large area on an economically viable substrate with minimal processing time. We have carried out systematic studies to investigate the effect of flowing different gases during the cooling phase on CVD graphene growth. We found that uniform single or bilayer graphene can be a grown on large area copper foils by regulating the gases introduced during the cooling phase. We demonstrate that vacuum cooling enhances the growth of single layer graphene while the introduction of hydrogen gas during the cooling phase encourages the growth of continuous bilayer graphene. The effects have been confirmed by Raman Spectroscopy analysis and through the observation of changes in electrical characteristics of fabricated field effect transistor devices. In addition, optical properties and selected area electron diffraction (SAED) measurements confirmed the single and bilayer graphene growth. Our results demonstrate that hydrogen plays a crucial role during the cooling phase to encourage bilayer graphene growth. We explain observed results elucidating a crucial role of hydrogen leading to a growth of bilayer graphene.

Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357

C-19

Non-destructive Young's Modulus Measurement of Ultra-Nanocrystalline Diamond Films

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Young's Modulus (YM) measurements for thin films are generally hard to accomplish for thin films. One method is to fabricate free-standing cantilever structures and calculate the YM from resonant frequencies or deflection-load plots, but that is both laborious and destructive to the substrate. Another method is to measure wafer curvatures produced by films as deposited on two different substrates of known YM (e.g., Si(100) and sapphire), but the method is imprecise and also requires full wafers of another nature than Si, which can be expensive. The hereby reported method uses a stress-temperature plot obtained non-destructively for the very Si wafer analyzed, as obtained from wafer curvature measurements, and the known value of the expansion coefficient as function of temperature for Si and diamond. The method is well suited for materials containing dominantly diamond phase and small fractions of different phase (e.g., graphitic, such as on grain boundaries), and also shows if significant departures from this composition are encountered.

C-20

Development of a N-UNCD Based Field Emitter Array for a Flat Panel X-ray Source

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As an alternative to conventional x-ray sources, a flat panel transmission x-ray source is being developed. A field emitter array (FEA) prototype to be incorporated as cold cathode in this flat panel x-ray source was fabricated for this work. Using the Particle-in-Cell code OOPIC Pro, an initial FEA was designed through simulations. Based on the simulation results, a FEA prototype was fabricated using conventional microfabrication techniques. Planar nitrogen-incorporated ultrananocrystalline diamond (N-UNCD) films were used as field emitters. This N-UNCD based FEA prototype was composed of nine pixels distributed in a 3×3 square array, with a pixel size of 225×225 mm, and a 500-mm pitch. Each pixel was composed of an N-UNCD-based cathode and a free-standing copper grid used as extraction grid. Field emission from each pixel could be addressed individually. Emission currents per pixel in the order of 0.05–3.0 mA were obtained for extraction fields between 4 and 20 V/mm. Delamination issues were found in the microfabrication of the first FEA prototype. Consequently, a second generation N-UNCD based 3×3 FEA was designed and fabricated. In this design, the free-standing grid was replaced by a tungsten layer composed of a matrix of 11×11 extraction gates. Each extraction gate had a circular aperture of 6 mm in diameter. These design changes solved the delamination issues found for the first prototype. Also, for an extraction field of 7 V/μm, an emission current around 0.14 μA per pixel was measured; this value is higher than the 0.08 μA per pixel obtained from the initial FEA prototype at the same extraction field.

This work was supported by DARPA under Grant No. N66001-12-1-4237. Any opinions, findings and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of DARPA. Also, device fabrication was carried out at the Center for Nanoscale Materials, which is supported by DOE, Office of Science, BES (#DE-AC02-06CH11357). Special thanks to D. Rosenmann and L. Stan for their support with metal depositions at the CNM.

C-21

The Effects of Patterning Parameters on Metal-assisted Chemical Etching

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Silicon nanostructures have a wide range of uses, revolutionizing solar cells and sensors for biological systems. One method of fabricating such structures is metal-assisted chemical etching. The rate at which this etching occurs is very sensitive to a variety of parameters. This study observed the effects of different temperatures, solution concentrations, pattern geometry, and metal catalysts on the rate of etching. Higher temperatures were observed to correlate with faster etching rates, but also with higher delamination of the metal catalyst from the silicon structures. Lower temperatures correlated to slower etching rates and less delamination. Ideal etching conditions would result in high etching rates and low delamination rates. Varying concentrations of the etching solution result in different etching rates. Smaller areas of metal result in higher etching rates. Ag catalyzes the reaction faster than Au, but it is also harder to control.

C-22

Surface Plasmon Polariton Enhanced Upconversion in Rare Earth Doped Nano Crystals on Plasmonic Substrates

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We use spectroscopic imaging to investigate the intensity enhancement and modification of radiative rates of infrared to visible upconversion from rare-earth doped nanoparticles ($NaYF_4$:Yb:Er [Tm]) supported on plasmonic substrates; including square lattices of Au nano-pillars fabricated by electron beam lithography, and hexagonal nanocavity arrays formed by self-assembly, each designed to support a surface plasmon polariton at frequencies which are nearresonant with the rare-earth sensitizer (Yb^{3+}) absorption. We observe a systematic enhancement in the efficiency of upconversion associated with the interaction of the co-doped nano-particles with the plasmonic substrates. Spectrally resolved imaging provides a massively parallel means of assessing the range of achievable enhancement, and its relation to the specific configuration of the substrate/upconverting nano-particle system. Spectrally resolved reflectivity of the plasmonic substrates confirms the role of the surface plasmon polariton in the upconversion enhancement. Experimental results are compared to finite difference time domain (FDTD) simulations of the frequency-dependent reflectivity of these nanostructures.

C-23

Modeling of Nano-Textured Tungsten Surfaces for Surface Emissivity Control

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The viability of micro/nano textured tungsten as efficient solar absorbers and thermal emitters for solar thermophotovoltaic systems is explored via computational electrodynamics simulations. Pseudo-random and grating type structures are investigated, along with the effects of protective oxide coatings and varied geometries. The absorbing structures show extremely high absorption across the solar spectrum while the emitting structures show close matching with photovoltaic cell absorption spectra.

C-24

Integrated Photonics for Cavity-QED with Non-transverse Photons

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Magneto-optical phenomena are powerful tools for studying spins in materials, but existing optical probes of spin dynamics do not harness the coherent interactions achievable in traditional two-level quantum systems. Using non-transverse photons in cavity-QED can overcome this limitation by providing spin-sensitive light-matter interactions in microphotonics [1]. By integrating solid-state nanosystems with photonic microcavities, we plan to realize non-transverse photon interactions that will pave the way for coherent magneto-optical phenomena such as optical non-reciprocity [2]. This project focuses on integrating nanocrystal quantum dots with high-Q silicon nitride (SiN) ring resonator cavities on silicon substrates. Taking the advantages of state-of-the-art fabrication facilities at CNM, we fabricate SiN ring resonators that operate at visible wavelengths with high-Q and small mode volume. These photonic devices will be a platform to test cavity-QED in a strong coupling regime with non-transverse photons.

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C-26

Si (311) – A Novel, Precious Substrate for Nanofabrication

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Si(311) offers a series of particular features for crystal-orientation-dependent etching, such as the possibility to form 3-sided pyramid shape V-grooves and deep, tilted parallel wall trenches. These can be useful for tips fabrication through molding and fabrication of blazed gratings and 3D gratings if combined with deep reactive ion trench etching. The present poster presents the comparison between Si(100) and Si(311) etching characteristics obtained with the "wagon wheel" pattern technique using KOH and TMAH solutions, common for nanofabrication.

Polymers

C-27
Nano-scale Mechanical Properties Testing on Polymer Thin Films via AFM indentation

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The nanoconfinement effect in polymer thin film has been a major interest in past decades. It was observed by using various experimental methods, that the glass transition temperature (T_g) differs from bulk material value at both polymer/substrate interfaces and free surfaces [1,2,3], which indicates the altered polymer molecular structure under confinements. To approach this topic from another angle, local elastic moduli of polymer thin films near interfaces and free surfaces were also investigated by different methods. However, due to the limitations of those methods, no convincible results have been published so far. In this work, an AFM nanomechanical testing based method was developed to study the elastic modulus change at both polymer interfaces and free surfaces. The new method is capable of providing the local modulus mapping with nanometer resolution inside sub-micron spatial range. Therefore the full gradient of modulus change can be revealed for the first time with ultrahigh resolution on both sides of the film, which facilitates the further understanding of polymer confinement effects. The experiments have been done on PMMA films spin coated on silicon substrates. The results showed that, on the interface side, PMMA modulus starts from 1.5 times of the bulk material value, and declines exponentially to the bulk value in 50-nm range. On free surface side, the modulus starts around half of the bulk value, then fast increase to normal in just 10-nm distance. To further investigate the mechanism of confinement effects, a proposal for using STM to scan molecular arrangement of first layer PMMA near interface has been submitted to CNM.

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C-28
From Block Copolymers to Metal Oxide Nanostructures via Sequential Infiltration Synthesis

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In sequential infiltration synthesis (SIS), selective self-limited interaction of metal precursors with only one block of self-assembled block copolymer films enables the fabrication of inorganic nanostructures with controlled and tunable dimensions. Here, we have utilized SIS in cylindrical and lamellar polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) block copolymer films to create metal oxide nanostructures, and explored the nanostructure morphology as a function of the block copolymer thickness. A combination of scanning electron microscopy imaging and grazing incident small angle x-ray scattering shows that by employing SIS in highly ordered directed self-assembled (DSA) lamellar films, ordered metal oxide nanostructures can be fabricated uniformly across millimeters. By varying the metal oxide precursors, the block copolymer thickness, and the substrate type, these nanostructures can be employed in various renewable energies applications.

Enviromental and Geology

E-1

Shock Features in Chelyabinsk LL Chondrite Meteorite: Preliminary Results

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Shock features within meteorite are the products of impacts and collisions in the asteroid belt that eventually led to the ejection of the meteorite from its parent body. Studying the shock effects within meteorites provide significant insights into the (P, T, t) conditions during the shock metamorphism process [1,2]. Although detailed studies of shock effects within various highly shocked L chondrites have been carried out, very few studies have been done on LL and H chondrites. Improved knowledge of shock effects within these meteorites is desirable due to their different origin.

We will present preliminary results from Chelyabinsk meteorite that exploded on Chelyabinsk region of Russia on February 15, 2013. The Chelyabinsk meteorite has been classified as LL5 ordinary chondrite but recent studies have shown that it is best described as a complex genomict breccia. We prepared polished section from Field Museum Chelyabinsk specimen ME6050 and studied it using the Field Museum`s Zeiss EVO 60 SEM. High-pressure mineral polymorphs form mostly within or near the shock melt veins. Raman spectra were collected using a custom built 458-nm confocal micro-Raman spectrometer in the mineral physics laboratory at the Northwestern University. Finally, FIB sections from suitable regions within the shock melt veins were extracted using the Zeiss 1540 XB FIB-SEM at the EMC facility of the Argonne National Laboratory. No high-pressure mineral phases were detected from the Raman and SEM studies but the TEM studies of the FIB sections prepared from the shock melt veins should provide more insights into shock events that led to the formation of melt veins and melt pools.

[1] Sharp, T.G. and DeCarli P.S. (2006). Meteorites and the Early Solar System II, p. 563-678.

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Materials Science

E-2

Hybrid $Sn_3O_2(OH)_2$/Graphite Nanomaterials as Anode for Lithium-ion Batteries

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Tin (Sn) anodes could three-fold increase the capacity if currently utilized in LIB carbon anodes (from 372 mAh/g for carbon to 994 mAh/g for Sn). However, structural stresses (up to 260% volumetric changes) during lithium intercalation/deintercalation create irreversible destruction of the anode, which quickly reduces the overall capacity and efficiency. The approaches to mitigating this effect are reduction of particle size where the stress on the crystal is reduced or addition of lithium-inactive elements to act as a buffer during volumetric changes. In our research we designed unique hybrid nanomaterials that would incorporate both approaches. High-energy-density tin and tin oxide nanoparticles were formed directly on nano-graphite sheets through a wet chemistry route. With the modified particle morphology we were able to achieve good electrical conductivity to an ensemble of individual $Sn_3O_2(OH)_2$ nanoparticles, while also keeping the size of individual Sn nanoparticles under the self-healing threshold which allowed us to by-pass Sn amorphization due to the volume expansion and achieve stable cycle life performance. X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirm $Sn_3O_2(OH)_2$ phase and 40-50 nm particle size of $Sn_3O_2(OH)_2$ on the surface of the larger GnP through both XRD peak broadening and visual inspection of SEM images. Initial reversible capacity of this hybrid anode materials is 680 mAh/g.

In-situ x-ray absorption spectroscopy (XAS), specifically extended x-ray absorption fine structure (EXAFS) spectroscopy measurements were made to determine local structural changes around Sn during different points of charge/discharge. As expected, large structural changes occur during charging, and in a discharged state the particles show Sn in a more metallic crystal structure. In addition, the more it is charged/discharged, the more prominent this Sn-Sn metallic peak becomes. This suggests the destructive nature of cycling such anodes is the tendency of Sn to agglomerate to larger structures, particularly to the point where the volumetric instability of pure Sn metal once again takes over.

E-3

Nanocrystallization in Fluorochlorozirconate Glasses

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Heat-treating fluorochlorozirconate (FCZ) glasses nucleates $BaCl_2$ nanocrystals in the glass matrix, resulting in a nanocomposite glass ceramic that has optical properties suitable for use as a medical imaging plate [1].Understanding the way in which the nanocrystal nucleation proceeds is critical to controlling the optical behavior. The nucleation and growth of nanocrystals in FCZ glass ceramics was investigated with *in situ* x-ray diffraction (XRD) heating experiments and transmission electron microscopy (TEM). These experiments showed that the nucleation of hexagonal $BaCl_2$ nanocrystals first occurs at 220°C, and undergoes a phase transformation to the orthorhombic phase at 280°C. The morphology of the $BaCl_2$ crystals changed with phase from spherical to spheroidal nanocrystals. The $BaCl_2$ nanocrystals continue to grow and coalesce to micron sized crystals with extended heat treatments, potentially damaging the optical performance of the $BaCl_2$ crystals. Through the use of different heat treatments it was found that the nucleation and phase transformation processes are kinetically controlled processes.

[1] J.A. Johnson, S. Schweizer, and A.R. Lubinsky, *J. Am. Ceram. Soc.* **90**, 693-698 (2007).

Nanoscience and Nanotechnology

E-4

Imaging the Atomic Surface Structures of CeO_2 Nanoparticles

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Cerium dioxide (CeO_2) is widely used in catalysis for the remarkable redox ability of the surfaces. The catalytic properties of CeO_2 can be further tuned by synthesizing nanoparticles with different facets exposed. The (100), (110) and (111) facets often demonstrate distinct catalytic properties, which was attributed to the different redox capabilities of the three facets. Despite the importance, previous studies were incapable of direct observation of the surface structures of CeO_2 nanoparticles. The underlying problem is the difficulty of visualizing the O atoms in previous microscopy studies. By conducting the Cc and Cs corrected high resolution electron microscopy (HREM) at Argonne, we directly imaged both Ce and O atoms and solved the atomic structures of (100), (110) and (111) surfaces. The (100) surface has a mixture of Ce, O and reduced CeO terminations on the outermost surface as well as the partially occupied lattice sites in the near-surface region (~1 nm from the surface). The (110) surface has a combination of reduced flat CeO_{2-x} surface layers and "sawtooth-like" (111) nanofacets. The CeO_2 (111) surface is O-terminated. The surface structures derived from this HREM study are consistent with results from our infrared spectroscopy investigation.

[1] Y. Lin, Z. Wu, et al., Nano Lett., 14, (2014), 191.

Exemplary Student Research Program

ESRP-1

Micro X-ray Fluorescence Mapping of Pb Distribution in *Brassica juncea* Grown in Artificially Stimulated Soils

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The potential use of *Brassica juncea* in phytoremediation of lead contaminated soils has been examined using the x-ray microprobe. Five-centimeter portions were cut from the terminal roots of *Brassica juncea* samples that had been grown in artificially stimulated Pb concentrated environments. Terminal roots were fixed in ethanol/acetic acid upon removal from the soil, and roots were then cross-sectioned before being examined in the x-ray microprobe at 7-micron resolution. Cross sections from plants grown in 100 ppm Pb soil compared with those from 0 ppm Pb soil show significant amounts of Pb distributed throughout the root section indicating uptake of Pb from the soil into the interior of the plant. Potential implications for the use of *Brassica juncea* in phytoremediation are discussed.

ESRP-2

Presence of Metals and Metalloids in Wild Salmon Compared to Farmed Salmon Studied with Hard X-ray Fluorescence Microscopy

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The presence of metals in fish is an issue of food safety due to the persistence of these chemicals in the body as well as their tendency to bioaccumulate. It has been discovered that in multiple species the concentrations of metals present in the flesh of wild-caught fish differ from the metal concentrations in farmed fish. The origin of these metals and their implications for human health are not completely understood. Current research points to the diet of the farmed fish as the source of these metals. Through other studies, it has been discovered that the concentration of metals not only varies from species to species, but from one tissue to another in each individual fish [1]. Whether the concentrations reach harmful levels varies with the species as well as the conditions of the fish farm. Comparisons of wild and farmed salmon have found that the farmed salmon had significantly higher levels of arsenic while wild salmon had significantly higher concentrations of cobalt, copper, and cadmium, though none of the metals were present in high enough quantities to harm a person [2].

In prior experiments, many fish were pureed and then tested for metals [2]. We prepared small frozen sections of salmon flesh in order to preserve the cell structure and to identify in what part of the flesh the metals are most heavily concentrated. We used the hard x-ray fluoresence microprobe at 2-ID-E to map the metal concentrations with high spatial resolution. Methods for sample preparation and results of the x-ray fluorescence microscopy will be presented.

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ESRP-3

The Effects of Glyphosate on Metal Concentration and Distribution in Transgenic Soybean

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In the 1990's transgenic glyphosate resistant soybeans (*Glycine max*), commercially called Roundup Ready (RR), were developed. This genetic modification gave the soybean resistance to the effects of glyphosate by providing an alternative biochemical pathway for production of vital amino acids. In farming, the benefits of glyphosate resistant soybeans include less tilling and fewer applications of herbicide. The majority of soybean varieties being commercially grown are glyphosate resistant. There is concern regarding the nutritional value of the transgenic soybean seed crop. The literature shows conflicting data in regards to the effect glyphosate has on the photosynthetic capacity and the intracellular homeostasis of metals in the transgenic soybean. (Duke et al., 2012)

This experiment studied the effect of glyphosate on plant growth and metal homeostasis when applied to wild type (cv. *Dwight*) and transgenic soybean species. Wild type and transgenic soybean were grown in greenhouse conditions. Plant growth was evaluated by measures of height and biomass; there were no statistically significant differences in the growth measures of transgenic and wild type soybean, with or without applied glyphosate. Metal concentration and intracellular metal distribution were analyzed by synchrotron x-ray fluorescence at beamline 13-ID-E. Samples of stem and root were prepared for analysis by cryogenic embedding in OCT and sectioned by hand held microtome. Sections were preserved by dessication. Leaves were analyzed *in vivo* directly sampled off living plants at the time of analysis. All samples were mounted on Kapton film for XRF analysis. Although statistically significant reduced levels of calcium were found in leaf vascular and mesophyll tissue in both wild type and transgenic soybean treated with glyphosate, the leaves of wild type soybean sprayed with glyphosate display significantly larger overall decrease in Ca abundance in leaf vascular and mesophyll tissue. It is hypothesized that glyphosate may affect the homeostasis of calcium within the soybean leaf and that the glyphosate resistant mutation may partially provide an alternative pathway for Ca incorporation not seen in wild type.

ESRP-4

X-ray Crystallography of Co-crystallized Concanavalin-A and IF7

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The development of vascular supply is an essential source of the growth and metastasization of malignant tumors. Annexin 1, involved in human anti-inflammatory processes, is of use as a potential anticancer drug; it is capable of highly specific tumor vasculature recognition. Recent articles have identified the carbohydrate ligand-mimicking 7-mer peptide, IFLLWQR (IF7) as capable of targeting annexin A1 in mouse tumors. IF7 can exhibit "unprecedented tumor-targeting activity", and has been detected in mouse tumors within a few minutes of intravenous injection of the peptide [PNAS, 108(49),19587-19592 (2011)]. IF7 may have the potential to act as a delivery vehicle of anticancer drugs to the location of the tumor. Concanavalin-A is a carbohydrate-binding protein, originally extracted from Jack Bean *Canavalia ensiformis*. It binds to various sugars, glycoproteins and glycolipids, by recognition of a Î±-D-mannosyl or a Î±-D-glucosyl group. We grew crystals of Concanavalin-A, cross-link them with glutaraldehyde, then soaked in solutions of either IF7 or IF7CRR, to identify their biologically active conformation. We will attempt to grow co-crystals of the protein/peptide complexes, independent of the glutaraldehyde cross-linking process, and crystals of the IF7 and IF7CRR peptides alone.

ESRP-5

The Sustainability of Silver Nanoparticles

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Silver nanoparticles are becoming an increasingly important topic of study in material science. Valued especially for their antibacterial properties, silver nanoparticles are appearing in everything from socks to hospital gowns. At the current moment, a rising problem with Ag nanoparticles is their sustainability when woven into fabrics. After multiple washes, the nanoparticles may either be flushed out altogether or be reduced in their antibacterial effectiveness (Impellitteri et al., 2009). Therefore, with this study, we seek to examine the effects multiple washes of fabric with Ag nanoparticles may have on the nanoparticles themselves. If regular usage affects the properties of silver nanoparticle infused clothing, then the nanoparticles in an article of clothing will decrease in number and antimicrobial properties over time. To do so, we obtained five samples of socks implemented with nanoparticles and soaked each sample in a various detergent. At the end of the week, the socks are washed and then either re-worn for the next week or tested for the concentration of Ag nanoparticles. We will use the x-ray technology at Argonne to determine the interactions between the silver nanoparticles and socks before and after regular use. In the end, the results from this experiment may provide a guide for using silver nanoparticles in clothing with greater efficiency, allowing for a cleaner today and healthier tomorrow.

ESRP-6

The Effect of Halogen Ions on Insulin Crystallography

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The purpose of this experiment is to determine the relationship between the structure of insulin crystals and the presence of iodine and bromine. These relationships are determined using protein crystallography and x-ray diffraction to analyze the structure of insulin structures.

Procedure: From the stock solutions, prepare the 24 reservoir solutions for the crystallization experiments according to the table. The students can be split into small groups, each preparing some of the 24 different solutions. All groups can use the same stock solutions. Using the table for reference, pipette 0.5 ml of the corresponding reservoir solution into each of the 24 reservoir wells of a Cryschem™ plate. The table summarizes the conditions in each well and shows the position of the wells on the plate. Pipette 1 µl of the reservoir solution into the crystallization cup on the sitting drop post in each well. Add 1 µl of lysozyme stock solution to each 1 µl reservoir solution drop. Immediately after adding the drops of protein solution, close the crystallization vessel with crystal clear sealing tape to prevent evaporation from the vessel. Store the plate at 20°C. The crystals will start to grow immediately in some wells, and growth can be observed directly under the microscope at 1-2 hour intervals. The plates may be stored until the next lesson for final analysis. After about 1-2 weeks, crystals will have grown to their final size.

ESRP-7

Trace Element Mapping of Fish Otoliths Using Synchrotron Microbeam X-ray Fluorescence as an Indicator of Fish Movement in the Illinois River System

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Asian carp are heavy-bodied cyprinid fish that are considered invasive in North America. A number of distinct fish species are collectively referred to as Asian carp in the United States. Native to Asia and eastern Europe, several species have recently been discovered in the upper Illinois River within 50 miles of Lake Michigan. These fish are considered harmful to the ecosystem, consuming a third of their own body weight per day and competing with native fish. The presence of Asian carp is a growing problem in U.S. waterways and effective management practices require better understanding of migratory habits for individual species that are collectively lumped under the categorization of Asian carp.

In this study, we have evaluated the relative migratory patterns from two distinct species of Asian carp, silver carp and bighead carp, using trace element otolith microchemical analysis. Fish otoliths are bony biominerals that are part of the hearing and balance system of a fish. They are composed of aragonite ($CaCO_3$) and grow in a fashion similar to tree rings. Aragonite layers are deposited in discrete increments as the fish matures, with alkaline earth metals such Sr substituting for Ca in the mineral structure. The Sr/Ca ratio of each layer is thought to be proportional to that of the ambient water, which the fish inhabited at the time of otolith deposition. Synchrotron micro-XRF analyses of these otoliths were conducted using the GSECARS 13-ID-E beamline.

Whole otoliths were provided by Dr. Greg Whitledge from Southern Illinois University and extracted from silver and bighead carp collected from the Illinois River near Morris, IL in 2013. Otoliths were embedded in epoxy and then sectioned using a diamond saw to ~ 50 μm in thickness. They were then glued to quartz microscope slides and polished for analysis at the beamline. A focused spot size of 2 μm was used with an incident beam energy of 18.9 keV. Otoliths were compositionally mapped using continuous scanning with a pixel size of 3 μm and a scan time per pixel of 20 msec.

Upon analysis, it was discovered that Sr abundance in silver carp otoliths display strong variability within aragonite layers whereas Sr in bighead carp otoliths is generally more uniformly distributed. We speculate that the differences are consistent with silver carp migrating more broadly than bighead carp. We further speculate that the data show that silver carp are more likely to move downriver into the Mississippi River and then back into the Illinois River. The Mississippi River generally has a much higher molar Sr:Ca ratio than the Illinois River, which likely accounts for the variability in Sr across the silver carp otoliths. Once the migratory patterns of Asian carp are known, preventing them from entering Lake Michigan can be achieved.

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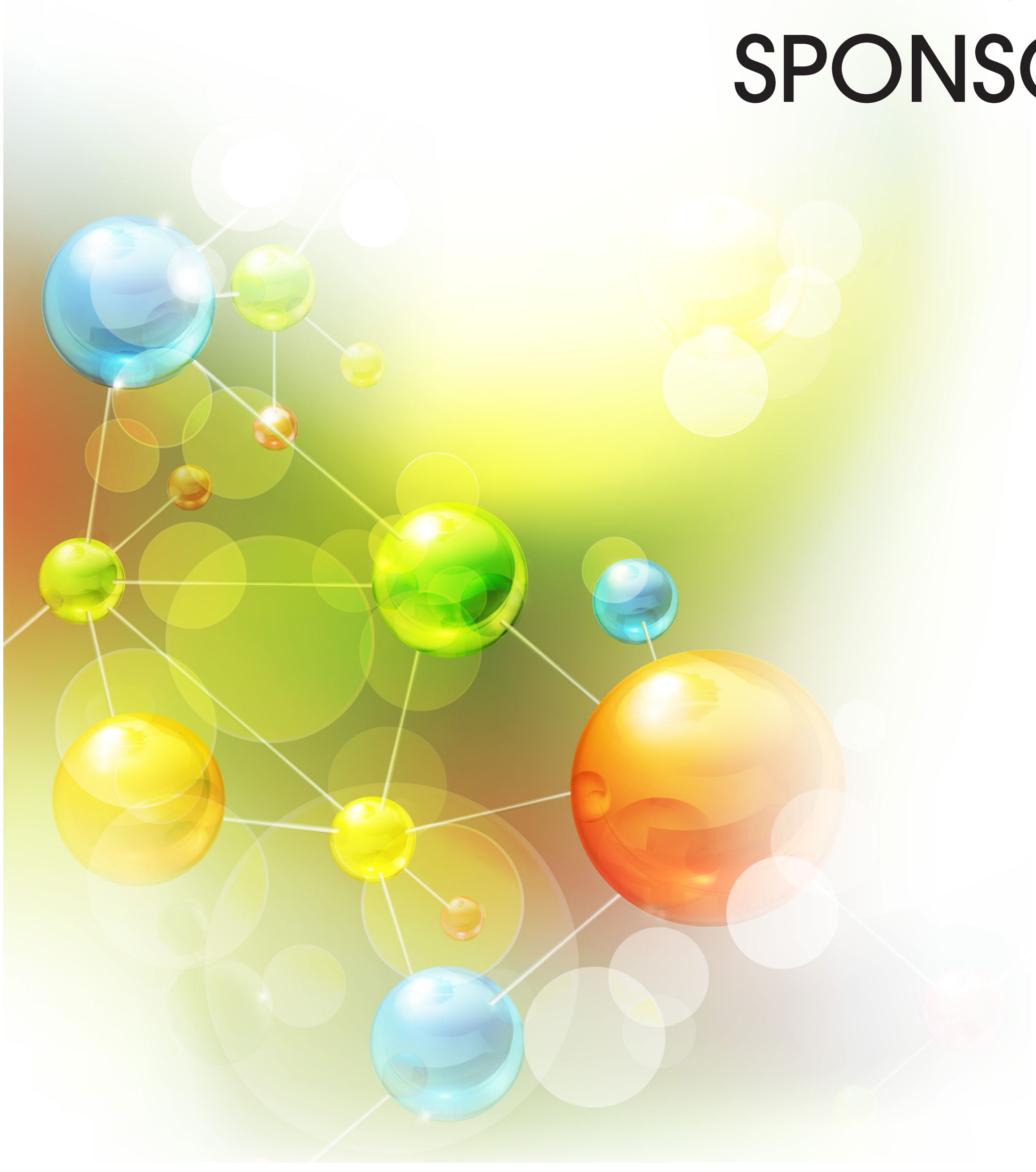

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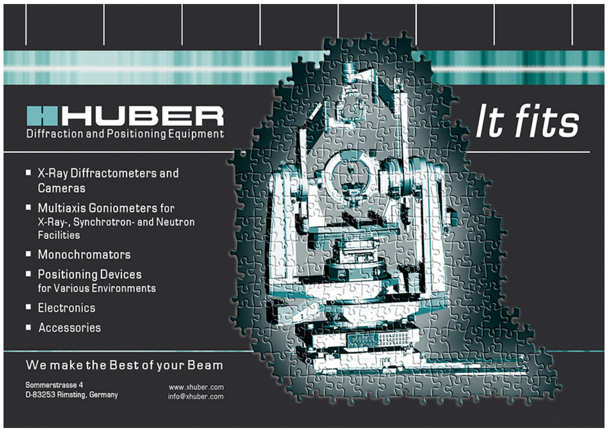
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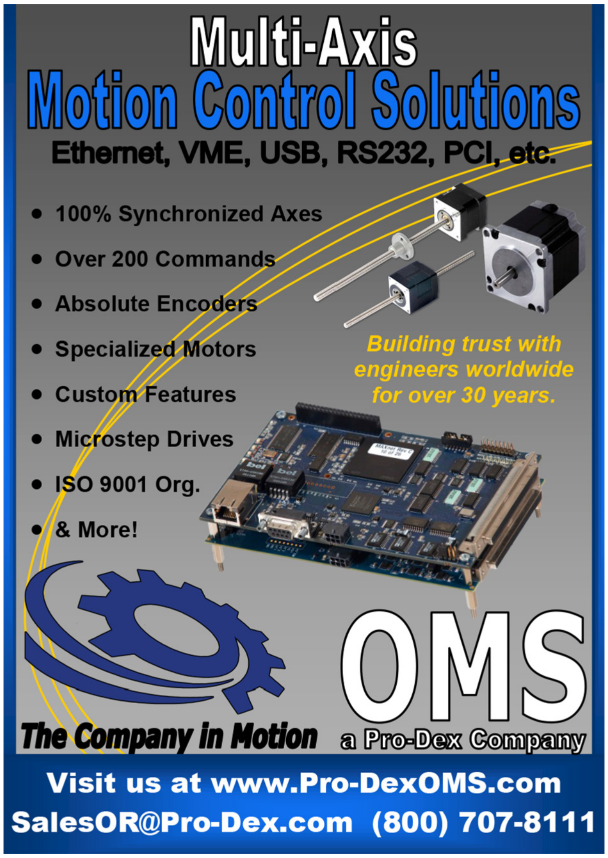

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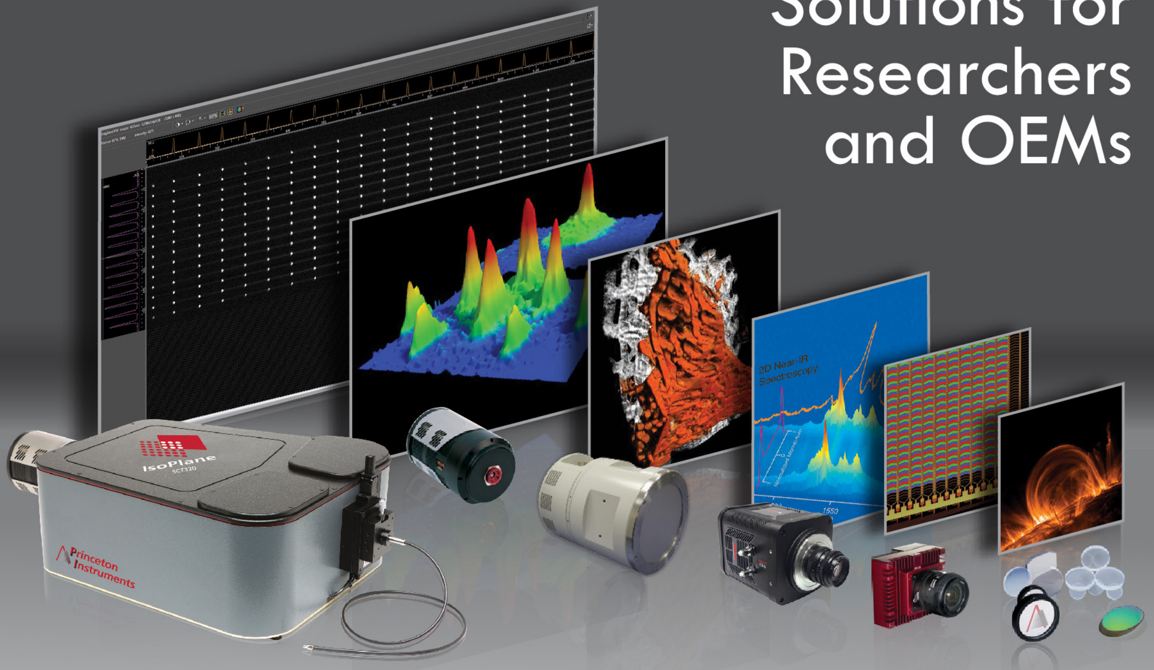
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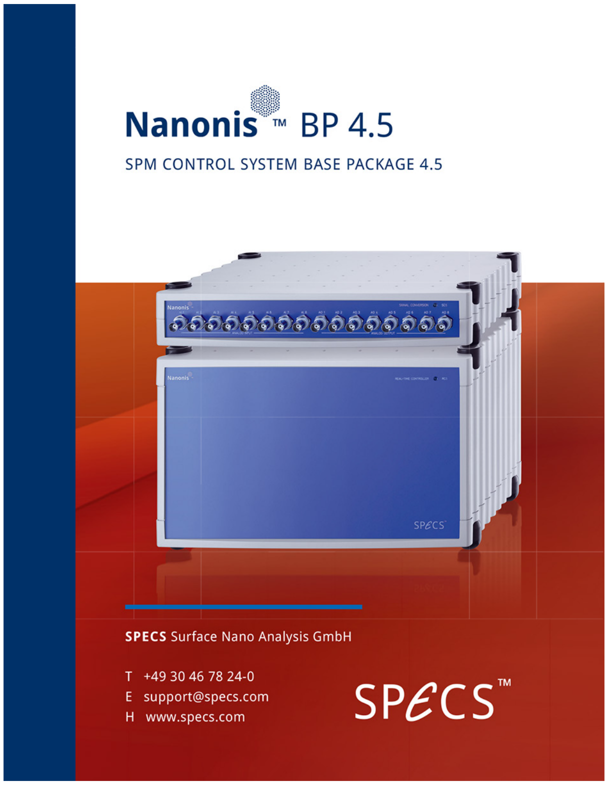

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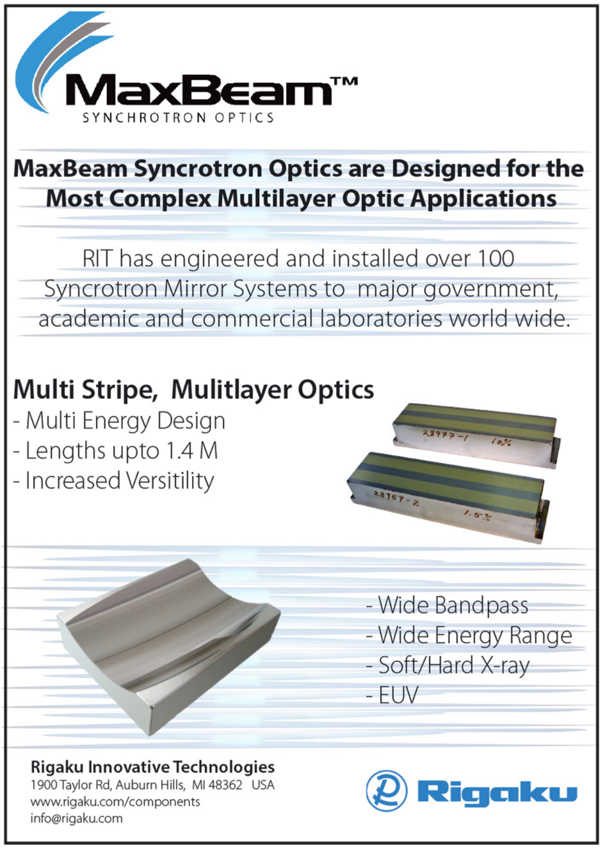

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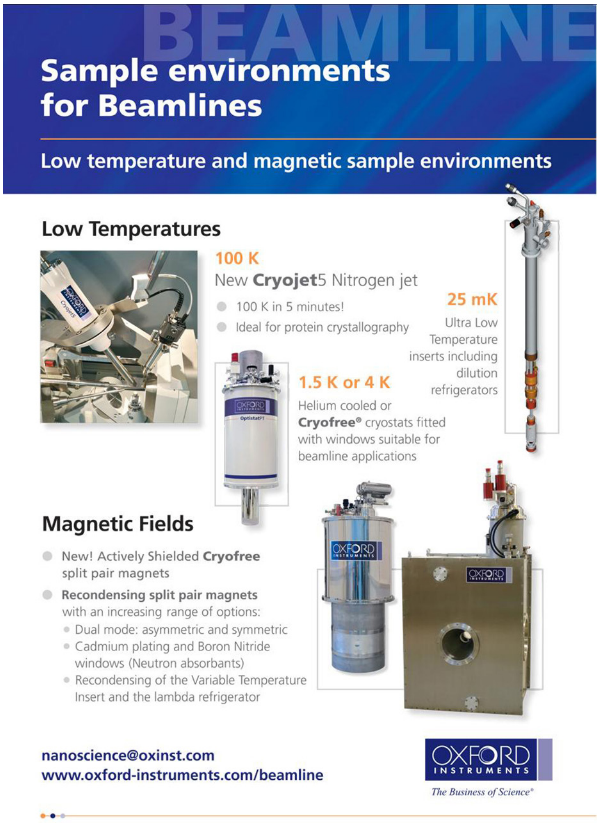

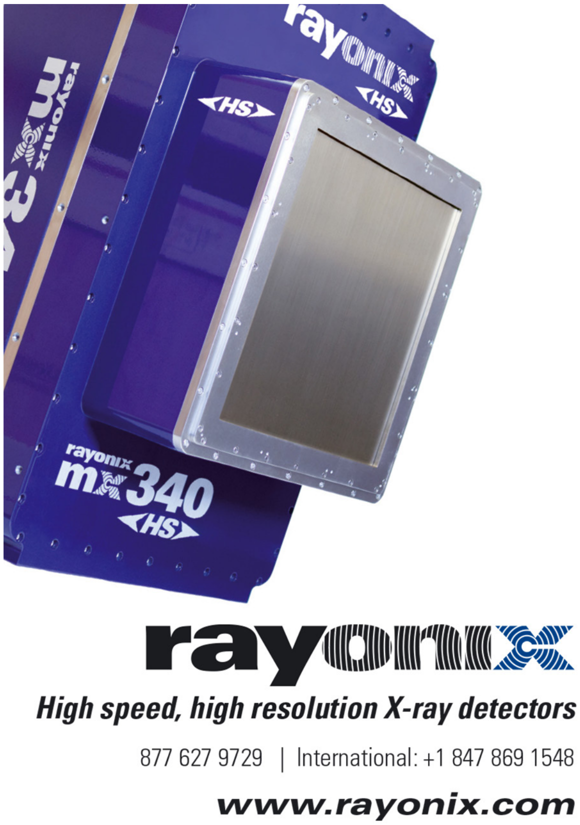

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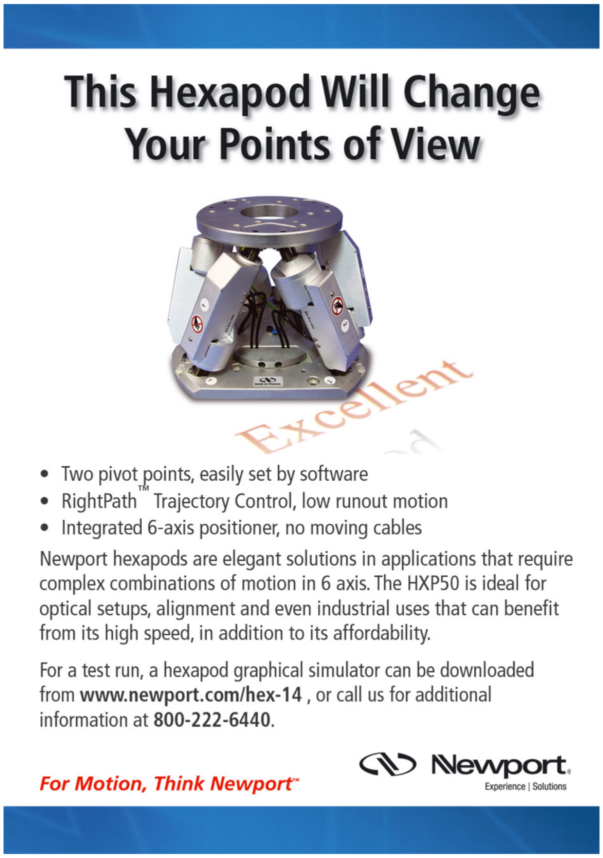

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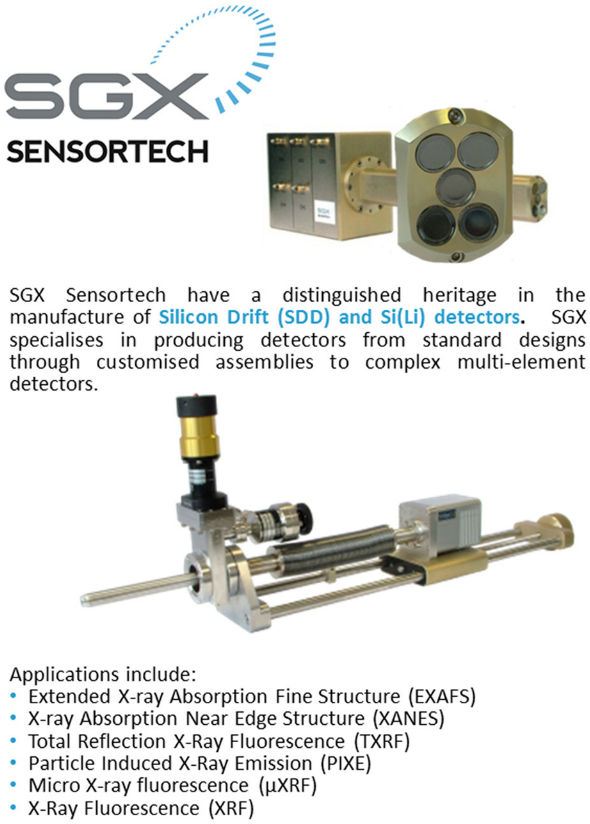

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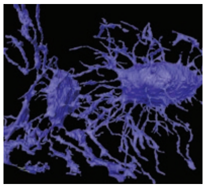
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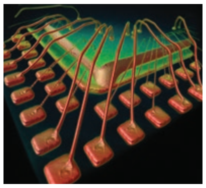
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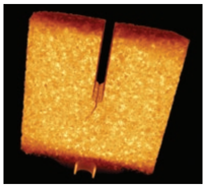
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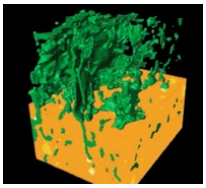
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General sessions will be held in the Auditorium on the first floor of the APS conference center, Bldg. 402. Vendor exhibits will be in the center's lower level and the atrium on the main level. Workshop locations are listed on the Comprehensive Program and posted at the registration desk.

Meals

The conference fee includes a continental breakfast and coffee breaks each day and the poster session reception. Buffet lunches will be served Monday through Wednesday in the tent outside of the Gallery on the lower level. If you pre-ordered lunches on your registration form, you will receive your tickets when you receive your meeting materials. (A limited number of extra lunch tickets are available for purchase at the registration desk.) Banquet tickets are nonrefundable. The Argonne cafeteria will be open for lunch; the Guest House restaurant it is open for dinner. The Beanline will be closed Monday through Wednesday during the meeting, re-opening on Thursday, May 15. The 401 Grill will be open for dinner throughout the meeting (closed for lunch, re-opening for both lunch and dinner on Thursday, May 15). A list of nearby restaurants is available on the APS home page (www.aps.anl.gov) under the side heading Visitor Information.

Telephones and Messages

Messages for you can be left at the registration desk; the telephone numbers there are 630.252.9580 and 630.252.9581. The messages will be posted on a bulletin board by the entrance to the Auditorium. If you need to make a telephone call, a pay phone is located downstairs near the restrooms at the back of the Gallery, lower level. If you need to send or receive a fax, a fax machine is located in the APS User Office (Bldg. 401, Rm. B1154). The number of this machine is 630.252.9250.

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Conference staff can make limousine reservations for you during the meeting as long as you make your request before 1:00 pm on Wednesday.

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Computer Access

Public computer terminals are available in the Bldg. 401 atrium behind the silver wall. Wireless access is also available in the Conference Center.

To use your laptop computer on the APS wireless networks, complete the following steps:

1. Open the wireless connection on your computer (either the 401 or 402 networks).
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If you have problems, please contact someone in the APS User Office (B1154, located immediately off the Conference Center atrium).

Exhibitor Locations – 2014 APS/CNM/EMC Users Meeting
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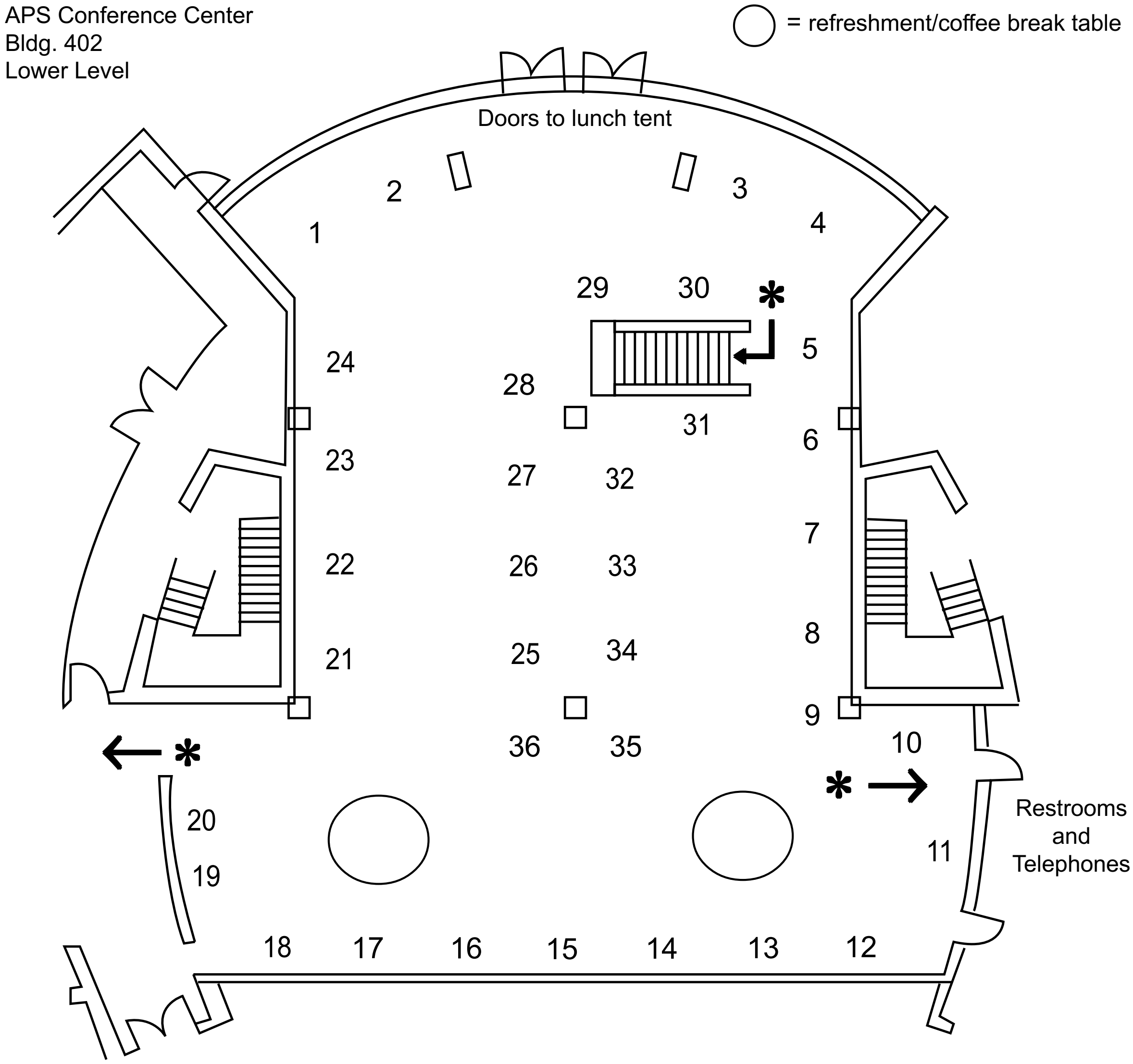

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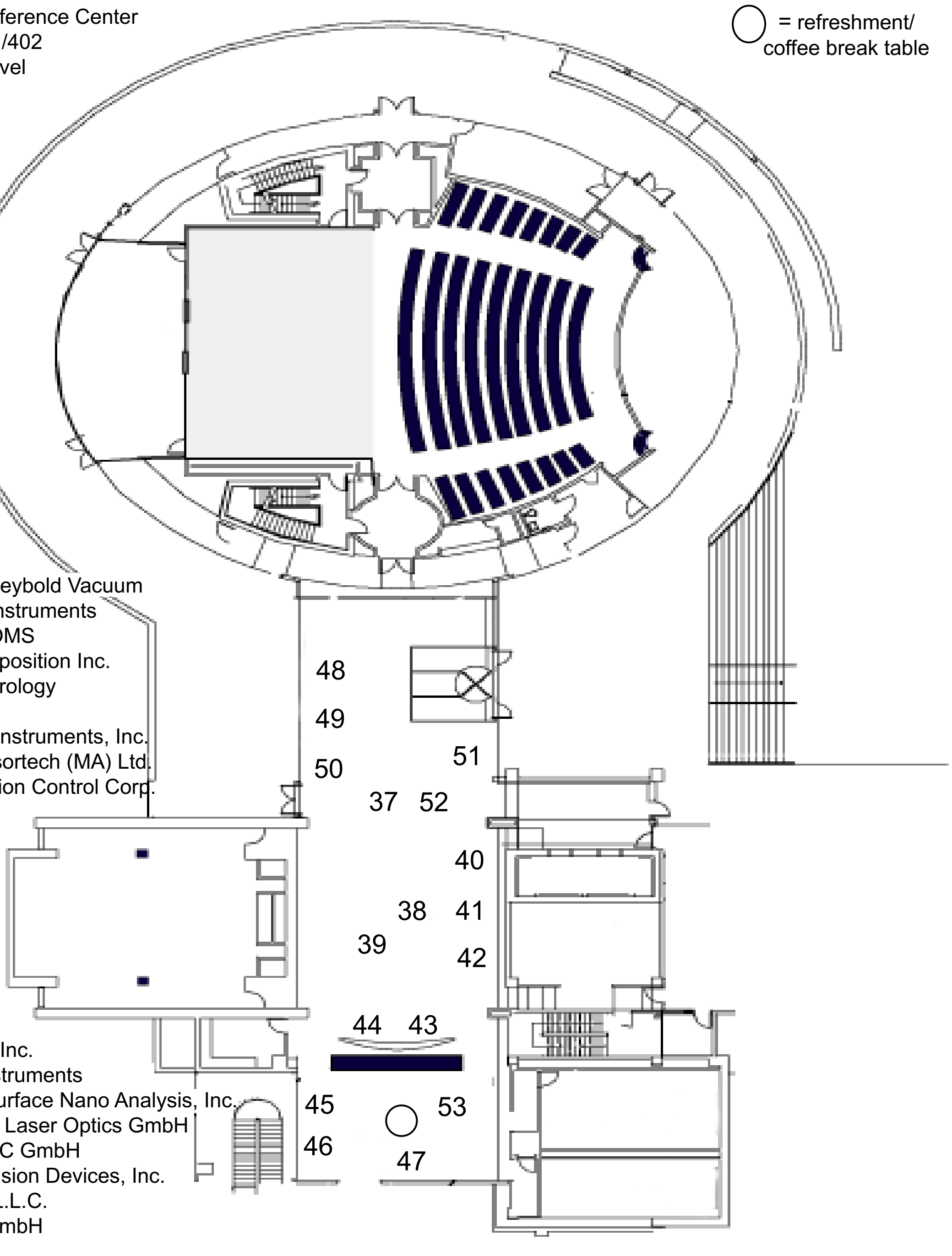

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