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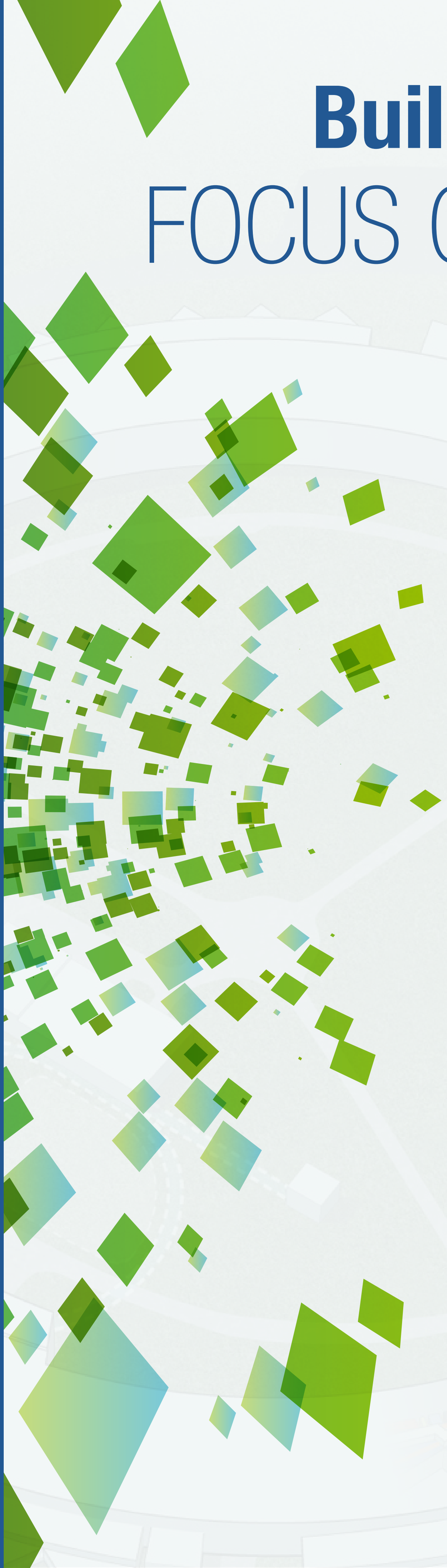


Building on Success:
FOCUS ON THE FUTURE

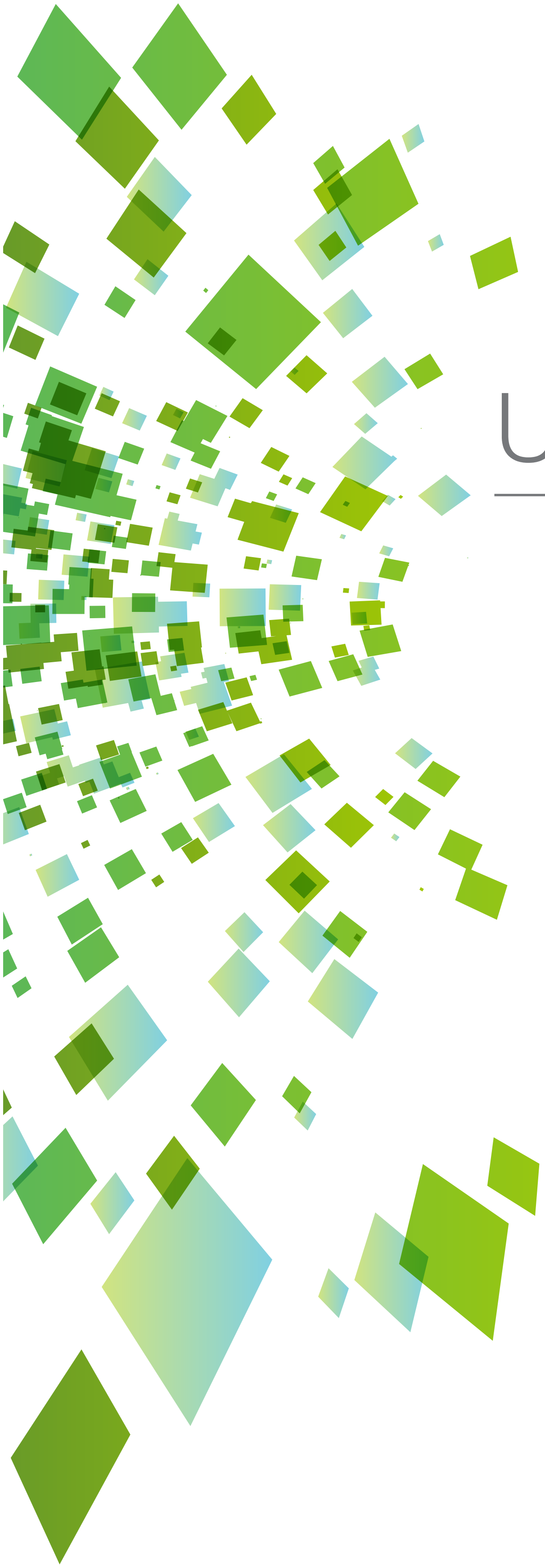
2013
Users Meeting

Argonne National Laboratory
May 6-9, 2013

Program and Abstracts

Argonne
NATIONAL LABORATORY

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



2013
Users Meeting

PROGRAM & ABSTRACTS

Argonne National Laboratory
May 6-9, 2013

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
630-252-6952
cnm_useroffice@anl.gov

Electron Microscopy Center
http://www.emc.anl.gov
630-252-4987

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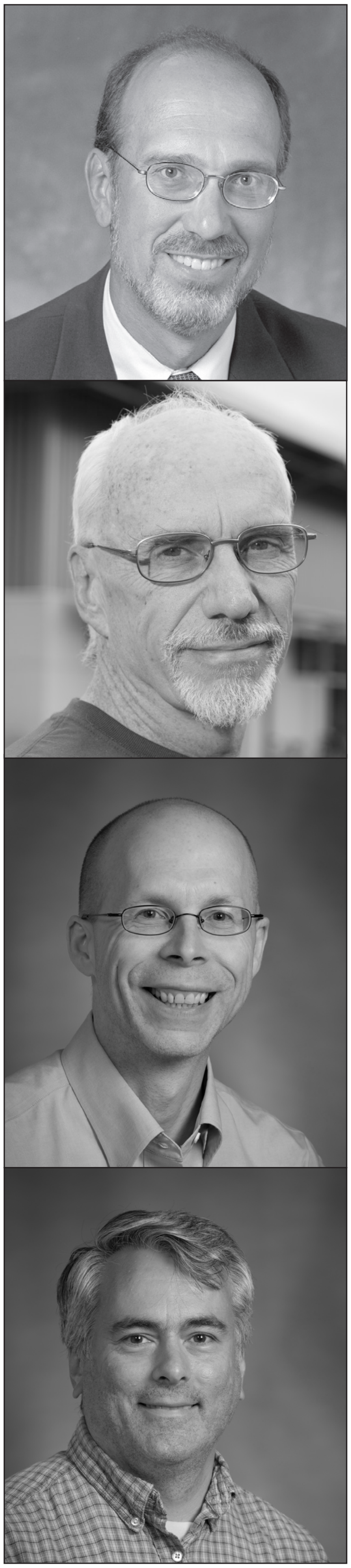


David E. Moncton, John N. Galayda
Michael Borland, Louis Emery

Eleventh Arthur H. Compton Award

The Department of Energy's Advanced Photon Source (APS) and the APS Users Organization present the 2013 Arthur H. Compton Award jointly to David E. Moncton, John N. Galayda, Michael Borland, and Louis Emery. The award recognizes the recipients' visionary leadership and technical ingenuity in introducing "top-up" operation to the synchrotron radiation community.

Top-up operation has substantially improved both the intensity and the quality of the x-ray beam for experiments. The method is now used in most third-generation light sources worldwide and is integral to the design of new sources, such as the Diamond Light Source and the National Synchrotron Light Source-II.

"It has fundamentally changed the operational paradigm for all the world's synchrotron facilities," said Moncton. "Facilities can now run at their maximum x-ray output all the time, significantly increasing the production of x-rays around the world. Perhaps more important, beam stability and operational flexibility have been greatly enhanced as well," he added.

The key issue addressed by top-up is the inevitable loss of stored electron beam, or current, in the storage ring. In the original APS operating modes, current was added, or injected, every 12 hours, and the current decreased 35% between injections, causing the x-ray intensity to decrease as well. This paradigm posed problems for users: X-rays were not available during injection, and the large drop in intensity was very problematic for many experiments because it introduced thermal errors and intensity variations and often limited the length of an experiment.

With top-up, injection is done every two minutes. The current drops only 1%, thermal and intensity transients are minimal, and x-ray production is never interrupted. The result is radically improved operation. Top-up provides higher average photon flux and better beam stability, while also stabilizing heat loads on storage ring magnets and beamline optics.

Furthermore, top-up also allowed changes to the storage ring that significantly reduced x-ray beam size (and thus increased brightness) and allowed new modes that support time-resolved studies. These changes—small emittance, small coupling, and fill patterns with few bunches—significantly decrease the lifetime of the electron beam in the storage ring, but because top-up continually compensates for gradual loss of beam, these much shorter beam lifetimes became practical. Thus, top-up opened the door to many new kinds of experiments that benefit from increased brightness and different time structures in the x-ray beam.

Two advances were crucial to the adoption of top-up. The first was to prove that current could be injected safely while the shutters that separate the storage ring from the beamlines remained open. There was concern that a failure of a storage ring magnet could send the electron beam into the x-ray beam pipe and thus into the x-ray optics, which did not have sufficient shielding. Borland and Emery conducted exhaustive studies to demonstrate conclusively that this could not happen.

The second advance was to minimize disruption to user experiments. Many users were initially highly skeptical, fearing glitches in their data every couple of minutes. "The team did an excellent job of minimizing such transients and documenting their magnitude to the users," said Mark Rivers of GSECARS/University of Chicago.

In their roles as director of the APS and director of the APS Accelerator Systems Division (ASD), respectively, Moncton and Galayda identified the critical developments for implementing and verifying top-up operation and advocated for it in the face of significant resistance from users. Borland, a member of ASD, carried out a massive tracking study of the injection process, co-opting many employee workstations after hours. Emery, also a member of ASD, did analytical studies of top-up safety as an independent confirmation, and led the technical effort to implement quiet, automated top-up, overseeing major improvements to many APS accelerator systems. Borland and Emery also collaborated to reduce the electron beam emittance (a measure of beam size) from about 8 nm to about 3 nm, employing top-up to compensate for the attendant lifetime reduction.

The effort began in September 1996, around the time APS began full user operations, and the first tests with shutters open were done in June 1999. In February and March of 2000, sympathetic users made their first tests during machine studies periods, then from June 2000 to June 2001, a week or two of top-up was offered to users during each run. Finally, in October 2001, top-up became the default mode, offered for 75% of user time.

The impact of top-up has been important across the spectrum of APS experiments. For example, protein crystallography and extended x-ray absorption fine structure (EXAFS) experiments have particularly benefited from stable beam intensity. "Top-up had a major impact on the quality of x-ray crystallography data, especially in the most challenging experiments," according to Andrzej Joachimiak of Argonne National Laboratory. For example, data collected soon after the implementation of top-up mode provided crucial information for solving ribosomal structures, work that was recognized with the Nobel Prize in Chemistry in 2009. The reduction of systematic errors has been important for low-count-rate experiments, such as inelastic and magnetic scattering. Finally, top-up allows APS to offer unique operating modes (such as 24-bunch and hybrid modes) that would be impossible without the improvements made to the injection process. "I can now do experiments which I could not do before," said Mark Sutton of McGill University. In sum, top-up has permitted remarkable scientific achievements and pushed synchrotron radiation sources to new levels of performance.

by Jane Marie Andrew
APS User Office

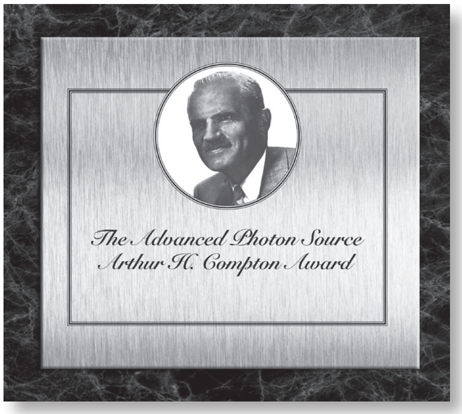
David E. Moncton was Associate Laboratory Director for the APS from 1987 to 2001; he is now a professor of physics and director of the Nuclear Reactor Laboratory at MIT.

John N. Galayda was director of the APS Accelerator Systems Division (ASD) from 1990 to 1999 and then deputy associate director of APS. In 2001 he left the APS to head the Linac Coherent Light Source (LCLS) Project; he is now directing the development of its successor, LCLS-II.

Michael Borland is the associate division director of the APS Accelerator Systems Division.

Louis Emery is an Argonne senior scientist and a group leader in the APS Accelerator Systems Division.

About the Award



The Arthur H. Compton award was established in 1995 by the APS Users Organization (APSUO) to recognize an important scientific or technical accomplishment at the Advanced Photon Source. The awards are generally made at APS User Meetings.

Compton was an American physicist who won the Nobel Prize for Physics in 1927 for discovering and explaining changes in x-ray wavelengths resulting from x-ray collisions with electrons, the so-called Compton effect. This important discovery in 1922 confirmed the dual nature (wave and particle) of electromagnetic radiation. A Ph.D. from Princeton University, Compton held many prominent positions including professor of physics at The University of Chicago and chairman of the committee of the National Academy of Sciences that studied the military potential of atomic energy. His position on that committee made Compton instrumental in initiating the Manhattan Project, which created the first atomic bomb.

Previous award recipients
Nikolai Vinokurov and Klaus Halbach (1995)
Philip M. Platzman and Peter Eisenberger (1997)
Donald H. Bilderback, Andreas K. Freund, Gordon S. Knapp, and Dennis M. Mills (1998)
Sunil K. Sinha (2000)
Wayne A. Hendrickson (2001)
Martin Blume, L. Doon Gibbs, Denis McWhan, and Kazumichi Namikawa (2003)
Günter Schmahl and Janos Kirz (2005)
Andrzej Joachimiak and Gerold Rosenbaum (2007)
Gerhard Grübel, Simon Mochrie, and Mark Sutton (2009)
Edward Stern, Farrel Lytle, Dale Sayers (posthumously), and John Rehr (2011)

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

2013
Users Meeting

COMPREHENSIVE PROGRAM

Monday, May 6

8:00 – 5:00	Exhibits *Bldg. 402, Gallery (lower level); Bldg. 401, Atrium and outside E1100-1200*
7:00 – 5:00	Registration *Bldg. 401, Atrium*
12:15 – 1:45	Lunch *Argonne Guest House (shuttle buses depart from Gallery lower level)*

Opening Session—Morning
Bldg. 402, Auditorium

8:30 – 8:40	Pamela Focia, APSUO Chair *Welcome*
8:40 – 9:00	Eric Isaacs, Argonne National Laboratory Director *Welcome from the Laboratory*
9:00 – 9:15	The Honorable Bill Foster, U.S. Representative, 11th Congressional District of Illinois *Welcome from the Laboratory*
9:15 – 9:30	The Honorable Daniel Lipinski, U.S. Representative, 3rd Congressional District of Illinois *Washington Perspective*
9:30 – 9:50	James Murphy, Director of Scientific User Facilities, Basic Energy Sciences, U.S. Department of Energy *Office of Science Perspective*
9:50 – 9:55	Brian Stephenson, Associate Laboratory Director for Photon Sciences, Argonne National Laboratory *Introduction of Keynote Speaker*
9:55 – 10:35	Brian Kobilka, 2012 Nobel Prize Winner in Chemistry, Professor in the departments of Molecular and Cellular Physiology at the Stanford University School of Medicine *Keynote Address*
10:35 – 11:00	Coffee Break (Gallery, Atrium, and outside E1100-1200)
11:00 – 11:25	Brian Stephenson, Associate Laboratory Director for Photon Sciences, Argonne National Laboratory *Update on the Advanced Photon Source*
11:25 – 11:45	Amanda Petford–Long, Director, Center for Nanoscale Materials, Argonne National Laboratory *Update on the Center for Nanoscale Materials*

11:45 – 12:00	Dean Miller, Director, Electron Microscopy Center, Argonne National Laboratory *Update on the Electron Microscopy Center*
12:00 – 12:20	Yves Idzerda, Vice Chair, National User Facility Organization *National User Facility Organization (NUFO) Report*
12:20 – 1:45	Lunch *AGH Dining Room, shuttle buses depart from Gallery level*

Parallel Facility Plenary Sessions—Afternoon

APS Session
Bldg. 402, Auditorium

1:45 – 2:15	Peter Abbamonte (University of Illinois at Urbana-Champaign) *Whither Inelastic X-ray Scattering?*
2:15 – 3:00	Compton Award winners (see page vii)
3:00 – 3:30	Mark Stalzer (California Institute of Technology) *Trends in Scientific Discovery Engines*
3:30 – 3:55	Coffee Break
3:55 – 4:25	Jay Schuren (Air Force Research Laboratory) *Changing the Paradigm for Engineering Design by Merging High Energy X-ray Data with Materials Modeling*
4:25 – 4:55	Paul G. Evans (University of Wisconsin–Madison) *Opportunities for Picosecond Science in the APS Upgrade*
4:55 – 5:15	Christopher M. Dettmar (Purdue University – Invited Student Talk) *Second Harmonic Generation for Monitoring X-ray Damage*
5:15	Adjourn

CNM Session
Bldg. 402, Room E1100-1200

1:30 – 2:15	Paul Nealey (The University of Chicago) *Directed Assembly of Nanoscale Materials*
2:15 – 2:45	Junhong Chen (University of Wisconsin at Milwaukee) *Graphene-based Hybrid Nanomaterials for Gas Sensing*
2:45 – 3:15	Chad Folkman (Argonne National Laboratory) *Catalysis and Electronic Structure of Complex Epitaxial Oxide Thin Films Studied by* In situ *X-ray Scattering and Cross-sectional STM*

3:15 – 3:25	John Freeland (Argonne National Laboratory) *CNM User Executive Committee Update*
3:25 – 3:50	Coffee Break
3:50 – 4:20	Greg Wurtz (King’s College London) *Ultrafast Dynamics and Spectral Behavior of Nanorod-based Plasmonic Metamaterials and Their Excitonic Hybrids*
4:20 – 4:50	Sanja Tepavcevic (CNM, Argonne National Laboratory) *Nanoarchitectures for Batteries: Beyond Lithium*
4:50 – 5:05	Daniel Hannah (Northwestern University – Invited Student Talk) *Optical and StructuralProperties of Si Nanoparticles at High Pressures*
5:05	Adjourn

EMC Session
Bldg. 401, Room A1100

1:45 – 2:15	J.G. Wen (EMC, Argonne National Laboratory) *Contribution of C_c and C_s Correction to High-resolution TEM at All Energy-loss Regimes*
2:15 – 2:45	Jim Zuo (University of Illinois at Urbana-Champaign) *Uncovering Nanoscale Structural Complexities by Scanning Electron Nanodiffraction*
2:45 – 3:15	Dave McComb (Ohio State University) *EELS and EDX Spectrum Imaging: Can We Measure Compositional Gradients on the Atomic Scale?*
3:15 – 3:45	Coffee Break
3:45 – 4:15	Martha McCartney (Arizona State University) *Electron Holography of Nanoscale Electric and Magnetic Fields*
4:15 – 4:45	Masashi Watanabe (Lehigh University) *Nanocharacterization of Materials by Spectrometry-based Approaches in STEM and TEM*
4:45 – 5:15	Wenpei Gao (University of Illinois at Urbana-Champaign – Invited Student Talk) *Imaging of Interfacial Oxygen Using Chromatic Aberration-corrected TEM*
5:15	Adjourn

5:30 – 9:00	Banquet *Morton Aboretum (buses depart promptly at 5:30 from in front of APS)*

Tuesday, May 7

8:00 – 5:00	Exhibits *Bldg. 402, Gallery (lower level); Bldg. 401, Atrium and outside E1100-1200*
8:00 – 5:00	Registration *Bldg. 401, 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 – 1:45	Lunch *Argonne Guest House (shuttle buses depart from Gallery lower level)*
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

9:00 – 5:05	APS Upgrade Workshop: Beamlines and Scientific Opportunities (see page 21) *Bldg. 402, APS Auditorium*
8:30 – 5:00	Workshop A: Driving Discovery: Visualization, Data Management, and Workflow Techniques (see page 26) *Bldg. 401, Rm. A5000*
8:45 – 5:00	Workshop B: Nanoscale Imaging of Next-generation Materials (see page 32) *Bldg. 402, Rm. E1100/E1200*
8:30 – 5:20	Workshop C: Pushing the Boundaries of Energy Technology: Materials Design for Battery Applications (see page 36) *Bldg. 401, Rm. A1100*
5:00 – 7:30	Poster Session and Reception *TCS, Bldg. 240 (shuttle buses provided)*

Wednesday, May 8

8:00 – 12:00	Exhibits *Bldg. 402 Gallery, Bldg. 401 Atrium and outside E1100-1200*
8:00 – 12:00	Registration *Bldg. 401 Atrium*
12:00 – 2:00	Lunch *Argonne Guest House (shuttle buses depart from Gallery lower level)*
12:15 – 1:30	APSUO Steering Committee Meeting *Bldg. 401, Fifth Floor Gallery*

Parallel Facility-specific Workshops

APS

Workshop 1 (full day): APS Life Science Future Directions (see page 44)
Bldg. 402, APS Auditorium

Workshop 2 (full day): Combining Experiments and Theory in f-Element Research (see page 49)
Bldg. 440 (CNM), Rm. A105/106

Workshop 3 (full day): Ultrafast Dynamics in Strongly Correlated Materials, Atoms, Molecules, and Clusters (see page 55)
Bldg. 401, Rm. A1100

Workshop 4 (morning): Engineering Materials (see page 62)
Bldg. 402, Rm. E1200

Workshop 5 (morning): The Future of High-throughput Nonresonant IXS at “Lower” Energy Resolution (see page 65)
Argonne Guest House, Conf. Rm. A

Workshop 6 (afternoon): High-energy X-rays on Single Crystals: A Unique Capability at the APS (see page 69)
Bldg. 402, Rm. E1200

Workshop 7 (afternoon): Resonant Inelastic X-ray Scattering (RIXS): Frontiers and Perspectives (see page 74)
Argonne Guest House, Conf. Rm. A

CNM

Workshop 8 (full day): Nanostructured Carbon Materials for MEMS/NEMS and Nanoelectronics (see page 77)
Bldg. 401, Rm. A5000

EMC

Workshop 9 (full day): Characterizing Energy Materials: Today and Tomorrow (see page 82)
Bldg. 402, Rm. E1100

Thursday, May 9

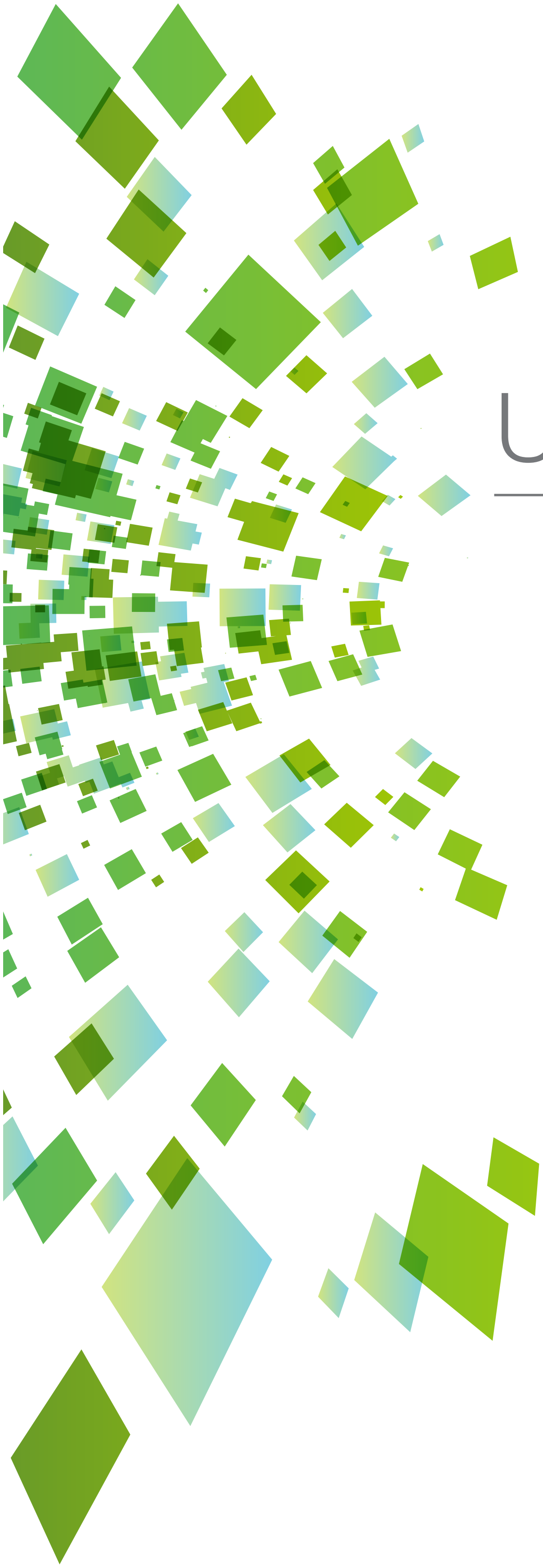
CNM Short Courses

8:30 – 5:00	Short Course A: Modeling and Simulation of Nanofabrication Processes Instructor: Ralu Divan *Bldg. 440, Rm. A105/106*
8:30 – 12:00	Short Course B: Confocal Raman Spectroscopy Instructor: Dave Gosztola *Bldg. 440, Rm. B108*
8:30 – 12:00	Short Course C: Using the Hard X-Ray Nanoprobe Instructor: Martin Holt *Sector 26 Control Room*
8:30 – 12:00	Short Course D: High-performance Computing Techniques for Materials Modeling and Nanophotonics Instructor: Michael Sternberg *Bldg. 440, Rm. A201*

Satellite Workshops

The following meetings are being held in conjunction with the Users Meeting workshops as a convenience to the attendees.

Workshop 10: 9:00 – 3:30	User Facilities for Industry 101 (see page 87) *Bldg. 401, Rm. A5000*
Workshop 11: 8:00 – 4:50	Introduction to the GSAS-II Crystallographic Analysis System (see page 90) *Bldg. 401, Rm. A1100*
Workshop 12: 8:30 – 5:00	Workshop on Next-generation Fast Orbit Feedback Systems for Storage Rings (see page 92) *Argonne Guest House, Conf. Rm. A*
Workshop 13: 8:45 – 4:15	Time-resolved X-ray Science at BioCARS: Past, Present, and Future (see page 94) *Bldg. 402, Auditorium*



2013
Users Meeting

GENERAL SESSION ABSTRACTS

Monday, May 6

APS

Trends in Scientific Discovery Engines

Mark Stalzer

Center for Advanced Computing Research, California Institute of Technology, Pasadena, CA 91125

This talk is about trends in computing technology that are leading to exascale-class systems for both scientific simulations and data reduction. The underlying themes are power consumption, the massive increase in parallelism, and architectural balance for "Big Data" systems. There is an opportunity for the computer science and materials science communities to work together in Pasteur's Quadrant, thereby accelerating the advancement of both fields.

APS

Changing the Paradigm for Engineering Design by Merging High-energy X-ray Data with Materials Modeling

Jay C. Schuren

U.S. Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433

The strategic development of new engineering materials with improved performance rests on establishing computational models that link materials processing, microstructure, and properties/performance. Researchers within the greater scientific community have long sought these linkages, but without access to experimental data at the relevant length scales, validated models capable of predicting complex phenomena such as fatigue initiation and small-crack propagation have remained elusive. Without validated models, adoption of advanced computational methods will remain at the mercy of traditional large-scale testing programs, which inherently limit the adoption of new materials or innovative design due to fiscal and time constraints. Emerging experimental techniques such as high-energy x-ray diffraction microscopy (HEDM) address a critical need with respect to validation experiments for models focused on the prediction of mechanical properties below the continuum scale, where the response of grains and similar microstructural features are explicitly tracked (e.g., Crystal Plasticity Finite Element Model, Field Dislocation Mechanics, etc.). These experiments consist of *in situ* loading at ambient and elevated temperatures, where synchrotron x-rays are used to quantify the average elastic strain and stress tensor for each grain, map both the morphology and local crystallographic orientation within and between grains, and track the formation and propagation of voids/cracks in the sample. The presentation will provide an overview of HEDM techniques, a detailed discussion of the type of data produced, and a discussion of how the data can be used for the development/validation of models and insight into deformation processes below the continuum length scale.

APS

Opportunities for Picosecond Science in the APS Upgrade

Paul Evans

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

The challenge of understanding and controlling how the states of atoms, molecules, and materials evolve as a function of time is an interdisciplinary issue of vast scientific importance. A common thread across disciplines is that a range of important fundamental processes in materials science, biology, and chemistry have characteristic times between 1 and 100 ps. These include the dynamics of chemical and biomolecular reconfiguration and the propagation of fundamental magnetic and structural excitations in solids. The upcoming upgrade of the Advanced Photon Source will create the short-pulse x-ray source (SPX), which will offer a significant advance in the scope of the experimental capabilities of synchrotron-radiation techniques in this important time regime. Significant opportunities arise because the picosecond-duration pulses of x-ray radiation produced by the SPX retain the favorable properties of third-generation sources: widely tunable photon energies spanning from below 1 keV to several tens of keV, excellent stability in the position and pulse-to-pulse reproducibility of the beam, and parallel and independent operation of several simultaneous experiments. The experimental facilities planned for the SPX will provide a unique series of experimental capabilities, including new instruments based on the time-angle correlation of the x-ray beam, time-resolved x-ray microscopy, and picosecond time-resolved x-ray spectroscopy and scattering. The results of recent ultrafast x-ray experiments point to promising directions for the initial use of the SPX facilities.

APS

Second Harmonic Generation for Monitoring X-ray Damage

Christopher M. Dettmar[1], Justin A. Newman[1], Scott J. Toth[1], Michael Becker[2], Robert Fischetti[2], and Garth J. Simpson[1]

[1]Department of Chemistry, Purdue University, West Lafayette, IN 47907
[2]GM/CA@APS, Argonne National Laboratory, Argonne, IL 60439

X-ray diffraction is a powerful tool for determining the atomic resolution structure of proteins, accounting for ~89% of the structures in the World Wide Protein Data Bank. However, x-rays are not a gentile probe and can perturb the order within a protein crystal, which often limits resolution achievable. The exact mechanism of this damage is still under debate. Second harmonic generation (SHG), the frequency doubling of light, is a sensitive probe for asymmetric polarizability and high degrees of order. SHG has been shown to detect protein crystals with a high degree of contrast due to their intrinsic chiral nature and highly ordered crystal lattices. In this work, SHG has been shown to be a good monitor of x-ray-induced damage within crystals. Careful examination into the conditions under which SHG arises also gives new evidence for the mechanism of x-ray damage.

CNM

Graphene-based Hybrid Nanomaterials for Gas Sensing

Junhong Chen

University of Wisconsin-Milwaukee, Department of Mechanical Engineering, Milwaukee, WI 53211

Miniaturized gas sensors that rapidly and accurately detect and differentiate trace amounts of chemical species are attractive for environmental monitoring, medical diagnosis, and lab-on-a-chip analytical devices. Graphene is worth evaluating for chemical and bio sensing due to its outstanding physical and chemical properties. We first report on the fabrication and characterization of room-temperature gas sensors using a back-gated field-effect transistor platform with chemically reduced and thermally reduced graphene oxide (RGO) as the conducting channel. These sensors exhibit significant responses when exposed to low-concentration NO_2 and NH_3 in air and their sensitivity is tunable through varying gate voltages. We then demonstrate the sensitivity and the selectivity of the RGO-based gas-sensing platform can be tuned through coating the RGO surface with various nanocrystals (NCs). For example, the hybrid RGO-SnO_2 NC platform shows enhanced NO_2 but weakened NH_3 sensing response compared with bare RGO. However, RGO-Ag NC hybrids exhibit a higher sensitivity to NH_3 than NO_2. By doping SnO_2 NCs with indium, the sensor selectivity could be further improved. Nanohybrids of indium-doped SnO_2 NCs on an RGO surface show excellent selectivity to NO_2 when other common gases, such as NH_3, H_2, CO, and H_2S are present. Our findings pave a way for the real-world application of graphene-based chemical sensors.

CNM

Catalysis and Electronic Structure of Complex Epitaxial Oxide Thin Films Studied by *In Situ* X-ray Scattering and Cross-sectional STM

Chad M. Folkman

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

The electronic structure of complex oxides materials underpins functionality ranging from superconductivity to resistive switching. To further our understanding of these fascinating systems, new experimental approaches combined with appropriate theory are required. In this talk, I will share two rather unconventional experiments used to access information about the detailed electronic structure of epitaxial complex oxide thin films. The first is cross-sectional scanning tunneling microscopy, which was performed on fully coherent epitaxial oxide heterostructure of $BaTiO_3$/ $SrRuO_3$/(001) Nb-doped $SrTiO_3$. The samples were UHV fractured in ultrahigh vacuum to expose a cross-section of the oxide metal-semiconductor interface and an oxide ferroelectric-metal interface. Nanometer-scale resolved images of the normally buried interfaces were captured at 55 K along with spectroscopy probing the local density of states. The depth resolved dI/dV results are compared with previous I-V and photoelectron spectroscopy type measurements on similar heterostructures. In a second experiment, catalytic activity measurements were conducted to gain insight into the chemical reactivity and indirectly probe the electronic surface structure. We performed an *in operando* catalytic study of the CO oxidation reaction using synchrotron x-ray diffraction and spectroscopy on epitaxial thin films of oxygen-deficient $SrCoO_{3-\delta}$. At elevated temperatures, we measured a CO_2 turn over frequency of ~1 nmoles/ cm^2/s using an in-line gas chromatograph; simultaneous x-ray measurements allowed the reactivity to be compared with changes in the surface roughness, stoichiometry and phase behavior during the reaction. The talk will conclude with a discussion of possible connections between the observed chemical reactivity and electronic structure of the $SrCoO_{3-\delta}$ thin film.

CNM

Ultrafast Dynamics and Spectral Behavior of Nanorod-based Plasmonic Metamaterials and Their Excitonic Hybrids

G. Wurtz[1], G. Wiederrecht[2], D. Gosztola[2], and A. Zayats[1]

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In this presentation we show that the recently discovered nonlocal optical behavior of plasmonic nanorod metamaterials enables an enhanced, ultrafast, and nonlinear optical response of this hyperbolic structure. In particular, a large (80%) change of transmission through this subwavelength thick slab of metamaterial subjected to a low control light fluence of 7 mJ/cm^2, is observed when the conditions of non-locality are satisfied. The picosecond temporal response of the system leads to switching frequencies in the terahertz range [1]. Coupling the metamaterial to a molecular aggregate supporting excitonic excitation, leads to an hybrid material with exciton-plasmon eigenstates [2]. Ultrafast spectroscopy reveals the dynamics of the hybrid metamaterial in both strong and weak coupling regimes, demonstrating drastic differences in both their temporal and spectral dynamic response.

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CNM

Nanoarchitectures for Batteries: Beyond Lithium

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Rechargeable battery systems with different transporting ions will bring substantial relief and expansion of the existing energy storage market, which is primarily based on Li-ion technology. Sodium-based batteries are an attractive alternative due to the abundance of sodium and their enhanced operation stability, while magnesium batteries with the divalent nature of Mg-ion are expected to achieve substantially greater energy density. Due to shorter electron and ion diffusion path length, nanostructured electrode materials are one of the most attractive strategies to dramatically enhance battery performance. To achieve fast mass transport and high power density, unique hierarchical nanoarchitectures such as nanotubes and nanoribbons have been investigated and will be presented. We found that size matching of the transporting ions and host atoms (e.g., Li^+ in TiO_2) enable the use of the high-density packed crystalline nanoscale materials as electrodes reaching theoretical capacity, highest rate capability, improved cycling life, and safety. On the other hand, our approach to achieving larger size ion/multiple charge intercalation is to use nanoscale materials that have adjustable d-spacing and two-dimensional layered structure that can accommodate large volume/charge changes. Most of the known conventional battery materials start out as highly crystalline and pulverize to an amorphous state upon cycling: their predetermined crystalline structures often undergo phase transitions upon intercalation of transporting ions. These phase transitions cause swelling of the electrode materials resulting in local atomic rearrangements, limited diffusion of ions, and ultimately capacity degradation. We will present how counter intuitively starting from amorphous, low-crystalline materials we were able to create interconnected nanoporous electrodes that undergo self-organization upon repeated cycling. Amorphous TiO_2 nanotubes convert into cubic titania, while open-frame bilayered V_2O_5 structure adopts long range order upon intercalation of transporting ions. Both of these structures naturally choose and optimize their crystalline structure in order to achieve fast cycling (high power), high permeability (energy density), and mechanical resistance to cycling (stability).

CNM

Optical and Structural Properties of Si Nanoparticles at High Pressures

Daniel Hannah[1], Maria Chan[2], Jihua Yang[3], Paul Podsiadlo[2], Arnaud Demortiere[2], David J. Gosztola[2], Uwe Korsthagen[3], Vitali Prakapenka[4], George Schatz[1], and Richard Schaller[1, 2]

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Nanocrystalline silicon has generated a great deal of interest as a material that offers improved optical performance with respect to bulk Si. Here, we report on the use of hydrostatic pressure as a tool to investigate the origin of photoluminescence in Si nanocrystals. A combination of classical molecular dynamics and first principles density functional theory is used to calculate the optical, electronic, and structural properties of Si nanocrystals under applied hydrostatic pressure [1]. These results are experimentally corroborated with pressure-dependent photoluminescence spectroscopy and x-ray diffraction [1]. This work extensively leveraged user resources at the Advanced Photon Source (APS) and Center for Nanoscale Materials (CNM). Molecular dynamics calculations were carried out on the Carbon high-performance computing cluster at the CNM. Optical characterization of Si nanocrystals was also carried out using laser spectroscopy facilities at CNM. Pressure-dependent structural characterization was carried out at sector 13 of the APS (GeoSoilEnviroCARS).

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EMC

Contribution of C_c and C_s Correction to High-rResolution TEM at All Energy-loss Regimes

Jianguo Wen

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The advent of spherical aberration correction (C_s) has led to significant improvements in TEM imaging. For example, the Negative C_s Imaging Method developed by Jia *et al* that allows direct structural mapping including oxygen columns is enabled by C_s correction. Now, the much more recent development of C_c correction offers a new opportunity to improve imaging further, especially for high-resolution TEM (HRTEM) at zero loss and energy-filtered HRTEM at high-loss regimes. Here, I will first present the contribution of C_c correction to conventional HRTEM including directly interpretable HRTEM imaging for thicker TEM specimens and obtaining atomic resolution channeling contrast in directly interpretable HRTEM images. Then, I will report the contribution of C_c correction to HRTEM imaging at high energy-loss regimes up to 500 eV.

EMC

Uncovering Nanoscale Structural Complexities by Scanning Electron Nanodiffraction

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Acquiring texture information is essential to further understand the properties of many technologically important materials. The conventional techniques used to characterize crystallite orientation are bright- and dark-field transmission electron microscopy (TEM) and electron backscatter diffraction (EBSD) performed in a scanning electron microscope. While EBSD allows a quantitative determination of crystal orientations, it has the disadvantage of relatively low spatial resolution and sensitivity to crystal surfaces. TEM has the advantage of high resolution, but diffraction contrast recorded in bright- or dark-field TEM is difficult to interpret. Therefore, it is required to develop new imaging techniques in TEM in order to detect the crystal orientation and structure information for nanocrystalline materials. Electron nanodiffraction is a TEM-based diffraction technique that can obtain diffraction patterns using electron probes of few nanometers in diameter. At University of Illinois, we have further developed electron nanodiffraction capability by combining with scanning, symmetry determination, and statistical analysis of diffraction patterns. Here, we report the progress we have made in characterizing nanodomains in piezoelectric single crystal of $(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3})O_3\text{-}xPbTiO_3$ single crystals in the morphotropic phase boundary region at x=0.31, gold nanowires, and high-entropy alloys of $Al_{0.5}CoCrCuFeNi$.

EMC

EELS and EDX Spectrum Imaging: Can We Measure Compositional Gradients on the Atomic Scale?

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There have been numerous reports in the literature of significantly enhanced ionic conductivity in multilayer heterostructures formed from ionic conductors and insulators [1–3]. There have also been a number of reports suggesting that these enhancements are due to electronic rather than ionic conductivity [4, 5]. Many of these reports have focused on heterostructures between $SrTiO_3$ (STO) and yttria-stabilized zirconia (YSZ) [3, 5].

It would be highly informative to understand how the lattice mismatch (>7%) between STO and YSZ is accommodated. It has been suggested that a highly disordered region is present at each interface in a trilayer structure, which results in high local concentration of oxygen vacancies. Electron energy-loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) has been used to address this question but close proximity of the atomic numbers (Sr:38, Y:39, Zr:40) make overlap of ionization edges problematic [5, 6].

In this contribution we will compare results obtained by EELS spectrum imaging with those obtained using high-resolution energy-dispersive x-ray (EDX) analysis in the STEM. In particular we will consider the reliability of measurements of atomic scale compositional fluctuations in the context of previous results discussing the limits of spatial resolution in EELS and EDX spectrum imaging [7].

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EMC

Electron Holography of Nanoscale Electric and Magnetic Fields

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Off-axis electron holography in the transmission electron microscope provides a unique and powerful approach to visualizing electric and magnetic fields within materials with resolutions approaching the nanometer scale. The ability to image phase shifts at medium resolution opens up a wide field of interesting and important materials problems. In this work, the technique has been successfully used to quantify electrostatic and magnetic fields in and around deep-submicron devices and patterned nanomagnets. An important extension of this work has involved *in situ* application of magnetic fields to image local magnetic response during hysteresis loops. Applications include asymmetric pinning of domain walls at notches in nanowires. Electrostatic field examples include, imaging of electrostatic phase shift at quantum dots to allow for quantification of charge capture and measurement of piezoelectric fields and two-dimensional electron gas densities.

This work was supported by U.S. Department of Energy under Grant No. DE-FG02-04ER46168.

EMC

Nanocharacterization of Materials by Spectrometry-based Approaches in STEM and TEM

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Chemical analysis at atomic-level spatial resolution with single-atom detection sensitivity is one of the ultimate goals in materials characterization. Such atomic-level materials characterization would be feasible by electron energy-loss spectrometry (EELS) and x-ray energy dispersive spectrometry (XEDS) in the latest aberration-corrected scanning transmission electron microscopes (STEM) because more probe current can be added into the incident probe by aberration correction. Especially for EELS analysis, sufficient amounts of core-loss signals can be generated within a short acquisition time by higher current probes, and hence atomic-resolution EELS mapping has already been applied [1–3]. For XEDS analysis, spatial resolution reaches ~ 0.4 nm [4], which implies atomic-level analysis is feasible in aberration-corrected STEM. However, atomic-level chemical analysis is even more challenging in the XEDS approach since detection of x-ray signals is more limited than that in EELS (~100 times difference). The limited signals can be improved by recently developed large, solid-angle detector configurations. In this presentation, the latest attempts to obtain atomic-level elemental distributions by EELS and XEDS approaches will be presented.

Conversely, it is also very important to obtain elemental information from a larger field of view. Energy-filtering transmission electron microscopy (EFTEM) in combination with spectrum imaging (SI) enables the determination of spatially resolved elemental distributions over a large field of view with a relatively high spatial resolution. However, the signal intensities in EFTEM images are generally lower, which may degrade following processing. Therefore, a new acquisition scheme for EFTEM SI, called SmartEFTEM-SI, has been developed by incorporating a number of improvements: (1) initialization of dark current in a CCD camera prior to acquisition, (2) measurement of individual dark currents prior to every filtered-image acquisition, (3) acquisition of the core-loss image series from the higher energy loss side, (4) multiple-frame acquisition of individual filtered images, (5) acquisition of a zero-loss image between successive filtered images for superior spatial drift correction, and (6) acquisition of a low-loss image series after the core-loss image series acquisition for further advanced spectral processing and quantification [5]. In addition to atomic-resolution chemical analysis, the latest development in EFTEM will also be presented.

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EMC

Imaging of Interfacial Oxygen Using Chromatic Aberration-corrected TEM

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[2]Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801
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Gold nanocrystals (Au NCs) on rutile TiO_2 surfaces have attracted considerable interest as a model system for studying the remarkable size-dependent catalytic activities of supported Au NCs, especially for catalyzing the oxidation of carbon monoxide [1]. Several mechanisms have been proposed to explain the surprising chemical activities of Au and almost all of them involve interactions at the Au NCs and support interface [2], which renders the study of interfacial structure tremendously important. Cross-sectional transmission electron microscopy (TEM) provides a powerful way for studying interfaces. While high-angle scattering of electrons (Z-contrast) in scanning transmission electron microscopy (STEM) with aberration correction can characterize interfacial cations at atomic resolution, oxygen atoms are much more difficult to detect due to its low atomic number. High-resolution TEM, in principle, is sensitive to light atoms in phase contrast. But the resolution and information transfer in conventional TEM are limited by both spherical and chromatic aberrations. The chromatic aberration correction enabled by ACAT (Argonne chromatic aberration-corrected TEM) located in Argonne National Lab significantly improves the information transfer and resolution in recorded images. Furthermore, the ability to adjust individual aberration coefficients using the C_c corrector also allows a precise control over the contrast transfer function (CTF) and the use of CTF for optimizing the contrast between heavy and light atoms, and thus improves the sensitivity to light elements for thin samples using phase contrast.

To enable high resolution C_c-corrected TEM investigation, we have developed a novel NC synthesis technique for preparing Au NCs on rutile (TiO_2) surfaces. Au nanoparticles about 2–5 nm in diameters were first deposited onto the single crystal TiO_2 substrate, pre-thinned and annealed in air, by e-beam evaporation deposition at room temperature. Then the sample was annealed in air at 500°C to form epitaxial Au NCs (the same annealing procedure is used for the activation of Au catalyst).

Using ACAT, we recorded HREM images in a focal series using optimized C3 and C5 coefficients. By reconstructing the focal series, we have succeeded in obtaining the exit wave function from several Au NCs supported on TiO_2. Focal series reconstruction improves the signal and noise ratio, removes the lens effect from the recorded images and allows a direct comparison between experiment and simulations. Results show resolved surface bridging oxygen on TiO_2 surface at 1.4 Å distance away from Ti, and oxygen reduction at the interface, which brings the Au atoms closer to Ti. Interfacial oxygen can be seen at stepped, or rough, Au/TiO_2 interfaces. Thus, chromatic aberration correction in ACAT now enables the study of full atomic details at nanocrystal and support interface, and a study of NC and support interaction, which potentially will have a large impact on our understanding of the atomistic mechanism of catalytic activities.

We would like to thank Dr. Jon M. Hiller at EMC, ANL for his help on sample preparation. The work reported here is supported by the NSF Grant No. DMR 0449790. High Resolution Electron microscopy was carried out on ACAT at the Electron Microscopy Center, an Office of Science User Facility 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.), and AC-STEM was carried out in the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois.

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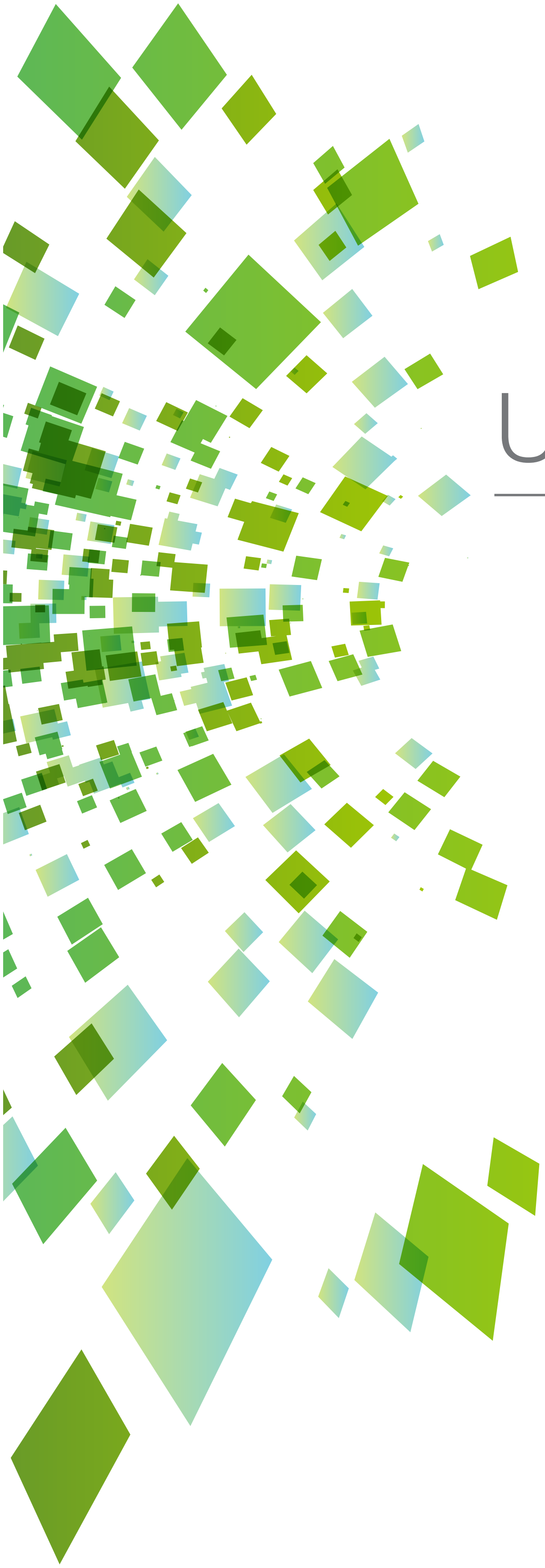

2013
Users Meeting

WORKSHOP AGENDAS AND ABSTRACTS

Tuesday, May 7
APS Upgrade Workshop

Beamlines and Scientific Opportunities

Location:	Bldg. 402, APS Auditorium
Organizers:	George Srajer, Dean Haeffner, Mark Beno, and Mohan Ramanathan (Advanced Photon Source)

The APS Upgrade Project will provide new state-of-the-art beamlines and enhanced capabilities to all APS users. To do this, the APS Upgrade Project will construct a dozen new or upgraded beamlines with orders-of-magnitude improvement in spatial, time, and energy resolutions in areas such as high-energy diffraction, *in situ* studies of materials synthesis, wide-field imaging, ultrafast diffraction, and spectroscopy. For all APS users, the scope of the Project also includes construction of insertion devices optimized to deliver the highest brightness, long straight sections, superconducting RF cavities to produce picosecond X-ray pulses, higher electron current, and improved beam stability.

Since the last Users Meeting in 2012, the Project received approval by DOE and has started the construction of the Resonant Inelastic X-Ray Scattering beamline, and has also successfully passed the Preliminary Design Review. In addition, significant progress has been made in many areas, such as the installation and commissioning of the prototype superconducting undulator, testing of the new beam position monitor, and the first integrated test of the prototype superconducting RF deflection cavity in the laboratory. The workshop will be an opportunity to discuss the current status of the APS Upgrade Project, recent design and technical advances, and future plans.

All speakers from Advanced Photon Source, Argonne National Laboratory

9:00 – 9:35	George Srajer *APS Upgrade Overview and Status*
9:35 – 10:00	Thomas Gog *Resonant Inelastic X-ray Scattering Beamline and Early Science*
10:00 – 10:25	Wenjun Liu *Sub-micron Three-Dimensional Diffraction (S3DD) Beamline*
10:25 – 10:40	Break
10:40 – 11:05	Vadim Sajaev *Producing Short Pulses*
11:05 – 11:35	Eric Dufresne *The APS-U Short-Pulse X-ray Beamline Facilities*
11:35 – 12:00	Robert Bradford *Proposed Detector Development Initiatives for the APS Upgrade*
12:00 – 2:00	Lunch

2:00 – 2:30	Yury Ivanyushenkov *First Experience with Superconducting Undulator at the APS*
2:30 – 2:55	Jörg Maser *The APS* In Situ *Nanoprobe Beamline: A Next-generation Tool for Study of Energy Materials and Devices*
2:55 – 3:20	Glenn Decker *APS Upgrade Beam Stability Enhancements*
3:20 – 3:35	Break
3:35 – 4:00	Hawoong Hong *X-ray Interface Science (XIS) Beamline*
4:00 – 4:25	Sarvjit Shastri *High-Energy X-Ray Diffraction (HEXD) at 1-ID*
4:25 – 4:50	Kamel Fezzaa *Wide-field Imaging Beamline*
4:50 – 5:05	Dean Haeffner, Marion White, and Mohan Ramanathan *Wrap-up*
5:05	Adjourn to Poster Session in Building 240

Upgrade

Resonant Inelastic X-ray Scattering Beamline and Early Science

Thomas Gog, Diego Casa, Mary Upton, Jungho Kim, XianRong Huang, Bran Brajuskovic, and Jason Carter

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

The resonant inelastic x-ray scattering (RIXS) program at the APS is one of the leading efforts of its kind in the world. Its main focus is on studying correlated electron systems in novel materials of great scientific and technological importance, including complex metal oxide compounds, and other electronically active substances such as graphene. The proposed upgrade will make possible entirely new contributions in the domain of "real materials in real conditions in real time" by virtue of substantially improving the energy resolution of the technique, increasing the incident flux and experimental throughput of the RIXS facility, and enhancing the spectrometer with polarization analysis and various extreme and *in situ* sample environments. Emphasis will initially be placed on 5d-TMOs such as iridates and osmates, which recently have emerged as materials with great promise.

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

Upgrade

Sub-micron Three-dimensional Diffraction (S3DD) Beamline

Wenjun Liu

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

The sub-micron three-dimensional diffraction (S3DD) beamline is an upgraded insertion device beamline to be developed at sector 34. Canted undulators will allow for simultaneous and independent use of microbeam diffraction and nanoscale diffraction facilities. A new experiment hutch will be constructed downstream of the existing microbeam diffraction hutch for dedicated x-ray polychromatic and monochromatic nanofocusing platforms. Both K-B mirror and zone-plate-based nanoprobes will be instrumented for quantitative detection and structural characterization of crystalline materials in the sub-100-nanometer scale in three dimensions.

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

Upgrade

Producing Short Pulses

Vadim Sajaev

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

One of most challenging aspects of the APS Upgrade will be creation of a short-pulse x-ray (or SPX) facility. We will discuss the method for generating picosecond-long x-ray pulses using deflecting cavities, describe its implementation at APS, and give the expected radiation parameters. We will also briefly show the present status of the project.

Upgrade

The APS-U Short-pulse X-ray Beamline Facilities

Eric Dufresne

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

The short-pulse x-ray (SPX) beamline facilities will extend time-resolved x-ray scattering and spectroscopy to the picosecond time scale while retaining the powerful characteristics of synchrotron radiation, i.e., user-controlled continuous tunability of energy, polarization, and bandwidth combined with exquisite x-ray energy and pulse length stability over a wide energy range. Experiments at the SPX facility will produce 2 ps stroboscopic snapshots of molecular rotations, molecular excited-state transient structures, stress/strain wave propagation, magnetic domain wall dynamics, phase transitions, and the coupling between electronic, vibrational, and magnetic degrees of freedom in condensed matter systems. Time-resolved studies of transient dynamics will be possible with simultaneous picosecond time resolution and picometer structural precision for a variety of atomic, molecular, supramolecular, nanoscale, and bulk material systems. Transformational developments are now taking place in high-average-power pulsed laser technology with substantially increased repetition rates that promise to make highly efficient use of the MHz x-ray repetition rates of the SPX. This talk will discuss the two hard x-ray beamlines and laser facilities developed in the APS Upgrade scope with five end stations with scattering, diffraction, spectroscopy, imaging, and microscopy capabilities.

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

Upgrade

Proposed Detector Development Initiatives for the APS Upgrade

Robert Bradford[1], Gabriella Carini[2], Grzegorz Deptuch[3], Angelo Dragone[2], Farah Fahim[3], Jasmine Hasi[2], Sven Herrmann[2], Chris Kenney[2], Tim Madden[1], Apurva Mehta[4], Julie Segal[2], and Tom Zimmerman[3]

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[4] Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Facility, Menlo Park, CA 94025

This talk will discuss plans for two proposed detector development initiatives being considered for the APS Upgrade. Both detectors are based on hybrid pixel technology, with pixel logic optimized for specific experimental techniques. CPix2 is a counting detector for pump-probe beamlines. The pixel logic will incorporate dual counters and both upper-level and lower-level discriminators. FASPAX (Fermi-Argonne Semiconducting Pixel Array X-ray Detector) is a versatile integrating detector for high-flux time-resolved applications such as the Dynamic Compression Sector or high-flux pump-probe. This detector will be capable of acquiring a burst of 48 images at 6.5 MHz, with dynamic range approaching 10^5 photons/pixel/pulse.

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

Upgrade

First Experience with Superconducting Undulator at the APS

Y. Ivanyushenkov, K. Harkay, and J. Lang

Advanced Photon Source, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439

The first test superconducting undulator, SCU0, was installed in the APS storage ring in the winter 2012–2013 shutdown. After successful commissioning, the device was immediately employed as a new user device. The first experience of operating such a novel device at the APS is presented including the undulator cryogenic behavior as well as its effects on the machine operation and the first experience of using the device in Sector 6.

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

Upgrade

The APS *In Situ* Nanoprobe Beamline: A Next-generation Tool for Study of Energy Materials and Devices

Jörg Maser

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

The Advanced Photon Source is developing a suite of new hard x-ray beamlines to study materials and devices under real conditions. One of the flagship beamlines of the APS Upgrade is the *in situ* nanoprobe (ISN) beamline, which will provide *in situ* and *operando* characterization of advanced energy materials and devices. The ISN will enable materials studies at variable temperature, under flow of fluids and gases, and under applied electric fields, at previously unattainable spatial resolution and throughput. Using nanofocusing mirrors, the ISN will provide several orders of magnitude increase in photon flux at a spatial resolution of 50 nm. It will provide a highest spatial resolution of 20 nm using diffractive optics, and sensitivity to yet smaller sample structures using coherent diffraction. A high-throughput data acquisition system will be deployed to significantly increase beamline productivity, with the goal providing a user experience similar to that of a modern scanning electron microscope. The ISN will provide full spectroscopy to study the chemical state of most materials in the periodic table, and enable x-ray fluorescence tomography. *In situ* electrical characterization will enable *operando* study of energy and electronic devices. We will the present the preliminary design of the ISN beamline, and discuss initial scientific studies related to the science thrust of the ISN beamline.

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

Upgrade

APS Upgrade Beam Stability Enhancements

G. Decker

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

A variety of machine improvements are planned, with the goal to improve beam stability up to 1 kHz, and over time scales of days to weeks. Beam position monitor (BPM) electronics upgrades, a new fast-orbit feedback system with a high-speed real-time data network, mechanical motion sensing of BPM pickup electrodes, and a totally new high-power hard x-ray beam position measurement and alignment system will be described along with the expected levels of performance improvement.

Upgrade

X-ray Interface Science (XIS) Beamlines

Hawoong Hong

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

X-rays offer a unique opportunity to penetrate many complex environments to probe the structure and chemistry of surfaces and buried interfaces. These interfaces between media with distinct physical and chemical properties offer exciting possibilities for discovery in diverse scientific areas such as catalysis, oxide film growth, semiconductors, geochemistry, surface physics, biomembranes, corrosion, nanoscience, environmental science, tribology, and electrochemistry. By its very nature, interfacial science brings together a diverse community with interests in catalysis, biomembranes, oxide film growth, semiconductors, geochemistry, surface physics, corrosion, nanoscience, tribology, electrochemistry, and in the development of the next generation of energy-related technologies. One of many grand challenges in this interdisciplinary field is to understand through observation and control the organization of atoms and molecules at well-defined surfaces in complex environments. Increasingly sophisticated *in situ* x-ray methods that exploit the inherent spatial, temporal, and spectral properties of undulator radiation are being developed to meet these challenges. A dedicated x-ray interfacial science (XIS) facility at a sector of the APS will fully exploit the unique capabilities of the APS to advance our understanding of this area.

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

Upgrade

High-energy X-ray Diffraction (HEXD) at 1-ID

S.D. Shastri

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

Both an upgraded and a new beamline are proposed at 1-ID through a canted configuration building new, dedicated stations and having a long straight section with optimized sources, including one superconducting undulator. The properties of high-energy x-rays, which include penetration capability, enable bulk samples to be studied in complex environments, and programs already in operation at beamline 1-ID exploit these unique characteristics. These programs are well integrated with the user community (whose diverse base consists of academic, national laboratory, and industrial users) and have high demand, as 1-ID is consistently oversubscribed by a factor of five or greater. In addition to focusing optics, end-station instruments will be upgraded and/or developed for the following techniques: high-energy diffraction microscopy, combined small-angle x-ray scattering/wide-angle x-ray scattering, imaging, resonant scattering, fluorescence, and buried interfaces. These programs are scientifically aligned with Argonne strategic initiatives, including materials for energy, nuclear materials, and advanced computation.

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

Upgrade

Wide-field Imaging Beamline

Kamel Fezzaa

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

The wide-field imaging (WFI) project is a 250 m long beamline that will enable x-ray imaging of centimeter-sized samples, with a spatial resolution in the 1–10 μm range and exposure times down to 80 ps using white beam or 10–60 keV monochromatic x-rays. It expands current capabilities at the APS in three crucial aspects: (1) increases the beam size from the millimeter to cemtimeter scale, (2) increases the sensitivity for phase-contrast imaging, and (3) improves the spatial resolution by reducing the source size effect.

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

Cross-facility Thematic Workshops

Workshop A
Driving Discovery: Visualization, Data Management, and Workflow Techniques

Location:	Bldg. 401, Rm. A5000
Organizers:	Nicholas Schwarz (Advanced Photon Source), Siwei Wang (Advanced Photon Source), Ian McNulty (Center for Nanoscale Materials), and C.D. Phatak (Electron Microscopy Center)

The great richness of data collected at the APS, CNM, and EMC plays critical roles in scientific exploration. As an example, imaging and microscopy experiments are adding dynamics and spectroscopic information to tomography. However, methods for understanding data have not kept pace; there is no "Moore's law" scaling that applies to by-hand examination of data. Manual management and analysis of data is too time consuming and cumbersome for large, complex datasets. State-of-the-art mathematics and computer science tools will help automate the understanding process for large datasets. Only then will scientific understanding be able to fully benefit from the coming deluge of data.

This workshop is organized to discuss the state of the art and future potential of advanced optimization, visualization, data management, and workflow techniques for Argonne's user facilities. It brings together experts in optimization, computer vision, visualization and data management alongside user scientists to discuss current and future applications. The goal is to elaborate on how users can benefit from these techniques to enable new scientific discovery.

8:30 – 8:50	Welcome & Introductory Remarks
8:50 – 9:20	Gayle Woloschak (Northwestern University) *Need for Correlative Imaging of Nanoparticles in Tissues*
9:20 – 9:50	Jean-Christophe Olivo-Marin (Institut Pasteur, France) *Mathematical Microscopy*
9:50 – 10:20	Yali Amit (University of Chicago) *Statistical Object Models: From Computer Vision to Biological Imaging*
10:20 – 10:50	Break
10:50 – 11:20	Rachana Ananthakrishnan (Argonne National Laboratory) *Globus Online Tools for Data Management and Analysis*
11:20 – 11:50	Daniela Ushizima (Lawrence Berkeley National Laboratory) *Analysis and Visualization of High-throughput Experiments*
11:50 – 12:15	Todd Munson (Argonne National Laboratory) *Numerical Optimization and Data Mining*
12:15 – 1:45	Lunch

1:45 – 2:15 Michael Groeber (Air Force Research Laboratory)
Digital Representation Environment for the Analysis of Microstructure in 3D (DREAM.3D): Who, What and Why

2:15 – 2:45 Subramanian Sankaranarayanan (CNM, Argonne National Laboratory)
Probing Structure-Functionality Relationship at the Mesoscale Using All-atom Molecular Dynamics Simulations

2:45 – 3:10 Josh Kacher (University of Illinois at Urbana-Champaign)
Progress and Development towards Four-dimensional Electron Microscopy for Defect Characterization

3:10 – 3:40 Break

3:40 – 4:10 Salman Habib (Argonne National Laboratory)
Inverting the Universe: How to Stuff a Supercomputer Inside a Laptop

4:10 – 4:40 Anton Barty (Center for Free-Electron Laser Science, Germany)
Processing the Deluge of Data from X-ray Free-electron Lasers

4:40 – 5:00 Discussion

WKA

Mathematical Microscopy

Yoann LeMontagner[1, 2], Elsa Angelini[2], and Jean-Christophe Olivo-Marin[1]

[1] Institut Pasteur, CNRS URA 2582, 75015, Paris, France
[2] Institut Mines –Télécom, 75013, Paris, France

Important improvements and breakthroughs in microscopy acquisition methods can be achieved by incorporating innovative signal/image processing ingredients directly into the acquisition and/or reconstruction protocols, and by developing the new paradigm of mathematical microscopy. We will present some recent developments of smart acquisition methods in biological imaging whereby it is possible with mathematical tools to recover a high quality image from very fewer samples than the full acquisition and to design smart dynamic imaging protocols. They are based on theoretical tools from compressed sensing (CS), a recent mathematical theory for sampling and reconstructing signals in an efficient manner. Indeed, the use of CS-based computational tools does provide a novel mathematical framework to enable faster frame rates, better preservation of biological samples and higher qualities of image reconstruction. We will show examples of how the use of mathematical microscopy makes it possible the design of new imaging protocols, dedicated to specific biological paradigms and experimental conditions.

Le Montagner, Y., Angelini, E., and Olivo-Marin, J.-C. (2012) Video reconstruction using compressed sensing measurements and 3D Total Variation regularization for bio-imaging applications, *IEEE Intern. Conf. on Image Processing, ICIP 2012*, Orlando, September 2012.

Marim, M., Angelini, E., Olivo-Marin, J.-C., Atlan, M. (2011) Off-axis compressed holographic microscopy in low light conditions, *Optics Letters*, 36, 1, pp. 79-81.

Le Montagner, Y., Angelini, E., and Olivo-Marin, J.-C. (2011) Comparison of reconstruction algorithms in compressed sensing applied to biological imaging, *IEEE Intern. Symp. on Biomedical Imaging, ISBI 2011,* Chicago, April 2011.

Marim, M., Atlan, M., Angelini, E., and Olivo-Marin, J.-C. (2010) Compressed sensing with off-axis, frequency-shifting holography, *Optics Letters*, 35, 6, pp. 871-3.

WKA

Statistical Object Models: From Computer Vision to Biological Imaging

Yali Amit

Departments of Statistics and Computer Science, University of Chicago, Chicago, IL 60637

The goal of computer vision is the automatic labeling of images containing multiple objects as well as noise and clutter. Similar issues arise in biological imaging, where massive amounts of images are generated at multiple scales: molecular, cellular, and organismal. In all these settings, several objects can interact creating configurations that may not have been encountered in the learning phase. I will present a unified approach, which starts from simple statistical models for individual objects. With these models the important notion of invariance can be clearly formulated, as well as geometric instantiations. Furthermore the individual object models can be composed to define models for object configurations. Decisions are likelihood based and do not depend on pre-trained decision boundaries. The model formulation also leads to a coarse-to-fine strategy for efficient computation of the optimal scene annotation. These ideas will be illustrated in a range of applications reading handwritten zip codes, detecting faces, tracking vesicles in fluorescent microscopy, and detecting worms and their shapes in light microscopy.

WKA

Globus Online Tools for Data Management and Analysis

Ian Foster

Argonne National Laboratory, Argonne, IL 60439

Globus Online provides hosted, software-as-a-service solutions for common research data management tasks. I describe the production services that we operate for file and folder transfer, synchronization, and sharing, and for identity, credential, and group management. I also introduce new services that we are developing for data collection and catalog management and for data analysis pipelines. I report on experiences with the use of these services at the Advanced Photon Source and the Advanced Light Source.

WKA

Analysis and Visualization of High-throughput Experiments

Daniela Ushizima

Lawrence Berkeley National Laboratory, Berkeley, CA 94720

One of the main challenges in microtomography analysis is to extract information from very large and high-resolution datasets, often with billions of pixels per image stack. We can access relevant structures through graphical visualizations of the solid volumes; however, the hardest task is to provide accurate differentiation among the components of the imaged materials. In this realm, our mission has been to develop algorithms that combine tuning procedures for image processing and analysis and to shield the user from implementation details while delivering measurements from the experimental outcomes. This talk will describe a computational analysis workflow to access internal and external properties of geological samples using synchrotron x-ray tomography. Our workflow, Quant-CT, can recover the porous media volume from microtomographies and extract features as volume, surface area, granularity spectrum, and porosity, among others. Quant-CT supports quick user interaction, so that the user trains algorithms for automated function parameterization. Quant-CT plugin is part of a research on porous materials related to geologic sequestration of CO_2. We will overview the materials science problem, describe our implementation, and demonstrate our plugin on microtomography.

WKA

Numerical Optimization and Data Mining

Todd Munson

Argonne National Laboratory, Argonne, IL 60439

I will give a general overview of numerical optimization and the methods available in the Toolkit for Advanced Optimization. I will use data mining applications to motivate the numerical optimization problems that we solve.

WKA

Digital Representation Environment for the Analysis of Microstructure in 3D (DREAM.3D): Who, What, and Why

Michael A. Groeber

Air Force Research Laboratory, Wright Patterson Air Force Base, OH 45433

DREAM.3D is an open and modular software environment that allows users to reconstruct, instantiate, quantify, mesh, handle and visualize microstructure digitally. It is being developed by the Air Force Research Laboratory in conjunction with a host of collaborators from Carnegie Mellon University, the Naval Research Laboratory, Ohio State University, Johns Hopkins University, Los Alamos National Laboratory, and others. This presentation will detail the architecture of the environment and its data formats, along with the current functionalities. This presentation is meant to educate the community on the existing state-of-the-art tools and build a developers network for advancing these tools in the future. Further, this presentation will attempt to identify areas of high return that are currently under-addressed in DREAM.3D's current form.

WKA

Probing Structure-Functionality Relationship at the Mesoscale Using All-atom Molecular Dynamics Simulations

Subramanian K. R. S. Sankaranarayanan

Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

Nanomaterials exhibiting complex multiproperty behavior and response have become important in key technological areas including solar conversion, energy storage, efficient electronics, medicine, and sensing. In functional devices employing these nanomaterials, it is critical to identify the structure-functionality correlation for an ensemble of nanoparticles. The factors determining such correlations vary over a wide range of length and time scales (intermolecular interactions at nanoscale to mesoscopic interfacial interactions and particle-particle interactions). This talk will focus on large-scale molecular dynamics simulations involving several-million-atom systems to probe structure-functionality at the mesoscale as well as mesoscale phenomena that are of importance for materials synthesis and design. The rapid advances in computational power as well as the need to understand the full functionality of new materials with atomistic resolution has led to an exponential growth in the size and complexity of the data used to describe them. Using representative systems ranging from solvated thermo-sensitive polymer relevant to biomedical application to reactive complex oxides, this talk highlights the computational challenges and evaluates the data-intensive nature of such million-atom atomistic simulations. The atomistic simulations of these multi-million-atom systems generate an enormous amount of data (several hundred TB). These simulations will be used as examples to illustrate the current bottlenecks in the post-processing step, visualization as well as the need for efficient algorithms to manage and analyze the large data sets.

WKA

Progress and Development towards Four-dimensional Electron Microscopy for Defect Characterization

Josh Kacher[1, 2] and Ian M. Robertson[2, 3]

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[2] Department of Materials Science and Engineering, University of Illinois, Urbana-Champaign, IL 61801
[3] Department of Materials Science and Engineering, College of Engineering, University of Wisconsin, Madison, WI 53706

Diffraction-contrast electron microscopy is a vital tool in materials science, allowing both the direct visualization and characterization of defects in crystalline materials. However, the data obtained is a snapshot in the evolution of the microstructure and is in the form of a two-dimensional projection of the three-dimensional structure as projected on the electron exit surface of the space. Consequences of this are that the pathway by which the evolved microstructure was attained is unknown and interpretation of complex microstructures can be ambiguous. These inherent ambiguities can be overcome by combining *in situ* transmission electron microscopy (TEM) experiments with electron tomography. The latter through the reconstruction of a series of images acquired over a wide angular range recovers the through-thickness information lost in the projection images, allowing the extraction of true three-dimensional data. As the contrast of defects in crystalline materials is directly related to the relationship between the electron beam and crystal orientation, care must be taken to carefully align the tilt axis with a single crystallographic plane when acquiring the images needed for tomographic reconstructions. This restriction inhibits the application of electron tomography during *in situ* TEM experiments as the stages used generally require a specific sample geometry and have limited tilting capabilities. In this talk, strategies to relax the geometrical requirements associated with electron tomography as well as to reduce the number of images needed for a high fidelity reconstruction of a defect state will be presented. It will be shown that these strategies facilitate the periodic acquisition of images needed for the reconstruction of an electron tomogram at interrupted points during *in situ* TEM deformation experiments. Additionally, it will be shown that through the addition of a real-space coordinate system to the tomograms, the dislocation character becomes directly accessible. Applications to dislocation interactions in ion-irradiated materials as well as grain boundary/dislocation interactions will be presented.

WKA

Inverting the Universe: How to Stuff a Supercomputer Inside a Laptop

Salman Habib

High Energy Physics and Mathematics & Computer Science Divisions, Argonne National Laboratory

The puzzles of cosmology constitute some of the grandest of inverse problems: How can mapping the distribution of galaxies, the underlying density field, the cosmic microwave background, and combining this information with other cosmological probes, yield information about the Universe as a dynamical system? Sky surveys across multiple wavebands—ongoing, and in the near future—will provide an enormous amount of information that can only be interpreted using large-scale simulation campaigns on the biggest available supercomputers. In this talk, I will describe the computational and statistical methodologies that are being developed to render this problem tractable and to produce robust results at high accuracy. Armed with these techniques, we hope to be able to provide insights on the nature of dark matter and dark energy, the mysterious source of the late-time accelerating expansion of the Universe. The computational techniques developed in this work have ramifications for multi-particle simulations; the new statistical methods are particularly useful in solving inverse problems that can arise in materials contexts such as electron and x-ray diffraction data sets.

WKA

Processing the Deluge of Data from X-ray Free-electron Lasers

Anton Barty

Center for Free Electron Laser Science, DESY, Hamburg, Germany

The development of free-electron lasers (FEL) in the x-ray regime has opened up new frontiers in x-ray imaging. With x-ray pulses of only a few femtoseconds duration and sufficient peak power to produce high-quality diffraction patterns from biologically relevant samples using a single pulse, recent experiments at the Linac Coherent Light Source (LCLS) have demonstrated structural determination from both isolated viruses and streams of hydrated sub-micron crystals. Samples are continuously fed into the x-ray focal region producing a diffraction pattern each time a sample particle intersects the FEL beam. Such experiments produce large quantities of data: for example, the Linac Coherent Light source at SLAC National Laboratory delivers a pulse repetition rate of up to 120 Hz enabling the collection of over 432,000 diffraction patterns per hour. Using one fully populated CSPAD detector each diffraction measurement contains roughly 2.3 million pixels at 16-bits data depth, or 4.7 MB/image, resulting in a data stream of roughly 2 TB per hour. A single experiment at the LCLS can easily result in more than 30 million detector readout events per experiment with a data volume in excess of 120 TB. Efficiently reducing this data into useful forms is critical for both guiding user decisions during experiments, and for the rapid extraction of science output once the experiment is complete. We will describe the tools currently used in such experiments, and look ahead to future needs demanded by higher repetition rate facilities such as the European XFEL, which can deliver up to 26,000 pulses per second.

Workshop B
Nanoscale Imaging of Next-generation Materials

Location: Bldg. 402, E1100/E1200

Organizers: Jörg Maser (Advanced Photon Source), Jeff Guest (Center for Nanoscale Materials), and Jianguo Wen (Electron Microscopy Center)

The development, understanding, and application of new materials and molecular systems hinges on resolving deep correlations between their structure and their electronic, optical, magnetic, and chemical properties. These correlations need to be explored on the nanometer length scales where critical physical processes such as charge separation, photo physics, catalysis, magnetic-exchange interactions, among others, take place, and where unique opportunities arise in discovery of new phenomena and design of new materials with new properties. At the APS, the CNM, and the EMC, we are developing and using a powerful and complementary array of microscopy platforms to explore these materials at these critical length scales in a variety of environments. This workshop will showcase efforts at the laboratory and elsewhere to push the frontier of nanoscale imaging in order to extend our understanding of advanced materials and nanoscale structures and to harness their unique properties for next generation applications.

8:45 – 9:00	Welcome & Introductory Remarks
9:00 – 9:40	Cheng-Hsuan Chen (National Taiwan University) *Chemical Mapping at Atomic Resolution in an Aberration-corrected Scanning Transmission Electron Microscope*
9:40 – 10:20	Robert F. Klie (University of Illinois at Chicago) *Chemical Analysis with Sub-Å Resolution of Light Elements Using Aberration-corrected STEM*
10:20 – 10:50	Break
10:50 – 11:30	Wei Chen (Argonne National Laboratory) *Hierarchical Nanomorphologies in High-performance Polymer:Fullerene Bulk Heterojunction Solar Cells*
11:30 – 12:15	Mariana Bertoni (Arizona State University) In Situ *X-ray Microscopy: A Story of Solar Cells and Defect Kinetics*
12:15 – 1:50	Lunch
1:50 – 2:30	Charlie Sykes (Tufts University) *Single Atom Alloys as a Strategy for Selective Heterogeneous Hydrogenations*
2:30 – 3:10	Wenge Yang (APS, Argonne National Laboratory) *High-pressure Research Combining Synchrotron Radiation and Electron Microscopy*
3:10 – 3:40	Break

3:40 – 4:20 Sophie-Charlotte Gleber (Argonne National Laboratory)
Spatial Insight: High-resolution X-ray Fluorescence Tomography for Complex Materials

4:20 – 5:00 Nathan Guisinger (CNM, Argonne National Laboratory)
Graphene Synthesis, Characterization, and Processing: An Atomic-scale Investigation

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WKB

Chemical Analysis with Sub-Å Resolution of Light Elements Using Aberration-corrected STEM

Robert F. Klie

Department of Physics, University of Illinois at Chicago, Chicago, IL 60607

The last few years have seen a paradigm change in scanning transmission electron microscopy (STEM) with unprecedented improvements in both spatial and spectroscopic resolution being realized by aberration correctors, cold-field emission guns, and monochromators. The successful correction of lens aberrations has greatly advanced the ability of the STEM to provide direct, real space imaging at atomic resolution. Very complementary to reciprocal space methods, this is especially advantageous for aperiodic systems, nanostructures, interfaces, and point defects. Aberration-correction has also enabled the development of new imaging techniques, such as incoherent annular bright field imaging, which enables the direct visualization of light atoms such as hydrogen. While these instrumentation developments have brought notable successes in materials analysis, in particular for hetero-interfaces, catalysis, and thin-film studies, they have also challenged the established experimental protocols and our fundamental understanding of both imaging and spectroscopy in the STEM. Aberration correction also allows increased flexibility in choosing the appropriate electron energy to minimize beam-induced damage while maintaining atomic-resolution (e.g., 60 keV electrons for studying graphene with 1.3 Å resolution).

Here, I will present the latest results from the new probe aberration-corrected cold-field emission JEOL JEM-ARM200CF at the University of Illinois at Chicago, which allows *in situ* characterization with 78 pm spatial resolution and an energy resolution of 350 meV in the temperature range between 10 K and 1,300 K using a variety of *in situ* heating, cooling, tomography, and electrical feedback holders. The primary electron energy can be chosen between 80 and 200 kV. I will show how low-energy imaging can now be used to characterize beam-sensitive materials without significant loss in spatial resolution and how such experiments enable direct correlation with other techniques, including atom-probe tomography and first-principles modeling.

WKB

Hierarchical Nanomorphologies in High-performance Polymer:Fullerene Bulk Heterojunction Solar Cells

Wei Chen

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439
Institute for Molecular Engineering, the 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 due to their low-cost and scalability. In the last 15 years, research efforts have led to organic photovoltaic (OPV) devices with power conversion efficiencies (PCEs) >8%, but these values are still insufficient for the devices to become widely marketable. To further improve solar cell performance, a thorough understanding of the complex structure-property relationships in OPV devices is required. In this work, we have determined that the superior performance of PTB7:fullerene bulk heterojunction (BHJ) solar cells, one of the best-performance OPV systems, is attributed to hierarchical nanomorphologies with optimum crystallinity and nanoscale intermixing of copolymers with fullerenes, which together promote exciton dissociation, and consequently, contribute to photocurrent. We have also discovered that the formation mechanism of hierarchical nanomorphologies is a competitive yet synergistic mechanism of crystallization and liquid-liquid phase separation (either nucleation and growth or spinodal decomposition). Fine-tuning morphologies from molecular ordering to nanophases enables us to understand the fundamental physics underlying the superior performance of PTB copolymers and, thereby, realize improvement in the performance of PTB:fullerene BHJ solar cells with power conversion efficiencies (PCEs) up to approximately 9%, very close to a commercially viable PCE of 10%.

WKB

In Situ X-ray Microscopy: A Story of Solar Cells and Defect Kinetics

Mariana Bertoni

Arizona State University, Tempe, AZ 85287

The vast majority of photovoltaic materials are highly sensitive to the presence of inhomogeneously distributed nanoscale defects, which commonly regulate the overall performance of the devices. The defects can take the form of impurities, stoichiometry variations, microstructural misalignments, and secondary phases—the majority of which are created during solar cell processing. In order to understand the severe efficiency limitations that currently affect solar cell materials, it is necessary to understand in detail the role of defects and their interactions under actual operating and processing conditions. This talk will discuss our work to develop an *in situ* stage for x-ray microscopes with the capabilities of temperature and ambient control. Insights into the defect kinetics in silicon solar cells will be discussed with an emphasis in creating a strong modeling tool for predicting and optimizing solar cell efficiency. Our most recent work on chalcogenide cells will be presented and the outlook for *in situ* x-ray microscopy in photovoltaic science will be discussed.

WKB

Single Atom Alloys as a Strategy for Selective Heterogeneous Hydrogenations

Charlie Sykes

Tufts University, Medford, MA 02155

Hydrogenation reactions are central to the petrochemical, fine chemical, pharmaceutical, and food industries and are of increasing interest in energy production and storage technologies. Typical heterogeneous catalysts often involve noble metals and alloys based on platinum, palladium, rhodium, and ruthenium. While these metals are active at modest temperature and pressure, they are not always completely selective and are expensive. We have demonstrated that single palladium atoms can convert the otherwise catalytically inert surface of an inexpensive metal into an ultraselective catalyst. We used high-resolution imaging to characterize the active sites and temperature programmed reaction spectroscopy to probe the chemistry. The mechanism involves facile dissociation of molecular hydrogen at individual palladium atoms followed by spillover onto the copper surface, where ultraselective catalysis occurs by virtue of weak binding. The reaction selectivity is in fact much higher than that measured on palladium alone, illustrating the unique synergy of the system.

WKB

High-pressure Research Combining Synchrotron Radiation and Electron Microscopy

Wenge Yang

High Pressure Synergetic Consortium, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, IL 60439

High-pressure research has made great achievements in the last half century, largely due to the advanced technique developments from both synchrotron radiation and electron microscopy. As for *in situ* high pressure research, high-energy x-ray synchrotron takes the major role with its large penetration and its high-brilliance, high-coherence, wide energy spectrum, short-pulse timing mode, and the fast developments on the x-ray optics. The state-of-the-art dedicated synchrotron beamlines allow high pressure scientists to conduct frontier diffraction, spectroscopy, imaging, and time-resolved *in situ* studies. The atomic resolution of modern electron microscopy also provides detailed characterization of the materials before and after high pressure processes. The *in situ* high-pressure research is also possible in transmission electron microscopy with the localized electron beam irradiation. In this talk, the most recent developments on both synchrotron and electron microscopy work will be presented, and the outlook will be discussed.

WKB

Spatial Insight: High-resolution X-ray Fluorescence Tomography for Complex Materials

Sophie-Charlotte Gleber, Chris Roehrig, Evan Maxey, and Stefan Vogt

X-Ray Science Division, Argonne National Laboratory, Argonne, IL 60439

X-ray fluorescence (XRF) tomography is uniquely capable of revealing the elemental composition of complex samples in three dimensions. With high sensitivity and high spatial resolution, various elements get detected simultaneously while at the same time absorption and differential phase contrast provide complementary information of the sample. 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 but at the same time the instrumentation needed basic improvements prior to opening to our user community. Today, the beamline runs routinely in tomography mode, and the applications thus far span the geological, biological, environmental, and material sciences. As our setup is under ambient conditions, we were even able to collect the first XRF tomography data set on aqueous samples [Gleber et al, accepted]. Ambient conditions also allow for controlled sample environments as currently under development for air moisture control.

In the presentation the capabilities of x-ray fluorescence tomography will be introduced and demonstrated showing a range of applications.

WKB

Graphene Synthesis, Characterization, and Processing: An Atomic-scale Investigation

Nathan P. Guisinger

Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

Graphene is nature's ideal two-dimensional conductor that is comprised of a single sheet of hexagonally packed carbon atoms. Since the first electrical measurements made on graphene, researchers have been trying to exploit the unique properties of this material for a variety of applications that span numerous scientific and engineering disciplines. In order fully realize the potential of graphene, large-scale synthesis of high quality graphene and the ability to control the electronic properties of this material on a nanometer length scale remain key challenges. This talk will focus on atomic-scale characterization of graphene synthesis on various materials [SiC, Cu(111), Cu foil, Ag(111), etc.] via scanning tunneling microscopy. These fundamental studies explore growth dynamics, film quality, and the role of defects. The chemical modification of graphene following exposure to atomic hydrogen will be discussed, while additional emphasis will be made on graphene's unique structural and electronic properties.

Workshop C
Pushing the Boundaries of Energy Technology: Materials Design for Battery Applications

Location: Bldg. 401, A1100

Organizers: Elena Shevchenko (Center for Nanoscale Materials), Mahalingam Balasubramanian (Advanced Photon Source), and Mitra Taheri (Drexel University, representing Electron Microscopy Center)

Development of transformational battery technologies requires tailoring novel materials and/or incorporating new chemical processes. Energy storage devices are intrinsically complex with the relevant materials processes covering time-scales from picoseconds to years and length-scales from angstroms to millimeters. Materials design in terms of morphology, chemical composition, size, structure, etc., can lead to advanced properties of lithium and beyond-lithium ion batteries, and new ways of electrode fabrication allowing ultrathin and flexible batteries. Advanced x-ray and electron microscopy methods have opened a new window by which vital structural and electronic properties of battery materials can be obtained at the appropriate spatio-temporal scales using a variety of spectroscopic, scattering and imaging techniques under real world operating conditions. This workshop will focus on different aspects of nanomaterials and advanced characterization of battery materials under operando conditions.

8:30 – 8:35	Welcome and Introductory Remarks
8:35 – 9:10	Shirley Meng (University of California, San Diego) *Pathways to Design and Develop New Energy Storage Materials*
9:10 – 9:45	Bruce Dunn (University of California, Los Angeles) *Pseudocapacitive Properties of Nanostructured Transition Metal Oxides*
9:45 – 10:05	Jason Croy (Argonne National Laboratory) *Challenges of Composite, High-Capacity, Lithium-ion Cathodes*
10:05 – 10:25	Matthew McDowell (Stanford University) *Watching Batteries Work: Understanding the Electrochemical Lithiation of Silicon Nanostructures with* In Situ *TEM*
10:25 – 10:50	Break
10:50 – 11:25	Debra Rolison (Naval Research Laboratory) *Architecturally Rewriting Energy Storage—3D Zn and 3D Air Cathodes*
11:25 – 12:00	Yury Gogotsi (Drexel University) *Two-dimensional Titanium-carbide-based Materials for Li-ion Batteries*
12:00 – 12:20	Maria Chan (CNM, Argonne National Laboratory) *Combining Advanced Characterization and First Principles Computation to Understand Surface and Interfacial Effects in Lithium Batteries*
12:20 – 1:50	Lunch
1:50 – 2:25	Jun Liu (Pacific Northwest National Laboratory) *Recent Progress in Na-Ion and Li-S Battery Chemistry*

2:25 – 3:00	Tim Fister (APS, Argonne National Laboratory) *Electrochemical Phase Stratification of Intermetallic Multilayers*
3:00 – 3:20	Andrea Paolella (University of Genova, Italian Institute of Technology) *Colloidal Synthesis of Ultrathin and High-performance Lithium Iron Phosphate and Lithium Iron Manganese Phosphate Nanoplatelets*
3:20 – 3:40	Break
3:40 – 4:15	Joy Andrews Hayter (SLAC National Accelerator Laboratory) *Mesoscale Phase Distribution in* $LiFePO_4$
4:15 – 4:50	Gerald Seidler (University of Washington) *Nonresonant IXS of Critical Materials for Energy Sciences: Opportunities and Instrumentation for the APS-U*
4:50 – 5:10	Sanja Tepavcevic (CNM, Argonne National Laboratory) *Nanostructured Na-ion Full Cells*
5:10 – 5:20	Closing remarks

WKC

Pathways to Design and Develop New Energy Storage Materials

Shirley Meng

Department of NanoEngineering, University of California San Diego, San Diego, CA 92093

Energy storage in the electrochemical form is attractive because of its high efficiency and fast response time. New and improved materials for energy storage are urgently required to make more efficient use of our finite supply of fossil fuels and to enable the effective use of renewable energy sources. In this seminar, I will discuss a few new perspectives for energy storage materials including new Li intercalation compounds, new Na intercalation compounds, and their micro and nanostructured electrodes. I will demonstrate how to combine knowledge-guided synthesis/characterization and first-principles computation to develop and optimize new higher energy/power density electrode materials for lithium ion and sodium ion batteries. With recent advances in characterization tools and computational methods, we are able to explore intrinsic ionic mobility and phase transformations in electrode materials, and develop an approach to map out the structure-properties relations in functional materials for energy storage and conversion.

WKC

Pseudocapacitive Properties of Nanostructured Transition Metal Oxides

Bruce Dunn

Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, CA 90095

Batteries and electrochemical capacitors (ECs) represent the most widely used types of electrochemical energy storage devices. ECs are frequently overlooked as an energy storage technology despite the fact that these devices can deliver greater power, have much faster response times, and longer cycle life than batteries. A key limitation to this technology, which is based on electric double-layer capacitance, is its low energy density, and for this reason there is considerable interest in exploring materials that exhibit pseudocapacitive charge storage. The fast and reversible redox reactions associated with pseudocapacitor-based materials lead to energy densities, which are an order of magnitude larger than traditional double-layer capacitors. In this paper some of the advantages of mesoporous architectures for transition metal oxides will be highlighted. The interconnected porosity enables the electrolyte to access the redox-active pore walls, thus ensuring that the entire film is electrochemically active. Among the different transition metal oxides, we find the charge storage properties of Nb_2O_5 to be especially attractive. *In situ* x-ray diffraction shows that lithium ion insertion into the orthorhombic phase produces a pseudocapacitive response that leads to high specific capacitance in short charging times. Recent studies have identified several structural and kinetic features that characterize this intercalation-based pseudocapacitance process.

WKC

Challenges of Composite, High-capacity Lithium-ion Cathodes

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Lithium- and manganese-rich composite cathode structures have received worldwide attention as some of the most promising candidates for the next generation of lithium-ion batteries. This class of materials boasts capacities of ~250 mAh/g [1] and uses abundant, inexpensive, and environmentally benign manganese as the major transition metal component. As such, composite electrode structures are poised to make their entry into high-energy-density batteries for electric and plug-in hybrid electric vehicles. However, several major challenges remain that compromise cell performance. For example, high voltage cycling is necessary to access the desired capacity, which leads to oxygen loss, surface damage, electrolyte decomposition, transition metal dissolution, and a large hysteresis [2, 3, 4, 5]. Furthermore, and perhaps most challenging, is the phenomenon of voltage fade [6]. Specifically, after the composite structure has been "activated" at high voltage (≥4.5 V) on the first charge, continued cycling over high states of delithiation leads to a continuous decay of the voltage profile and an overall decrease in energy output. Therefore, the "activation" process itself, necessary for obtaining high capacities, triggers the slow and continual decay of these composite electrode structures.

In this talk, an overview of recent results pertaining to the aforementioned challenges will be presented. In addition, examples of how Argonne National Laboratory's Advanced Photon Source is being used to characterize these highly complex materials and to aid in the design of new composite cathode structures and compositions will be given.

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WKC

Watching Batteries Work: Understanding the Electrochemical Lithiation of Silicon Nanostructures with *In Situ* TEM

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Improvements in Li-ion battery technology are urgently needed for emerging applications such as electric vehicles and grid storage. Silicon (Si) is an especially attractive negative electrode material because it has ten-times higher theoretical specific capacity than conventional anodes. However, silicon undergoes different reaction and degradation mechanisms than traditional battery materials, and for stable electrochemical cycling it is vital to understand these processes in detail. Here, the electrochemical lithiation reaction of single silicon nanostructures is studied with *in situ* transmission electron microscopy (TEM) and *ex situ* techniques. The experiments reveal the effects of crystallography, size, and shape on volume expansion and fracture, along with uncovering the controlling influence of mechanical stress on the kinetics of the reaction in crystalline Si nanoparticles. These results provide general guidelines for engineering silicon nanostructures for better performance in Li-ion battery anodes.

WKC

Architecturally Rewriting Energy Storage—3D Zn and 3D Air Cathodes

D.R. Rolison, C.N. Chervin, J.F. Parker, E.S. Nelson, and J.W. Long

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Bringing rechargeable metal–air batteries to practical fruition intersects all of the challenges inherent to fuel cells, electrolyzers, and batteries. For energy stored in the metal anode to be released (battery function), oxygen must be catalytically reduced at a porous air cathode (fuel-cell function); for the battery to be recharged, oxygen must be catalytically regenerated from the products of metal oxidation (electrolyzer function). Redesigning the air cathode via an architectural, nanoscopic, and three-dimensional (3D) perspective has brought technologically relevant O_2-reduction activity to carbon nanofoam paper derived from nanoscopic coatings of manganese oxide (~10-nm thick MnO_x) at the carbon walls [1] plus a new function difficult to achieve in metal–air cells: pulse power from the pseudocapacitance of the oxide paint [2]. We now show that converting standard Zn powder composite anodes to a 3D form factor (we use the aperiodic sponge) permits Zn electrodes to be (i) charged and discharged in symmetric cells without generating dendrites; and (ii) discharged vs. an air cathode to ~90% Zn utilization [3].

J.F.P. is a National Research Council Postdoctoral Fellow (2010–2013) in Code 6170; E.S.N. is a Pathways Research Aid in Code 6170.

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WKC

Two-dimensional Titanium-carbide-based Materials for Li-ion Batteries

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Recently, we discovered a new family of two-dimensional (2D) early transition metal carbides produced by the exfoliation of the MAX phases. The latter is a large family (+60 members) of machinable layered ternary carbides and nitrides, with a $M_{n+1}AX_n$ composition, where "M" is an early transition metal, "A" is a group 13 to 16 element, "X" is C and/or N, and n = 1, 2, or 3. The exfoliation process was carried out by selective etching of the A-group element from from $M_{n+1}AX_n$ at room temperature, resulting in 2D $M_{n+1}X_n$ layers, we labeled MXene to emphasis their similarity to graphene [1, 2]. Herein we focus on the first synthesized and most studied members of the MXenes family: Ti_3C_2 and Ti_2C produced by HF etching of Ti_3AlC_2 and Ti_2AlC, respectively. The effect of synthesis parameters (temperature, time, particle size) on etching will be discussed. Not only are individual layers formed after exfoliation, but also multi-layer particles and conical scrolls of radii < 20 nm have been demonstrated. Density functional theory simulations showed that band gap of Ti_3C_2 can be tuned from metallic to semiconductor by changing its surface termination (O, OH, and F), and its elastic properties along the basal planes ($c_{11} \approx 523$ GPa) are higher than that of the binary carbide TiC. One of the potential applications for 2D Ti_3C_2 is in energy storage systems as anodes for lithium ion batteries. Oxygen-terminated MXene layers offer excellent wetting with aqueous and organic electrolytes, while having metallic character of conductivity. This is a unique combination of properties that can be used in battery and supercapacitor electrodes [3, 4]. Additive-free Ti_3C_2 anodes produced by filtering an aqueous dispersion of delaminated Ti_3C_2 showed capacity of 410 mAh•g^{-1} at cycling rate of 1C and 110 mAh•g^{-1} at 36C after 200 cycles [5].

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WKC

Combining Advanced Characterization and First Principles Computation to Understand Surface and Interfacial Effects in Lithium Batteries

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Surface and interfacial effects play an important role in lithium-ion and lithium-oxygen batteries. For example, solid-electrolyte interphase products form from electrochemical processes at the electrode-electrolyte interface in batteries, discharge products form on the surface of the oxygen electrode in Li-O_2 batteries, surface orientation dramatically affects the lithium insertion process in silicon anodes, and underpotential surface reactions cause stress in metallic anodes. In this talk, I will discuss how first principles computation can be used in conjunction with characterization techniques such as non-resonant inelastic x-ray scattering, x-ray diffraction, pair-distribution function analysis, and cantilever stress measurements to understand these surface and interfacial effects. I will show how the first principles computation of configurations, spectra, and stresses, in corroboration with measurements of the same, allows us to form an accurate atomistic picture of electrochemical processes.

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WKC

Recent Progress in Na-Ion and Li-S Battery Chemistry

Jun Liu

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Recently, non-Li-based energy storage chemistry has attracted wide attention. In this talk we will discuss recent progress in Na-ion and Li-S battery chemistry focusing on research conducted at the Pacific Northwest National Laboratory. Na-ion could be an inexpensive alternate to Li-ion chemistry for stationary storage, but the intercalation and diffusion of Na ions are difficult. We will summarize our effort to optimize the nanostructured cathode and anode materials to improve the reversibility and the rate capacity of the electrode materials. We will also discuss potential approaches that are not dependent on the bulk diffusion. For Li-S chemistry, most studies have been focused on nanostructured cathode materials. We will discuss our current understanding of the reactions occurring on both the cathode and anode and new approaches to mitigate the undesirable reactions.

WKC

Electrochemical Phase Stratification of Intermetallic Multilayers

Tim Fister[1], Paul Fenter[1], Christian Schlepuetz[1], Bing Shi[1], Xiao Chen[2], Mike Bedzyk[2], Brandon Long[1, 3], Jen Esbenshade[3], and Andrew Gewirth[3]

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As candidate anode materials in lithium ion batteries, intermetallic compounds—like silicon, germanium, and tin—have charge densities up to ten times higher than traditional graphitic electrodes. As a result, these materials expand by ~300% when lithiated and will often suffer from rapid degradation over repeated cycles due to strain-induced delamination of the electrode from its current collector. Using x-ray reflectivity, we have studied the interfacial structure of amorphous thin film silicon electrodes grown on chromium current collectors in a working lithium ion half-cell. We find that silicon intermixes with its metallic current collector and stabilizes into well-defined layers with discrete intermediate densities. In such a structure, lithium insertion occurs reversibly at the *interface* of each layer, forming low-density lithiated silicides that alternate with higher-density metallic layers [1]. Inspired by this electrochemically driven phase stratification, we have also studied silicon/metal silicide multilayers using *in operando* reflectivity. Remarkably, the bilayer spacing of the multilayers coherently expands and contracts by nearly 400% during lithiation and delithiation. *Ex situ* cycling measurements confirm that multilayers are a promising approach to high-power, long lifetime intermetallic anodes.

This research was supported as a part of the Center for Electrical Energy Storage: Tailored Interfaces, an Energy Frontier Research Center funded by the US Department of Energy, Basic Energy Sciences under award number DE-AC02-06CH11.

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WKC

Colloidal Synthesis of Ultrathin and High-performance Lithium Iron Phosphate and Lithium Iron Manganese Phosphate Nanoplatelets

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Olivine lithium iron phosphate is an interesting material for energy storage. For its high theoretical capacity (170 mAh g^{-1}), high stability and layered structure, lithium iron phosphate has caught the interest of chemists as cathode material for secondary lithium ion batteries. After Goodenough's synthesis, lithium iron phosphate could be also synthesized through hydrothermal synthesis, solvothermal synthesis, pyrolisis, microemulsion, and sol-gel synthesis. A colloidal route was presented by Jiang et al. Here we present a new synthetic route that yields ultrathin LFP nanoplatelets with a thickness of 5–7 nm and a length of 60–70 nm. We can control the size and the shape of the crystals using different surfactants and different precursors. Respect to the bulk material lithium iron phosphate nanoplatelets show very facile intercalation and de-intercalation in the tryphilite structure.

Moreover $LiFe_{(1-x)}Mn_xPO_4$ was explored by Yamada and Zhao-Hui Wang. Here we present an easy colloidal synthesis of $LiFe_{(1-x)}Mn_xPO_4$ $(0 \le x \ge 1)$ nanoplatelets with tunable electrochemical properties in the potential range of 3–4 volts simply changing the molar ratio between Fe (II) and Mn (II) ions in the olivine structure. So in one single step it's possible to produce cathode materials with tunable redox potential synthesizing nanoplatelets with different intermediate phases between tryphilite $LiFePO_4$ and lithiophilite $LiMnPO_4$. All these procedures were recently patented: http://www.iit.it/en/technology-transfer/patents/smart-materials-patents/item/shape-control-synthesis-of-lithium-iron-phosphate-nanocrystals-via-colloidal-synthesis.html?category_id=8.

WKC

Mesoscale Phase Distribution in $LiFePO_4$

Ulrike Boesenberg[1, †], Florian Meirer[2], Yijin Liu[3], Rossana Dell'Anna[2], Alpesh K. Shukla[1], Tolek Tyliszczak[4], Guoying Chen[1], Joy C. Andrews[3], Thomas J. Richardson[1], Robert Kostecki[1], and Jordi Cabana[1]

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Li ion batteries are regarded as key players for efficient chemical energy storage from sustainable energy sources. For optimized performance, understanding of fundamental mechanisms of diffusion and phase transformation is mandatory. Although $LiFePO_4$ is widely considered as a cathode material that has achieved technological maturity, the fundamentals of the phase transformation remain poorly understood. The chemical state of the active metal within electrodes can be used to track the charge transfer as the state of charge/discharge. Using full-field transmission x-ray microscopy (TXM) coupled with x-ray absorption near edge spectroscopy (XANES) (FF TXM-XANES) at SSRL beamline 6-2C, maps of the distribution of species involved in the transformation ($LiFePO_4$ and $FePO_4$) were produced at high chemical and spatial (30 nm) resolution for partially delithiated, micron-sized $LiFePO_4$ plate-like crystals [1]. The results of this study stress the role of microstructure as a kinetic factor during the redox transformation of a particle between initial and final state, especially when defects are considered. It provides clues to the design of electrode materials with enhanced utilization and durability.

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WKC

Nonresonant IXS of Critical Materials for Energy Sciences: Opportunities and Instrumentation for the APS-U

Gerald Seidler

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Nonresonant inelastic x-ray scattering (NIXS), often also called x-ray Raman scattering, holds the potential to overcome a lingering experimental problem in research on electrical energy storage, catalysis, and f-electron science. Specifically, in many of the most interesting material systems x-ray spectroscopy from low binding energy edges would be especially valuable, but soft x-rays will not penetrate the necessary sample environments or otherwise conflict with standard sample morphology. NIXS avoids this issue by performing an energy transfer spectroscopy starting at a baseline photon energy of ~10 keV, and therefore exhibits at least modestly bulk-like penetration into even high-Z materials. In this talk, I'll summary a wide range of NIXS work at the APS and elsewhere on critical materials in energy sciences while also touching on the progress toward a final design for the LERIX-2 instrument for the APS-U.

WKC

Nanostructured Na-ion Full Cells

Sanja Tepavcevic[1], Hui Xiong[1], Christopher S. Johnson[2], and Tijana Rajh[1]

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Alternative rechargeable battery systems with transporting ions other than Li ion have attracted growing interests in recent years. While lithium-ion battery technology is quite mature, there remain questions regarding safety, lifetime, and cost. Sodium-based batteries are particularly attractive due to the promise of low cost associated with the abundance of sodium and enhanced stability of nonaqueous battery electrolytes due to the lower operating voltages. Creation of nanostructured electrode materials represents one of the most attractive strategies to dramatically enhance the transport of electrons, ions, and molecules associated with cycling, enabling the use of variety of nonconventional substrates as active electrode materials. To achieve fast mass transport and high power density, unique hierarchical nanoarchitectures such as nanotubes and nanoribbons have been investigated. Excellent electronic and/or ionic conductivity is required for unhindered charge flow through out the whole device. Nanomaterials can offer a possible solution to these requirements with their ability to connect materials and build up structures from the molecular level. Electronically interconnected nanoporosity enables full participation of every electrode atom in achieving theoretical capacity while short diffusion length of Na^+ transporting ions leads to exceptionally fast charging. We will present feasibility of development Na-ion full cell rechargeable batteries that operate at ambient temperature. Full battery was assembled by employment of electrodes (anodes and cathodes) with tailored nanoarchitectures. The most striking advantage of full cells composed of nanostructured electrodes is that they can deliver similar capacity in a much shorter time compared to their conventional counterparts. With repeating cycling nanostructured electrodes naturally choose and optimize their crystalline structure can achieve high power, energy density and stability needed for the next generation of hybrid systems. Furthermore, this Na-ion battery holds promise for the further development of new aqueous, ambient temperature Na-ion battery systems that combine novel electrodes to form energy storage devices that are inexpensive with good performance.

Wednesday, May 8
Facility-specific Workshops

APS Workshop 1
APS Life Science Future Directions

Location:	Bldg. 402, APS Auditorium
Organizers:	Keith Moffat (The University of Chicago), Robert Fischetti (Argonne National Laboratory), and Keith Brister (Northwestern University)

The APS life sciences community has a unique opportunity to leverage the advances planned by the APS-U to push forward on the next generation of life sciences experiments. This workshop will gather the community together to flesh out our plans for the next 5 to 10 years. The will enable us to present a coherent, APS-wide plan for beam line upgrades that will drive new science. The workshop will review the work we've accomplished so far as part of the original APS-U planning process, look at opportunities that have arisen since, and lay out a plan to achieve our goals.

8:30 – 8:50	Keith Moffat (Senior Advisor for Life Sciences at the APS) *Only Connect: Can Aspects of Our User Science Be Done Better Together?*
8:50 – 9:20	Gwyndaf Evans (Diamond Light Source) *Progress with* In Situ *Room-temperature Data Collection at Diamond Light Source*
9:20 – 9:50	Vadim Cherezov (The Scripps Research Institute) *Micro-crystallography of GPCRs*
9:50 – 10:20	Michael Malkowski (State Univeristy of New York at Buffalo) *Monotopic Membrane Enzymes: Structural Features Governing Catalysis at the Membrane Interface*
10:20 – 10:45	Break
10:45 – 11:15	Osman Bilsel (University of Massachusetts Medical School) *Continuous Flow Microsecond SAXS*
11:15 – 11:45	Tobin R. Sosnick (University of Chicago) *SAXS/WAXS Studies of Proteins and RNAs: What Have We Done and What Do We Want?*
11:45 – 12:15	Duncan Kilburn (Johns Hopkins University) *RNA Folding in Crowded Solutions by SAXS*
12:15 – 1:40	Lunch
1:40 – 2:10	Bi-Cheng Wang (University of Georgia) *A New Tool for Biology and Crystallography: Exploring Biophysical/Biochemical Information of Metals and Other Atoms Using Wavelength-dependent Diffraction Data*

2:10 – 2:40	Robert A. Scott (University of Georgia) *Metals in Biology: A Spectroscopist's View of High-energy-resolution Crystallography*
2:40 – 3:00	Vukica Srajer (University of Chicago/BioCARS) *Studies of Biological Macromolecules in Action: Current State and Challenges*
3:00 – 3:30	Break
3:30 – 4:00	James Penner-Hahn (University of Michigan) *Inorganic Physiology: Interconnected Metal Homeostasis Patterns in Yeast*
4:00 – 4:30	Thomas V. O'Halloran (Northwestern University) *Zinc Fluxes in Control of Cellular Physiology and Development*
4:30 – 4:45	Andrzej Joachimiak (Argonne National Laboratory) *Advanced Protein Crystallization Facility*
4:45 – 5:25	Round Table Discussion
5:25 – 5:30	Summary

WK1

Only Connect: Can Aspects of Our User Science Be Done Better Together?

Keith Moffat

The University of Chicago, Chicago, IL 60637

Structural biology collaborative access teams (CATs) have traditionally sought funding and operated independently of one another. Substantial scientific and technical collaborations exist between CATs, but these have largely sprung up after separate funding has been secured rather than acting as drivers for grant applications. Although the independent CAT funding model has been highly successful, the APS Upgrade (APS-U), pressures for cost-effective operation, and minimization of scientific redundancies offer the opportunity to consider other funding options. Are there areas in which we could effectively draw up inter-CAT, collaborative grant applications? Would federal agencies such as the National Institutes of Health be receptive? If so, on what scale? Would such applications concentrate on, for example, taking advantage of APS-U? On research and development? On support of user operations? On construction of a new sector? On joint purchases such as several detectors or robots?

WK1

Microcrystallography of G Protein-coupled Receptors

Vadim Cherezov

The Scripps Research Institute, La Jolla, CA 92037

Development of microcrystallography has strongly contributed to a recent explosion in structural studies of G protein-coupled receptors (GPCRs), the largest protein superfamily in the human genome, responsible for recognition a variety of extracellular signaling molecules and triggering intracellular responses. GPCRs are very unstable and highly dynamic molecules sampling many conformational states. Such dynamic behavior is essential for signal transduction but makes GPCRs challenging for structural studies. To overcome these hurdles, GPCRs are typically stabilized preferably in one conformational state and crystallized from a membrane-like environment producing well-ordered but limited in size microcrystals. In this talk, I will describe challenges and solutions applied to data collection from small GPCR crystals using minibeams at synchrotron sources. Alignment of microcrystals in the beam has been greatly facilitated by the development of automatic rastering and other approaches, such as SONICC (second-order imaging of chiral crystals). Obtaining high-resolution data from microcrystals is often limited by radiation damage, which can be reduced by collecting data on multiple microcrystals and merging multiple sets together. Further improvements in GPCR microcrystallography can be reached by improvements in detectors and data processing, as well as in further increasing the flux and decreasing the beam size. Recent experience with serial femtosecond crystallography on GPCR microcrystals at an x-ray free-electron laser source will be discussed.

WK1

A New Tool for Biology and Crystallography: Exploring Biophysical/Biochemical Information of Metals and Other Atoms Using Wavelength-dependent Diffraction Data

Bi-Cheng (B.C.) Wang

SER-CAT and the University of Georgia, Athens, GA 30602

During the 2011 APS workshop on “Soft X-ray Crystallography,” all the presentations were focused on the advantages of using longer wavelength x-rays for crystallographic phasing. Again, in the recent Scientific Session on “Extended Wavelength X-ray Crystallography” at the 2012 Boston ACA meeting, the majority of talks were centered on the advantages of using longer wavelength x-rays for direct S-SAD and P-SAD phasing. However, I opened the session with the simple question, “What additional…information can be obtained” from extended wavelength data and briefly touched on the topic I plan to present in detail at the APS Life Science Future Directions Workshop.

In this presentation, the theoretical possibility that biophysical/biochemical information of metals and other atoms in the crystal may be obtained by analyzing wavelength-dependent diffraction data (medium-to-low resolution data may be sufficient) will be discussed, together with recent results from some of our proof-of-concept/feasibility studies. An explanation will also be given on why a dedicated extended wavelength beamline, once realized, will allow the integration of one-dimensional spectroscopic information, such as the XAS-type “electronic structure” with the corresponding “3D crystallographic structure” to describe the true nature of molecules of interest. This means that X-ray crystallography will **no longer be limited to 3D structure determination**. It may also be used to carry out a **4D structural analysis** providing information about both position (3D coordinates) and identity (including valence states of metals) of all atoms in the crystal.

WK1

Metals in Biology: A Spectroscopist’s View of High-energy-resolution Crystallography

Robert A. Scott

Office of the Vice President for Research, University of Georgia, Athens, GA 30602

Biological inorganic chemistry has focused for 50-plus years on functions of inorganic elements (mostly metals) in biological systems. These elements serve structural roles, but their unique functionality involves the presence and movement of valence electrons (e.g., Lewis acid catalysis, oxidation- reduction). Structural biology, including crystallography, has increasingly provided the structural basis upon which to understand function, but traditional crystallographic techniques focus on core electrons (bulk electron density). On the other hand, spectroscopy, especially x-ray absorption spectroscopy, has a long-standing record of providing information about valence electrons (e.g., oxidation state, spin state), but without direct three-dimensional (3D) structural context (beyond local information). This presentation will focus on the premise that a leap forward in structure-function relationships is possible if we had a way of directly connecting valence electron information (oxidation state) with a specific site in a 3D macromolecular structure. The key concept is the ability of metal x-ray absorption edges to relate core electron changes to valence electron changes. High-energy-resolution “multiwavelength” x-ray diffraction data can go beyond simply providing element identification, but also provide oxidation state information, in a site-specific manner. Two overarching reasons for needing site-specific oxidation state information are: (1) mechanistic hypotheses depend on where the valence electrons are; "when I add an electron, to which site does it go, and how does that affect potential mechanisms of catalysis?" and (2) radiation damage often involves photoreduction; high-energy-resolution crystallography allows a direct monitor of damage at a given site. We will describe some of the structure-function information that could be accessed in multi-site, multi-electron biological systems with such a capability.

WK1

Studies of Biological Macromolecules in Action: Current State and Challenges

Vukica Srajer

BioCARS, The University of Chicago, Chicago, IL 60637

Studies of macromolecules in action are essential for understanding of how they perform their function. BioCARS focuses on such studies using time-resolved x-ray scattering techniques such as time-resolved crystallography and more recently time-resolved solution scattering. The goal is to elucidate structures of transient intermediates that facilitate functionally important structural transitions. The upgrade of the 14-ID beamline [1] extended the time resolution of such studies at BioCARS to 100 ps, significantly expanded beam time suitable for such studies, and improved the x-ray flux at the sample to ~4 × 10^{10} photons in a single 100 ps x-ray pulse focused to a 90 × 20 μm^2 beam size. Pump-probe time-resolved crystallography has reached a mature phase with demonstrated ability to detect small structural changes even at relatively low levels of reaction initiation of <10% [2, 3]. Solution scattering with 100 ps time resolution has also been successfully demonstrated [4, 5, 6]. However, many challenges for time-resolved studies remain: reaction initiation, studies of irreversible processes, resolving measured mixtures of states, extending time resolution beyond 100 ps, structural analysis of solution scattering results, etc. An overview of the challenges and efforts at BioCARS to address them will be presented.

[1] Graber et al., *J. Synchrotron Rad.*, **18**, 658 (2011).

[2] Schotte et al., *PNAS*, **109**, 19256 (2012).

[3] Jung et al., *Nat. Chem.*, **5**, 212 (2013).

[4] Cho et al., *PNAS*, 107, 7281 (2010).

[5] Kim et al., *Chem. Commun.*, **47**, 289 (2011).

[6] Kim et al., *J. Am. Chem. Soc.*, **134**, 7001 (2012).

WK1

Inorganic Physiology: Interconnected Metal Homeostasis Patterns in Yeast

James E. Penner-Hahn[1, 2], Carol A. Fierke[1], Nathan Zahler[1], Matthew Kidd[1], Andrea Stoddard[1], Lubomir Dostal[1], and Andrew Crawford[1]

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[2] Program in Biophysics, University of Michigan, Ann Arbor, MI 48109-1055

Metal ions play a critical role in virtually all biological processes including catalysis, electron transport, structural stability, and cellular signaling. In the absence of sufficient metal, critical cellular functions fail, frequently leading to pathological conditions. However, most metals are both bio-essential and, at sufficiently high concentrations, toxic, with the details being dependent on the metal, concentration, and organism; others are exclusively toxic. Consequently, metal ion levels within cells are tightly regulated, and a complex set of machinery has evolved to control the uptake, storage, and efflux of metals. A critical piece of information for understanding the control of this "inorganic physiology" is direct measurement of the concentration and speciation of metal ions, both in tissue and also on the sub-cellular length scale.

The importance of the biological x-ray nanoprobe will be illustrated with examples from studies of yeast metal homeostasis. We have used the 2-ID x-ray microprobe to study yeast metal homeostasis and in particular to characterize the consequences of cadmium (Cd) toxicity for the local cellular environment. These data provide new insights into the basis of Cd toxicity and the mechanisms of metal homeostasis. The opportunities that will be made available by the bio-nanoprobe will be discussed.

Supported in part by NIH GM70545 and GM38047. Synchrotron beam time at the Advanced Photon Sources is supported in part by the US Department of Energy.

WK1

Zinc Fluxes in Control of Cellular Physiology and Development

Thomas V. O'Halloran

The Chemistry of Life Processes Institute, and the Departments of Chemistry and Molecular Biosciences, Northwestern University, Evanston, IL 60208-3113

All cells must acquire large numbers of transition metals ions for use as essential cofactors in a multitude of housekeeping 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 and scanning transmission electron 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 zinc fluxes are essential in the blood stage of infectious cycle. Thus metal fluxes involving movement of millions to billions of metal ions between compartments of a single cell and the extracellular environment are key regulatory events in both infectious disease and mammalian development.

APS Workshop 2
Combining Experiments and Theory in f-Element Research

Location: Bldg. 440 (CNM), Rm. A105/106

Organizers: Mark R. Antonio and Lynne Soderholm (Argonne National Laboratory)

A combination of political, economic, and scientific factors is contributing to the current resurgence of interest in probing the fundamental behaviors of the f-elements. With a goal toward effective energy applications, lanthanide and actinide materials pose challenges to the scientific community in terms of a predictive understanding of their chemical and physical behaviors in a wide range of systems and under a wide variety of conditions. In combination with theory, synchrotron research is playing a key role in addressing these challenges. For example, the development of new reagents and processes as well as improvements to existing systems for the separation of lanthanides from each other, which are chemically very similar, and for separating lanthanides from actinides is just one area of active research that is being revolutionized by the availability of synchrotron radiation. The focus of this workshop will be on basic f-element science and its role in resolving strategic energy challenges. The workshop will pair discussions of new experimental approaches and technical applications with developments in theoretical modeling and computational simulations. The goal will be to socialize current issues with new opportunities afforded by the APS upgrade. Experimental results obtained at synchrotron radiation facilities, both national—with highlights of activities at the APS—and international will be discussed for a broad selection of f-element systems and a broad range of potential synchrotron techniques. Particular emphasis will be placed upon projecting the needs for the next generation of cutting edge experiments in areas as diverse as catalysis, magnetic and optical materials, phase stability in solid-state materials, hydrometallurgy, supramolecular and electroanalytical chemistry, and coordination chemistry research.

8:45 – 9:00	Welcome & Introductory Remarks *Mark Antonio & Lynne Soderholm (Argonne National Laboratory)*
9:00 – 9:40	Ross Ellis (Argonne National Laboratory) *Periodic Behavior of Lanthanide Coordination within Reverse Micelles*
9:40 – 10:20	Riccardo Spezia (CNRS, Université d'Evry, France) *A Combined Experimental/Theoretical Approach for Determination of Structural and Dynamical Properties of Lanthanoid(III) and Actinoid(III) Ions in Water*
10:20 – 10:50	Break
10:50 – 11:30	David Dixon (University of Alabama) *Computational Studies of Actinide Aggregation*
11:30 – 12:10	Valérie Vallet (Université Lille, France) *Revealing the Hydration of the Cm^{3+} Ion with Combined Techniques Involving EXAFS, HEXS, and Molecular Dynamics Simulations*
12:10 – 1:50	Lunch
1:50 – 2:30	Richard Martin (Los Alamos National Laboratory) *Covalency in the Actinides Probed with Ligand K-Edge X-ray Absorption Spectroscopy*

2:30 – 3:10 Corwin Booth (Lawrence Berkeley National Laboratory)
Multiconfigurational Nature of 5f Orbitals in Uranium and Plutonium and Their Intermetallic Compounds

3:10 – 3:40 Break

3:40 – 4:20 Zhengwei Pan (University of Georgia)
New Eu^{2+}-Activated (Alkaline Earth) Aluminate Nanoribbons

4:20 – 5:00 John Freeland (APS, Argonne National Laboratory)
Understanding the Atomic Level Synthesis of Layered Oxide Thin Films

5:00 – 5:15 Wrap Up

WK2

Periodic Behavior of Lanthanide Coordination within Reverse Micelles

Ross J. Ellis

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

Trends in lanthanide(III) (Ln^{III}) coordination were investigated within nano-confined solvation environments. Ln^{III} ions were incorporated into the cores of reverse micelles (RMs) formed with malonamide amphiphiles in *n*-heptane by contact with aqueous phases containing nitrate and Ln^{III}; both insert into pre-organized RM units built up of DMDOHEMA (N,N'-dimethyl-N,N'-dioctylhexylethoxymalonamide) that are either relatively large and hydrated or small and dry, depending on whether the organic phase is acidic or neutral, respectively. Structural aspects of the Ln^{III} complex formation and the RM morphology were obtained by use of x-ray absorption spectroscopy and small-angle x-ray scattering at the Advanced Photon Source. The Ln^{III} coordination environments were determined through use of L$_3$-edge x-ray absorption near edge structure and extended x-ray absorption fine structure, which provide metrical insights into the chemistry across the period. Hydration numbers for the Eu species were measured using time-resolved laser-induced fluorescence spectroscopy (or TRLIFS). The picture that emerges from a system wide perspective of the Ln-O interatomic distances and O coordination numbers for the extracted complexes of Ln^{III} in the first half of the series (i.e., Nd, Eu) is that they are different from those in the second half of the series (i.e., Tb, Yb): the O coordination numbers decrease from nine O for early lanthanides to eight O for the late ones—a trend that is consistent with the effect of the lanthanide contraction. The environment within the RM, altered by either the presence or absence of acid, also had a pronounced influence on the nitrate coordination mode where the larger, more hydrated, acidic RM core favors monodentate coordination whereas the small, dry, neutral core favors bidentate coordination to Ln^{III}. These findings show that the coordination chemistry of lanthanides within nano-confined environments is neither equivalent to the solid nor bulk solution behaviors. Herein we address atomic- and meso-scale phenomena in the under-explored field of lanthanide coordination and period behaviors within RMs, providing a consilience of fundamental insights into the chemistry of growing importance in technologies as diverse as nano-synthesis and separations science.

This work is supported by the U. S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Biosciences and Geosciences, under contract No DE-AC02-06CH11357 (for the parts performed at Argonne National Laboratory).

WK2

A Combined Experimental/Theoretical Approach for Determination of Structural and Dynamical Properties of Lanthanoid(III) and Actinoid(III) Ions in Water

Riccardo Spezia[1] and Paola D'Angelo[2]

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In the last ten years, a growing number of studies were devoted, both experimentally and theoretically, to the understanding of the hydration properties of lanthanoid(III) and actinoid(III) ions in water, and a clear picture did emerge. This was possible thanks to the improvements of the x-ray absorption spectroscopy (XAS) and the development of more sophisticated and reliable theoretical models.

Via an accurate and systematic combination of molecular dynamics simulations and XAS experiments, we obtained for both the lanthanoid and actinoid series: (i) polarizable force fields able to provide structural and dynamical hydration properties in agreement with experimental observations, (ii) accurate experimental determinations of the aqua-ions geometry, (iii) novel sets of ionic radii in aqueous solution replacing the Shannon's radii obtained in solid state.

A description of the protocol employed to combine experimental and theoretical data will be given and the potentiality of this approach will be discussed.

P. D'Angelo and R. Spezia, "Hydration of Lanthanoids(III) and Actinoids(III) : an Experimental/Theoretical Saga," *Chem. Eur. J.*, **18**, 11162–11178 (2012).

P. D'Angelo, A. Zitolo, V. Migliorati, G. Chillemi, M. Duvail, P. Vitorge, S. Abadie, and R.Spezia, "Revised ionic radii of lanthanoid(III) ions in aqueous solution," *Inorg. Chem.*, **50**, 4572–4579 (2011).

M. Duvail, P. Vitorge, and R. Spezia, "Building a polarizable pair interaction potential for lanthanoids(III) in liquid water: a molecular dynamics study of structure and dynamics of the whole series," *J. Chem. Phys.*, **130**, 104501 (2009).

M. Duvail, F. Martelli, P. Vitorge, and R. Spezia, "Polarizable Interaction Potential for Molecular Dynamics Simulations of Actinoids(III) in Liquid Water," *J. Chem. Phys.*, **135**, 044503 (2011).

I. Persson, P.D'Angelo, S. De Panfilis, M. Sandstrom, and L. Eriksson, "Hydration of Lanthanoid(III) Ions in Aqueous Solution and Crystalline Hydrates Studied by EXAFS Spectroscopy and Crystallography: The Myth of the Gadolinium Break," *Chem. Eur. J.*, **14**, 3056–3066 (2008).

WK2

Computational Studies of Actinide Aggregation

David A. Dixon[1], Monica Vasiliu[1], Virgil E. Jackson[1], and Ryan Flamerich[1], Karah Knope[2], and Lynda Soderholm[2]

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Advances in theory, algorithms, software, and computer architectures have made it possible to begin to calculate reliably the properties of actinide and lanthanide complexes. It is now possible to predict a range of properties that can be used to interpret experimental data. We are focused on the prediction of such properties, especially thermodynamic and spectroscopic properties in the gas and aqueous solution phases, using correlated (CCSD(T)) molecular orbital theory and density functional theory with effective core potentials (small core) and large basis sets. The self-consistent reaction field approximation with the COSMO parameterization is used for the prediction of properties in aqueous solution. The properties and hydrolysis of thorium oxide complexes will be described in detail beginning with small oxides and then to clusters of $(ThO_2)_n$ and their hydrolysis reactions. The properties of $Th_6O_8^{8+}$ and $Th_8O_{12}^{8+}$ clusters surrounded by oxyanions will be discussed including their structures, spectroscopic properties and energetic properties, for example, gas phase acidities and pK$_a$'s. The interpretation of vibrational and nuclear magnetic resonance spectra for such compounds will be discussed. The differences in the gas phase and solution phase acidities will be discussed. The properties of thorium fluorides and hydroxide clusters will also be discussed. Differences between thorium (IV) compounds and other metal (IV) compounds will be discussed.

Useful recent references

L. Andrews, Y. Gong, B. Liang, V.E. Jackson, R. Flamerich, S. Li, and D.A. Dixon, "Matrix Infrared Spectra and Predicted Properties of Thorium Oxide Species: ThO_x and and Th_2O_y," *J. Phys. Chem. A*, **115**, 14407–1441 (2011).

K.E. Knope, R.E. Wilson, M. Vasiliu, D.A. Dixon, and L. Soderholm, "Thorium(IV) molecular clusters with a hexanuclear core," *Inorg. Chem.*, **50,** 9696–9704 (2011).

K.E. Knope, M. Vasiliu, D.A. Dixon, and L. Soderholm, "Thorium(IV)-Selenate Clusters containing an Octanuclear Th(IV) Hydroxide/Oxide Core," *Inorg. Chem.*, **51**, 4239–4249 (2012).

M. Vasiliu, K.E. Knope, L. Soderholm, and D.A. Dixon, "Spectroscopic and Energetic Properties of Thorium(IV) Molecular Clusters with a Hexanuclear Core," *J. Phys. Chem. A*, **116**, 6917–6926 (2012).

Y. Gong, L. Andrews, V.E. Jackson, and D.A. Dixon, "Methane to Methanol Conversion Induced by Thorium Oxide through the $CH_3Th(O)H$ Intermediate in Solid Argon," *Inorg. Chem.*, **51**, 11055–11060 (2012).

WK2

Revealing the Hydration of the Cm^{3+} Ion with Combined Techniques Involving EXAFS, HEXS, and Molecular Dynamics Simulations

Valérie Vallet[1], Florent Réal[1], Michel Masella[2], Yung-Jin Hu[3], S. Skanthakumar[3], and L. Soderholm[3]

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[2] CEA Saclay, Laboratoire de Chimie du Vivant, Service d'ingénierie moléculaire des protéines, Institut de biologie et de technologies de Saclay, F-91191 Gif sur Yvette Cedex, France
[3] Chemical Sciences and Engineering, Argonne National Laboratory, Argonne, IL 60439

The hydration shells of an ion can be probed by various theoretical and experimental techniques that are complementary in their ability to accurately predict structural details, including coordination numbers and metal-solvent hydration shells. Accurate molecular-dynamics simulations reveal that very subtle changes in the metal-solvent and solvent-solvent interactions have a direct impact on the coordination shell, by displacing the equilibrium between competing isomers. Synchrotron experiments including high-energy x-ray scattering (HEXS) and x-ray absorption fine structure (XAFS) provide metrical information to compare with theory. Combining both new experimental and theoretical information, this presentation will focus on a detailed analysis of Cm^{3+} first and second hydration shells.

[1] S. Skanthakumar, M.R. Antonio, R.E. Wilson, and L. Soderholm, *Inorg. Chem.*, **46**, 3485 (2007).

[2] F. Réal, M. Trumm, B. Schimmelpfennig, M. Masella, and V. Vallet, *J. Comput. Chem.*, **34**, 707 (2013).

WK2

Covalency in the Actinides Probed with Ligand K-Edge X-ray Absorption Spectroscopy

Richard L. Martin

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The presence or absence of significant participation by the f-orbitals in actinide materials has been a subject of debate for many years. In this talk, I will discuss a relatively direct probe of actinide involvement in bonding, ligand K-edge x-ray absorption spectroscopy. Experimental and theoretical investigations for a number of actinide complexes and solids will be presented and the strong evidence for f-orbital-ligand bonding interactions discussed along with the consequences for actinide electronic structure.

WK2

Multiconfigurational Nature of 5f Orbitals in Uranium and Plutonium and Their Intermetallic Compounds

Corwin H. Booth

Lawrence Berkeley National Laboratory, Berkeley, CA 94720

The structural, electronic, and magnetic properties of U and Pu elements and intermetallics remain poorly understood despite decades of effort, and currently represent an important scientific frontier toward understanding matter. The last decade has seen great progress both due to the discovery of superconductivity in $PuCoGa_5$ and advances in theory that finally can explain fundamental ground state properties in elemental plutonium, such as the phonon dispersion curve, the non-magnetic ground state, and the volume difference between the α and δ phases. A new feature of the recent calculations is the presence not only of intermediate valence of the Pu 5f electrons, but of multiconfigurational ground states, where the different properties of the α and δ phases are primarily governed by the different relative weights of the $5f^4$, $5f^5$, and $5f^6$ electronic configurations. The usual method for measuring multiconfigurational states in the lanthanides is to measure the lanthanide L_{III}-edge x-ray absorption near-edge structure (XANES), a method that is severely limited for the actinides because the spectroscopic features are not well enough separated compared to the intrinsic resolution. Advances in resonant x-ray emission spectroscopy (RXES) have now allowed for spectra with sufficient resolution to resolve individual resonances associated with the various actinide valence states. Utilizing a new spectrometer at the Stanford Synchrotron Radiation Lightsource, RXES data have been collected that show spectroscopic signatures of each of these configurations and their relative changes in various uranium and plutonium intermetallic compounds. In combination with conventional XANES spectra on related compounds, these data indicate such states may be ubiquitous in uranium and plutonium intermetallics, providing a new framework toward understanding properties ranging from heavy fermion behavior, superconductivity, and intermediate valence to mechanical and fundamental bonding behavior in these materials.

WK2

New Eu^{2+}-Activated (Alkaline Earth) Aluminate Nanoribbons

Feng Liu[1, 2], Xufan Li[1], John D. Budai[3], Jane Y. Howe[3], Jonathan Z. Tischler[3], Chengjun Sun[4], Ru-Sheng Chen[5], Jiahua Zhang[6], Xiao-Jun Wang[7], Zhanjun Gu[8], Richard S. Meltzer[2], and Zhengwei Pan[1, 2]

[1] College of Engineering, University of Georgia, Athens, GA 30602
[2] Department of Physics and Astronomy, University of Georgia, Athens, GA 30602
[3] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[4] X-ray Science Division, Argonne National Laboratory, Argonne, IL 60439
[5] ChemMatCARS, Argonne National Laboratory, Argonne, IL 60439
[6] Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China
[7] Department of Physics, Georgia Southern University, Statesboro, GA 30460
[8] Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

Developing novel one-dimensional (1D) luminescent nanostructures (e.g., nanowires and nanoribbons) is highly desired for enabling progress in nanophotonics and other emerging optical technologies. Using a carbothermal reaction and evaporation technique, we have successfully fabricated three series in a total of 10 kinds of Eu^{2+}-activated (alkaline earth) aluminate nanoribbons that exhibit new compositions, new crystal lattice structures, and new luminescence properties and mechanisms. These nanoribbons are: ternary europium aluminates with luminescence colors of blue, green, and orange [1, 2]; quaternary strontium europium aluminates with luminescence colors of blue, green, and yellow; and quaternary barium europium aluminates with luminescence colors of blue, green, yellow, and red. Except for the three green-luminescent products, the other seven aluminates are new compounds with new lattice structures that were not reported before. Four beamlines in Advanced Photon Sources were used to characterize the crystal structures of these new materials: synchrotron powder x-ray diffraction at beamline11-BM-B, polychromatic Laue microdiffraction at beamline 34-ID-E, Eu L3 edge measurement at beamline 20-BM-B, and microcrystallographic study at beamline 15-ID-C. These new 1D luminescent nanoribbons have promising applications as nanoscale light generators and waveguides in nanophotonics and as light converting phosphors in warm-white light-emitting diodes [3].

[1] F. Liu, J.D. Budai, X.F. Li, J.Z. Tischler, J.H. Howe, C.J. Sun, R.S. Meltzer, and Z.W. Pan, "New Eu^{2+}-activated europium aluminate luminescent nanoribbons for advanced photonics," *Adv. Funct. Mater.*, doi: 10.1002/adfm.201202539 (Cover Art).

[2] F. Liu, R.S. Meltzer, X.F. Li, J.D. Budai, and Z.W. Pan, "New Localized/Delocalized Emitting State of Eu^{2+} in Orange-Emitting Hexagonal $EuAl_2O_4$," *Phys. Rev. Lett.* (in revision).

[3] X.F. Li, J.D. Budai, F. Liu, J.Y. Howe, C.J. Sun, J.H. Zhang, X.–J.Wang, Z.J. Gu, R.S. Meltzer, and Z.W. Pan, "New yellow $Ba_{0.93}Eu_{0.07}Al_2O_4$ phosphor for warm-white light-emitting diodes through single-emitting-center-conversion," *Light: Science & Applications* **2**, e50 (2013); doi:10.1038/lsa.2013.6.

WK2

Understanding the Atomic Level Synthesis of Layered Oxide Thin Films

John W. Freeland

Magnetic Materials Group, X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Functional materials based on complex oxides offer new and exciting strategies for meeting many of our outstanding energy challenges. Materials theorists can now design virtual crystals for specific applications and predict their properties. Unfortunately, the synthesis of a new oxide material is typically very difficult, particularly when there is a lack of quantitative feedback during growth. Furthermore, the desired structure may not be thermodynamically stable, such that a kinetic route is necessary for attaining the desired phase. The goal of this project is to couple quantitative information extracted from *in situ* probes with a theoretical synthesis framework that will allow us to rapidly grow desired phases of layered oxides. The *layered* complex oxides (so-called because their unit cell consists of stacked atomic sheets) offer an enormous span of functionalities ranging from intermediate temperature solid oxide fuel cell cathodes to novel water-splitting catalysts to colossal dielectric materials. Synthesis by oxide molecular beam epitaxy (MBE) offers the ability to build materials atomic plane by atomic plane to explore materials that do not exist in nature. Coupling *in situ* synchrotron techniques with oxide film synthesis offers quantitative understanding of the growth process. Here I will present recent results of *in situ* studies of growth using a unique reactive oxide MBE system, where we find a strong departure from the expected outcomes based upon a specific growth sequence. The growth of Sr_2TiO_4 on $SrTiO_3$ has been examined in detail and experimental findings clearly show a dynamic swapping of layers during growth to reach a lower energy configuration. Theoretical studies of the process clearly establish the underlying energetics, give insight into how the process occurs, and provide a solution to achieve the desired phase. Using this insight into these dynamic processes, we expanded this to use the layer swapping to our advantage and realized the stabilization of a single-crystal phase of layered nickelates that up to now only exist in polycrystalline form. These findings indicate that it is possible to use the coupling of experimental and theoretical efforts to understand the "Science of Synthesis" and offer pathways to create novel energy materials.

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

APS Workshop 3
Ultrafast Dynamics in Strongly Correlated Materials, Atoms, Molecules, and Clusters

Location: Bldg. 401, Rm. A1100

Organizers: Yuelin Li, David Keavney, Philip Ryan, and Steve Southworth (Advanced Photon Source)

Strongly correlated phenomena occur in many material systems. In solids, these are a wide class of electronic materials that show unusual coupling between electronic, structural, and magnetic degrees of freedom. They display interesting and technologically useful behaviors including superconductivity, photostriction, magnetostriction, magnetoresistance, and electromagnetic coupling. Correlated dynamics are also widely observed in chemical reactions and in atomic, molecular and optical systems. Pump-probe experiments provide unique opportunities to understand the origin and the dynamics of these phenomena at time scales that are intrinsic to the physics and relevant to their technical applications. In addition, selective excitation of the different degrees of freedom makes it possible to create states that are not accessible under conventional, adiabatic manipulation. The Advanced Photon Source is planning a major upgrade that will provide picosecond x-ray pulses, coupled with a wide array of laser pump energy and x-ray probing capabilities, including spectroscopy, scattering, and imaging. It is the goal of this workshop to bring together experts in sample growth and time-resolved experiments to discuss new scientific opportunities that this new x-ray facility will enable.

8:30 – 8:35	Opening remarks
8:35 – 8:55	Eric Dufresne (APS, Argonne National Laboratory) *The APS-U Short-Pulse X-ray Beamline Facilities*
8:55 – 9:15	Anne Marie March (APS, Argonne National Laboratory) *Capturing Ultrafast Molecular Dynamics with High-Repetition-Rate Laser-Pump, X-ray- Probe Techniques*
9:15 – 9:50	Paul Evans (University of Wisconsin–Madison) *Dynamics of Domains, Polarization, and Atomic-scale Distortion in Complex Oxide Superlattices*
9:50 – 10:25	Aaron Lindenberg (SLAC National Accelerator Laboratory) *Light-induced Processes in Ferroelectrics*
10:25 – 10:50	Break
10:50 – 11:25	Christoph Bostedt (SLAC National Accelerator Laboratory) *Clusters in Intense X-ray Pulses*
11:25 – 12:00	Chris Milne (Swiss-FEL, Paul Scherrer Institut) *High-repetition-rate Ultrafast Time-resolved XAS and XES: Investigating Chemical Dynamics*
12:00 – 12:10	Discussion
12:10 – 1:30	Lunch

1:30 – 2:05	Michael Först (University of Hamburg) *X-ray Probing of Ultrafast Lattice-driven Dynamics in Complex Oxides*
2:05 – 2:40	Wei-Sheng Lee (SLAC National Accelerator Laboratory) *Photo-induced Dynamics of Strongly Coupled Charge and Spin Order Parameters*
2:40 – 3:15	Urs Staub (Paul Scherrer Institut) *Ultrafast Electronic and Structural Changes in Photo-excited Manganites*
3:15 – 3:40	Break
3:40 – 4:15	Richard D. Averitt (Boston University) *Nonequilibrium Dynamics in Transition Metal Oxides*
4:15 – 4:50	Adrian Cavalieri (University of Hamburg and CFEL) *Ultrafast Capability at Accelerator-based X-ray Sources*
4:50 – 5:20	Discussion

WK3

The APS-U Short-Pulse X-ray Beamline Facilities

Eric M. Dufresne

X-ray Science Division, Argonne National Laboratory, Argonne, IL 60439

The short-pulse x-ray (SPX) beamline facilities will extend time-resolved x-ray scattering and spectroscopy to the picosecond time scale while retaining the powerful characteristics of synchrotron radiation, i.e., user-controlled continuous tunability of energy, polarization, and bandwidth combined with exquisite x-ray energy and pulse-length stability over a wide energy range. Experiments at the SPX facility will produce 2 ps stroboscopic snapshots of molecular rotations, molecular excited-state transient structures, stress/strain wave propagation, magnetic domain wall dynamics, phase transitions, and the coupling between electronic, vibrational, and magnetic degrees of freedom in condensed matter systems. Time-resolved studies of transient dynamics will be possible with simultaneous picosecond time resolution and picometer structural precision for a variety of atomic, molecular, supramolecular, nanoscale, and bulk material systems. Transformational developments are now taking place in high-average-power pulsed laser technology, with substantially increased repetition rates that promise to make highly efficient use of the MHz x-ray repetition rates of the SPX. This talk will discuss the hard and soft x-ray beamlines and laser facilities designed in the APS Upgrade preliminary design with seven end stations with scattering, diffraction, spectroscopy, imaging, and microscopy capabilities.

WK3

Capturing Ultrafast Molecular Dynamics with High-repetition-rate Laser-pump, X-ray-probe Techniques

Anne Marie March

X-ray Science Division, Argonne National Laboratory, Argonne, IL 60439

Laser-pump, x-ray-probe experiments are powerful tools for understanding and controlling the behavior of matter at the molecular level. Transient structural changes, both geometric and electronic, of single molecules after excitation by a laser pulse can be probed with high resolution and within complex or disordered environments such as gases and liquids taking advantage of the superior spatial resolution, elemental specificity, and penetration power of x-rays. The Short Pulse X-ray Facility (SPX) at the Advanced Photon Source (APS) will provide variable x-ray pulse durations down to ~2 ps while maintaining the high flux (10^{13} photons/second/0.01% bandwidth) and high repetition rate (6.5 MHz) that is presently available. Variable repetition rate lasers that can match the x-ray pulse repetition rate and accommodate sample recovery or refresh rates will be crucial to the efficient use of the SPX. In this talk I will describe progress that is being made at 7-ID-D at the APS developing these high-repetition-rate techniques.

WK3

Dynamics of Domains, Polarization, and Atomic-scale Distortion in Complex Oxide Superlattices

Paul G. Evans

University of Wisconsin-Madison, Madison, WI 53706

Complex oxide superlattices have a wide degree of chemical and structural versatility that leads to a wide range of dynamical phenomena. Superlattices composed of alternating dielectric and ferroelectric layers exhibit phenomena with characteristic lengths that range from the relatively large scale of nanodomain patterns to the far smaller scale associated with electric-field-induced piezoelectric distortion and changes in polarization. Each of these phenomena is in turn coupled strongly to the polarization and thus has significant effects on the electronic and optical properties of superlattices. Ultrafast x-ray scattering techniques offer a unique opportunity to study the dynamics across these length scales, and to determine how the structural complexity imposed by the domain structure influences atomic scale dynamics. X-ray nanodiffraction shows that the domain dynamics can have characteristic timescales as short as a few nanoseconds at high electric fields and that the dynamics are fit by an inhomogeneous switching of the domains across larger length scales. Analysis of the time-dependence of the superlattice domain reflections shows that the electric field induces a redistribution of the polarization among the component layers of the superlattice. We will also discuss prospects for inducing these phenomena with improved time resolution including the use of highly localized optical excitation.

WK3

Light-induced Processes in Ferroelectrics

A.M. Lindenberg

Stanford University/SLAC National Accelerator Laboratory, Menlo Park, CA 94025

Light couples to relevant structural and electronic degrees of freedom in ferroelectric oxides, opening up new opportunities for control and engineering of their functional properties. In this talk I will describe recent experiments probing the ultrafast dynamics of both visible light and THz-induced processes in $PbTiO_3$ and $BiFeO_3$ thin films using both femtosecond x-rays from the Linac Coherent Light Source as well as nonlinear optical techniques. We observe large-amplitude field-driven modifications in the ferroelectric order and will discuss the origin of these effects.

WK3

Clusters in Intense X-ray Pulses

Christoph Bostedt

Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

Free-electron lasers deliver extremely intense, coherent x-ray flashes with femtosecond pulse length, opening the door for imaging single nanoscale objects in a single shot. All matter irradiated by these intense x-ray pulses, however, will be transformed into a highly excited non-equilibrium plasma within femtoseconds. During the x-ray pulse complex electron dynamics and the onset of atomic disorder will be induced, leading to a time-varying sample.

We have performed experiments about intense x-ray pulse–matter interaction at both the FLASH and LCLS x-ray free-electron lasers using atomic clusters. Imaging experiments with xenon clusters in the soft x-ray regime have revealed power-density-dependent changes in the scattering patterns. The data show that the scattering signal carries information about transient charge states in the cluster. Single-shot, single-particle experiments with keV x-rays reveal that for the highest power densities, a highly excited and hot cluster plasma is formed for which recombination is suppressed. Studying the ionization dynamics of smaller clusters shows that the energy absorption depends on the particle size, which is attributed to changing Auger rates in the x-ray-induced nanoplasma. Recent single-shot experiments with hard x-rays yield insight into the crystalline order of the particles.

WK3

High-repetition-rate Ultrafast Time-resolved XAS and XES: Investigating Chemical Dynamics

C.J. Milne[1], J. Szlachetko[1], F.A. Lima[2], M.H. Rittmann-Frank[2], T.J. Penfold[1, 2], M. Reinhard[2], J. Rittmann[2], J. Sá[2], M. Silatani[2], F. Santomauro[2], R. Abela[1], and M. Chergui[2]

[1] Paul Scherrer Institut, 5232 Villigen, Switzerland
[2] Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Using x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) to probe laser-excited samples we can obtain excited-state structural and electronic dynamical information not available through other techniques. One of the restrictions of most synchrotron-based implementations of this technique is the three-orders of magnitude mismatch between x-ray and laser repetition rates (MHz vs. kHz). By using a laser capable of generating significant pulse energies at MHz repetition rates we can eliminate this discrepancy, thus greatly reducing measurement times and enhancing achievable signal-to-noise ratios [1, 2, 3, 4, 5]. Several examples that demonstrate the strength of this technique will be presented, including probing the electron relaxation in photoexcited TiO_2 nanoparticles in solution and resolving the dynamical structural changes associated with ligand rebinding in the protein myoglobin under physiological conditions. The ability to extend these high-repetition rate measurements down to the single ps timescale will have a significant impact on the range of fast dynamics that can be measured. Some examples of what would be possible with such a setup will be presented.

[1] F.A. Lima, C.J. Milne, D.C.V. Amarasinghe, M.H. Rittmann-Frank, R.M. van der Veen, M. Reinhard, V.-T. Pham, S. Karlsson, S.L. Johnson, D. Grolimund, C. Borca, T. Huthwelker, M. Janousch, F. van Mourik, R. Abela, and M. Chergui, "A high-repetition rate scheme for synchrotron-based picosecond laser pump/x-ray probe experiments on chemical and biological systems in solution," *Review of Scientific Instruments*, **82**, 6, 063111 (June 2011).

[2] A.M. March, A. Stickrath, G. Doumy, E.P. Kanter, B. Krässig, S.H. Southworth, K. Attenkofer, C.A. Kurtz, L.X. Chen, and L. Young, "Development of high-repetition-rate laser pump/x-ray probe methodologies for synchrotron facilities," *Review of Scientific Instruments*, **82**, 7, 073110 (2011).

[3] G. Vankó, A. Bordage, P. Glatzel, E. Gallo, M. Rovezzi, W. Gawelda, A. Galler, C. Bressler, G. Doumy, A.M. March, E.P. Kanter, L. Young, S.H. Southworth, S.E. Canton, J. Uhlig, G. Smolentsev, V. Sundstrom, K. Haldrup, T.B. van Driel, M.M. Nielsen, K.S. Kjaer, and H.T. Lemke, "Spin-state studies with XES and RIXS: From static to ultrafast," *Journal Of Electron Spectroscopy and Related Phenomena*, 1–6 (Oct., 2012).

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[5] K. Haldrup, G. Vankó, W. Gawelda, A. Galler, G. Doumy, A.M. March, E.P. Kanter, A. Bordage, A. Dohn, T.B. van Driel, K.S. Kjær, H.T. Lemke, S.E. Canton, J. Uhlig, V. Sundstrom, L. Young, S.H. Southworth, M.M. Nielsen, and C. Bressler, "Guest-Host Interactions Investigated by Time-resolved X-ray Spectroscopies and Scattering at MHz Rates: Solvation Dynamics and Photoinduced Spin Transition in Aqueous $Fe(bipy)^{2+}{}_3$," *The Journal of Physical Chemistry A*, **116**, 40, 9878–9887 (Oct., 2012).

WK3

X-ray Probing of Ultrafast Lattice-driven Dynamics in Complex Oxides

Michael Först

Max-Planck Institute for the Structure and Dynamics of Matter, Center for Free Electron Laser Science, University of Hamburg, 22761 Hamburg, Germany

Controlling the phase state of condensed matter in a non-thermal fashion is a particularly interesting challenge in ultrafast science. In quantum materials, where the competing phases are balanced by a complex interplay between charges, orbitals, spins, and the lattice, the macroscopic properties can be manipulated by direct excitation of specific

vibrational modes with intense mid-infrared light pulses. Examples include the control of insulator-metal transitions in, e.g., manganites and nickelates. Vibrational excitation also induces superconductivity in underdoped, stripe-ordered cuprate compounds.

In my talk, I will summarize our recent efforts in exploiting the Linac Coherent Light Source free-electron laser to shine light onto the dynamics of the complex physics at hand. Using time-resolved hard x-ray diffraction, the vibrationally induced nonlinear crystal lattice response could be disclosed. These dynamics are capable of unbalancing the interactions with charges and spins in order to drive ultrafast phase transitions. Using ultrafast resonant soft x-ray diffraction, we disclosed the transient changes in the lattice driven charge, orbital, and magnetic order parameters in the various complex oxides mentioned above. Beyond the presentation of these science cases, I will express our needs and wishes for intense mid-infrared and THz light sources that are necessary to conduct our future research.

WK3

Photo-induced Dynamics of Strongly Coupled Charge and Spin Order Parameters

W. S. Lee

Stanford Institute for Materials and Energy Science, SLAC National Accelerator Laboratory,
Stanford, CA 94305-4090

Photo-excited charge/spin ordering phenomena have recently dawn significant attention in the field of correlated materials research because it offers new opportunities to study and control the associated order parameters. With the availability of ultrafast x-ray pulses, time-resolved resonant x-ray diffraction can now be performed with picosecond or femtosecond resolution to directly monitor the time-evolution of the spin/charge/orbital order parameters.

In this presentation, I will discuss resonant x-ray diffraction measurements on striped nickelate $La_{1.75}Sr_{0.25}NiO_4$ [1, 2]. Upon photo-excitation, the length scales of spin and charge order remain unchanged, which is distinct from the thermal evolution of the charge and spin order. In the recovery process, the order parameters' amplitude and phase are separated into different timescales [1], showing that phase fluctuation is the bottleneck of order parameter's recovery. Further, time scale comparison reveals a real-time manifestation of strongly coupled spin and charge orders, which is indiscernible by the energy scale of the spin and charge degrees of freedom [2]. Finally, the dynamics of CDW state in $TbTe_3$ will also be presented to contrast the charge order dynamics in the limit of strong (nickelate) and weak coupling ($TbTe_3$) [3]. Based on the information learned from the Linac Coherent Light Source experiments, an outlook to the time-resolved experiment for correlated materials at the storage ring-based synchrotron will be briefly discussed.

[1] W.S. Lee *et al.*, Phase fluctuations and the absence of topological defects in photo-excited charge ordered nickelate, *Nature Communications*, **3**, 838 (2012).

[2] Y.D. Chuang et al., Energy scale independent order parameter dynamics in striped nickelate. Accepted by *Physical Review Letters*.

[3] R.G. Moore *et al.*, Ultrafast lattice dynamical response to the electronic excitation of the charge density wave in $TbTe_3$. In preparation.

WK3

Ultrafast Electronic and Structural Changes in Photo-excited Manganites

A. Caviezel[1], S.O. Mariager[1], S.L. Johnson[2], E. Möhr-Vorobeva[1], S.W. Huang[1], G. Ingold[1], H. Wadati[3], M. Sikorski[4], J.M. Glownia[4], H. Lemke[4], M. Chollet[4], A. Robert[4], C.J. Milne[5], M. Nakamura[6], V.A. Guzenko[7], M. Kawasaki[8, 9], Y. Tokura[8, 9], S.-W. Cheong[10], P. Beaud[1], and U. Staub[1]

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[9] Japan and Cross-Correlated Materials Research Group (CMRG), Advanced Science Institute, RIKEN, Wako [3]51-0198, Japan
[1]0Rutgers Center for Emergent Materials and Department of Physics & Astronomy, Piscataway, NJ 08854

Manganites represent an interesting class of materials, as they show peculiar magnetic and electronic properties. In this presentation, I will concentrate on charge and orbitally ordered systems, and discuss how the structure and the electronic states transform in real time after an excitation from a short optical pulse. We use an ultrafast x-ray pulse, created by beam slicing at the Swiss Light Source, or by the x-ray free electron laser (LCLS), to probe the material. Collecting intensities of superlattice reflections, caused by the charge and orbital order of the ordered low temperature phase, allows us to show both how and how fast the structure responds to the excitation. By using resonant diffraction we can also test how the charge and orbital order is affected by the excitation. In addition, I will discuss how the electronic structure reacts to weak excitations, which creates coherent motions of the lattice (coherent phonons).

WK3

Nonequilibrium Dynamics in Transition Metal Oxides

Richard D. Averitt

Boston University, Boston, MA 02215

The nascent field of photoinduced phase transitions utilizes sub-picosecond "optical" pulses to initiate cooperative quantum dynamics in complex materials. Goals include probing phase transition pathways and, ultimately, creating macroscopically ordered phases that are thermally inaccessible. Correlated transition metal oxides are of particular interest given their sensitivity to external perturbations deriving from spin, lattice, charge, and orbital degree-of-freedom competition. Advances in epitaxial thin film growth, concurrent with developments in terahertz time-domain spectroscopy, present new opportunities for well-controlled studies of nonequilibrium phenomena in transition metal oxides. I will present our recent results on the vanadates and manganites using optical excitation, electric fields, and coherent strain to drive nonequilibrium dynamics. In V_2O_3, we have observed coherent strain driven conductivity oscillations, indicative of electronic bandwidth modulation. In VO_2 we show that ~1 MV/cm picosecond electric fields initiate the insulator-to-metal transition. Finally, I will describe our observation of a persistent photo-induced metallic state in epitaxially grown charge-ordered manganite thin films. The metastable conductivity and distinctly non-exponential dynamics are consistent with glassy behavior.

WK3

Ultrafast Capability at Accelerator-based X-ray Sources

Adrian Cavalieri

**Max-Planck Institute for the Structure and Dynamics of Matter, Center for Free Electron Laser Science,
University of Hamburg, 22761 Hamburg, Germany**

Next-generation x-ray sources, including x-ray free-electron lasers (XFELs) can in principle be used to study dynamics occurring on timescales as short as the x-ray pulse duration. However, to achieve such high time resolution, the relative timing of the x-ray pulses must be characterized or controlled on a commensurate level and the pulse profile must be known to determine the x-ray intensity. Knowledge of the pulse profile is also critical when the dynamics are expected to evolve within the x-ray exposure.

To solve these problems, we extended the techniques of attosecond photoelectron streaking with the use of single-cycle laser-driven terahertz (THz) pulses, allowing for simultaneous online measurement of both the arrival time and temporal profile of XFEL pulses on a shot-to-shot basis. THz streaking is non-invasive and could be incorporated in pump-probe experiments, eventually characterizing pulses before and after the interaction with most sample environments. At the Linac Coherent Light Source, the x-ray pulse profile has now been measured with ~30 fs resolution, with the clear potential to reach the sub-10 fs regime. Furthermore, these measurements were made on a time base synchronized to the external experiment environment to better than 5 fs. In the future, THz streaking could provide real-time feedback, allowing for x-ray pulse shaping in the temporal domain. Streaking may also eventually provide access to the spectral phase of the x-ray pulse, opening a new dimension in time-resolved x-ray spectroscopy.

APS Workshop 4 Engineering Materials

Location: Bldg. 402, Rm. E1200

Organizers: Matt Miller (Cornell University), Bob Suter (Carnegie Mellon University), and Jon Almer (Advanced Photon Source)

A new generation of synchrotron-based characterization tools for structural (load bearing) materials are currently being developed around the world. The attributes of synchrotron x-rays (high flux, small beam size, high energy, etc.) are being widely exploited to change the very nature of engineering material characterization experiments including the way experimental data are being utilized within material performance models. This workshop will have presentations focused on methods, including high-energy diffraction microscopy, polychromatic micro-beam scans, tomography, and combinations of techniques; on applications, including non-destructive grain map reconstruction, *in situ* environments (loading, temperature, irradiation, etc.) to study material evolution, and residual stress measurements; on modeling, including virtual sample construction, elastic-plastic deformation, phase transformations, forward projections; and on facilities at APS sector 1, CHESS, ESRF, and Petra-III.

8:45 – 9:00	Matt Miller and Bob Suter *Welcome & Introductory Remarks*
9:00 – 9:40	Peter Voorhees (Northwestern University) *3D X-ray Diffraction Contrast Tomography of Grains and Grain Growth*
9:40 – 10:20	Armand Beaudoin (University of Illinois at Urbana Champaign) In Situ *Assessment of Lattice Strain in Al–Li Alloys*
10:20 – 10:50	Break
10:50 – 11:30	Jacob Ruff (CHESS, Cornell University) *Prospects for "Magnetic Loading" with the APS Pulsed Magnets*
11:30 – 12:15	Jun-Sang Park (APS, Argonne National Laboratory) *Understanding the State of Polycrystalline Structural Alloys and Components Using High-energy Synchrotron X-rays*

WK4

3D X-ray Diffraction Contrast Tomography of Grains and Grain Growth

Anthony E. Johnson[1], Erik M. Lauridsen[2], and Peter W. Voorhees[1, 3]

[1] Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60093
[2] Department of Energy Conversion and Storage, Technical University of Denmark, Denmark
[3] Department of Engineering Sciences and Applied Mathematics, Northwestern University, Evanston, IL 60093

Diffraction contrast tomography has been used at the European Synchrotron Radiation Facility to produce three-dimensional (3D) grain maps of a high-purity aluminum sample at seven time steps during an anneal. A new forward-projection algorithm that models the intensity of the peaks was then used to reconstruct the 3D grain morphology. The result is a much higher fidelity, but not completely space filling, reconstruction that is an improvement over that produced using the conventional back-projection method. Using this data we determine the evolution of the morphology of the grains, the texture of the sample, the grain boundary velocities, and the grain boundary misorientations. We also have reconstructed the 3D grain morphology of a barium-titanate sample that shows highly anisotropic grain morphologies. Comparisons between the forward- and back-projection reconstructions of this polycrystalline sample will be given.

WK4

In Situ Assessment of Lattice Strain in Al–Li Alloys

Armand J. Beaudoin

University of Illinois at Urbana-Champaign, Urbana, IL 61801

Aluminum-lithium alloys are under continuing development, with increasing use in aerospace structures. The practice of design—with consideration given to fault tolerance—is complicated by the interplay of kinetics and deformation incompatibility at the mesoscale. High-energy diffraction microscopy is applied to measure the crystallographic orientation and evolution of lattice strain in an Al–Li alloy. The relative spatial arrangement of the several pancake-shaped grains in a tensile sample is determined through *in situ* and *ex situ* techniques. In addition, a depth-defining aperture is used to isolate the diffraction of individual grains in this highly textured production alloy. A model for crystal plasticity with continuity of lattice spin is set developed, where grains are represented by layers in a finite element mesh following the arrangement indicated by experiment. Comparison is drawn between experiment and simulation. It is shown that hydrostatic stress, and in turn the stress triaxiality, can vary significantly from grain to grain.

WK4

Prospects for “Magnetic Loading” with the APS Pulsed Magnets

J.P.C. Ruff[1, 2], and Z. Islam[1]

[1] Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439
[2] CHESS, Cornell University, Ithaca, NY 14853

Recently, a suite of instruments has been developed at the Advanced Photon Source that enables precise x-ray diffraction measurements in pulsed magnetic fields as high as 30 tesla. Primarily, these instruments have been developed to address fundamental condensed matter physics questions in quantum magnets and superconductors, and in this regard they have been successfully used. In this somewhat speculative talk, we will explore some complementary opportunities offered by these instruments for “structural materials” studies. The availability of magnetic fields of sufficient magnitude to significantly perturb crystal lattice properties opens a new avenue for dynamic “loading” of materials. We will review what has been achieved at the APS thus far, and sketch out the types of measurements that are now possible. Opportunities for co-opting recent technique developments in strain loading and reworking them for high magnetic field studies will also be discussed.

WK4

Understanding the State of Polycrystalline Structural Alloys and Components Using High-energy Synchrotron X-rays

Jun-Sang Park

Advanced Photon Source, Argonne National Laboratory, Argonne IL 60439

High-energy synchrotron radiation is an attractive non-destructive tool for investigating the state and the micromechanical behavior of polycrystalline structural alloys. In this talk, I will focus on two high-energy x-ray diffraction techniques.

In the first part of the talk, I will talk about a suite of high-energy diffraction microscopy (HEDM) experiments that allow us to characterize the microstructure of a polycrystalline alloy and quantify its micromechanical state. A framework that combines HEDM data with polycrystal finite element simulation will also be discussed.

In the second part of the talk, I will talk about powder-diffraction-based experiments for quantifying the residual stress field in a polycrystalline material. An experimental setup that allows the measurement of lattice strains from a specific volume of material inside a polycrystalline component is described. A numerical framework that uses these spatially resolved measurements to obtain the full three-dimensional residual stress field in the component is also described.

APS Workshop 5
The Future of High-throughput Nonresonant IXS at “Lower” Energy Resolution

Location: Argonne Guest House, Conf. Rm. A

Organizers: Chengjun Sun (Advanced Photon Source) and Gerald Seidler (University of Washington)

Hard x-ray, nonresonant inelastic x-ray scattering (NIXS, also often called x-ray Raman scattering) at energy resolutions of a few tenths to 1 eV has seen a steadily growing range of applications at the APS. This method, which is regularly supported at three different sectors, has resulted in nearly 100 publications based on APS data. These manuscripts address high-pressure phases, battery materials and their underlying science, f-electron chemistry, numerous topics in materials chemistry, and even fundamental issues in quantum scattering theory. The purpose of this workshop is to look toward the future under APS-U and to discuss how to find the most productive overlap between the scientific demands of the broad user base and the technical opportunities provided by the upgrade process.

To this end, we propose a full-day workshop aimed at bringing together successful, prominent users of the LERIX spectrometer and related instruments at HP-CAT and GSE-CARS with the designers of the massively parallel NIX spectrometers in operation at the APS, SSRL, and ESRF. The workshop will, as a secondary point, also bring in members of the fusion energy science community who perform *in situ* NIXS experiments on dense plasmas at the National Ignition Facility (NIF); this will help to identify emerging synergies where NIXS studies at the APS may become important contributors to instrument validation and data interpretations at the NIF, OMEGA, and other large-scale laser-plasma facilities.

9:00 – 9:05	Welcome and Introductory Remarks *Gerald T. Seidler (University of Washington)*
9:05 – 9:30	Simo Huotari (University of Helsinki) *Understanding Bent Analyzer Crystal Properties for Advanced Applications*
9:30 – 9:55	Dimosthenis Sokaras (SLAC National Accelerator Laboratory/Stanford University) *The High-throughput X-ray Raman Spectroscopy End Station at the Stanford Synchrotron Radiation Lightsource*
9:55 – 10:20	Tilo Doeppner (Lawrence Livermore National Laboratory) *X-ray Thomson Scattering for Characterization of Dense Plasma States in High-energy-density Physics Experiments on Large-scale Laser Facilities*
10:20 – 10:50	Break
10:50 – 11:15	Mahalingam Balasubramanian (APS, Argonne National Laboratory) *Battery Science Using X-ray Raman Scattering*
11:15 – 11:45	Steve Heald (APS, Argonne National Laboratory) and Gerald T. Seidler (University of Washington) *The LERIX-2 End Station at the Advanced Spectroscopy Beamline*
11:45 – 12:10	Beamline developments session

WK5

Understanding Bent Analyzer Crystal Properties for Advanced Applications

A.-P. Honkanen[1], R. Verbeni[2], L. Simonelli[2], M. Moretti Sala[2], G. Monaco[2], and S. Huotari[1]

[1] **University of Helsinki, Finland**
[2] **European Synchrotron Radiation Facility, Grenoble, France**

As a part of the European Synchrotron Radiation Facility (ESRF) upgrade program, a new beamline ID20 for inelastic x-ray scattering (IXS) studies from electronic excitations is currently being commissioned. The new beamline will feature a spectrometer for non-resonant IXS using 72 crystal analyzers, and a five-crystal spectrometer suitable for resonant IXS and x-ray emission spectroscopy. The state-of-the-art applications require a thorough understanding of properties of the analyzer crystals that form the heart of the end station instrumentation.

During the two decades of IXS studies at the ESRF, hundreds of analyzer crystals have been used with different properties and manufacturing methods. An intensive research and development program has led to many advances in the analyzer crystal fabrication [1]. The current mass-scale production of spherically bent crystals relies on the anodic bonding technique with highly polished and thin wafers. A very useful addition to the IXS instrumentation was found to be photon-counting hybrid pixel detectors. The current ones in use are based on the Timepix [2] design. These detectors give information on not only on the mere resolution function but also on the focusing properties of analyzer crystals. This added information has led to advanced applications [3] and better understanding on the fundamental properties of macroscopic bent crystals and their diffraction properties [4]. This may eventually lead to improvements in the energy resolution of bent analyzer crystals. The current status of this development program at the ESRF will be presented.

[1] R. Verbeni, M. Kocsis, S. Huotari, M. Krisch, G. Monaco, F. Sette, and G. Vanko, *J. Phys. Chem. Sol.* **66**, 2299 (2005).

[2] X. Llopart, R. Ballabriga, M. Campbell, L. Tlustos, and W. Wong, *Nucl. Instrum. Meth. Phys. Res. A* **581**, 485 (2007).

[3] S. Huotari, T. Pylkkänen, R. Verbeni, G. Monaco, and K. Hämäläinen, *Nature Mater.* **10**, 489 (2011).

[4] A.-P. Honkanen, R. Verbeni, L. Simonelli, M. Moretti Sala, G. Monaco, and S. Huotari (submitted).

WK5

The High-throughput X-ray Raman Spectroscopy End Station at the Stanford Synchrotron Radiation Lightsource

Dimosthenis Sokaras, Tsu-Chien Weng, Dennis Nordlund, Roberto Alonso Mori, and Uwe Bergmann

Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

Recently we developed, installed, and operated a state-of-the-art x-ray Raman spectroscopy end station at the Stanford Synchrotron Radiation Lightsource (SSRL). The setup's features, in terms of energy resolution (~0.3eV) and solid angle of detection (0.9% of 4π sr) coupled with the performance of the beamline 6-2 and SPEAR3 storage ring, position the instrumentation as a unique alternative to soft x-ray absorption when samples under difficult conditions or bulk sensitive measurements are required. In this way, a systematic implementation of this photon-in/photon-out hard x-ray technique on emerging research of multidisciplinary scientific fields (such as energy-related science, physics, and material science) has been enabled at SSRL. First results from the SSRL's spectroscopy program and collaborations with various groups will be presented.

[1] D. Sokaras et al., *Rev. Sci. Instrum.*, **83**, 043112 (2012).

WK5

X-ray Thomson Scattering for Characterization of Dense Plasma States in High-energy-density Physics Experiments on Large-scale Laser Facilities

Tilo Doeppner[1], Paul Davis[2], Roger Falcone[2, 3], Luke Fletcher[2], Siegfried Glenzer[4], Stefan Hau-Riege[1], Andrea Kritcher[1], Otto Landen[1], HaeJa Lee[4], Tammy Ma[1], Art Pak[1], and Sebastien Le Pape[1]

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[2] UC Berkeley, Department of Physics, Berkeley, CA 96720
[3] Larwence Berkeley National Laboratory, Berkeley, CA 96720
[4] Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

In the last decade powerful laser facilities went into operation that have enabled the creation of unprecedented warm and hot dense plasma states. These experiments generate novel very dense states of matter. To characterize these plasma conditions new diagnostic methods are being developed. X-ray Thomson scattering (XRTS) is a powerful tool to measure relevant plasma properties [1].

It employs strong high-energy x-ray sources that are able to penetrate through such dense states of matter, and allows inferring macroscopic and microscopic plasma properties. While the forward scattering spectrum is sensitive to collective plasmon oscillations, the back-scattering spectrum is sensitive to the motion of individual electrons and provides accurate diagnostic information on the temperature, density and ionization state from the width and the shape of the Compton peak. In addition, measurement of the angularly resolved near-elastic scattering obtains the structure factor S(k) and yields independent information on compression and correlations in the plasma [5]. I will present results from experiments conducted at the Omega Laser (LLE Rochester) [3, 5], the Jupiter Laser Facility (LLNL Livermore) [2], and at LCLS at SLAC [4], and plans on fielding XRTS on the National Ignition Facility (NIF).

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

[1] S.H. Glenzer and R. Redmer, *Rev. Mod. Phys.*, **81**, 1625–1663 (2009).

[2] P. Neumayer et al., *Phys. Rev. Lett.*, **98**, 065002 (2010).

[3] A. L. Kritcher et al., *Phys. Rev. Lett.*, **107**, 015002 (2011).

[4] S. Hau-Riege et al., *Phys. Rev. Lett.*, **108,** 0217402 (2013).

[5] T. Ma, T. Doeppner et al., *Phys. Rev. Lett.*, **110**, 065001 (2013).

WK5

Battery Science Using X-ray Raman Scattering

M. Balasubramanian

X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Lithium-ion batteries with high energy and power density are needed for a variety of existing and emerging technologies. Knowledge of the redox chemistry and changes in the structure during electrochemical cycling is of paramount importance in designing new battery materials with superior properties. *In situ* x-ray diffraction and x-ray absorption (XAS) studies have played a vital role in elucidating the structural and electronic changes that accompany lithiation/delithiation. The advent of third-generation synchrotron sources coupled with dedicated and specialized instruments for specific types of x-ray scattering studies has opened a new window to systematically investigate the structure property relationship of advanced materials under operating conditions. Using a combination of XAS and x-ray Raman scattering (XRS) methods, we seek to provide definitive characterization of the redox chemistry of operating batteries, a topic of continuing fundamental and applied interest. XRS, which involves inelastic scattering of x-rays from core electrons, is becoming an important method to study the electronic structure of condensed matter systems. In the limit of small momentum transfer, XRS is equivalent to soft XAS or electron energy loss spectroscopy. In this talk I will highlight the work done at sector 20 using the lower-energy-resolution inelastic x-ray scattering spectrometer to understand battery materials.

WK5

The LERIX-2 End Station at the Advanced Spectroscopy Beamline

Steve Heald[1] and Gerald Seidler[2]

[1] **Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439**
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We will present a technical overview of the Advanced Spectroscopy beamline and the LERIX-2 (lower-energy-resolution inelastic x-ray scattering) end station for the APS Upgrade. Design and performance considerations for LERIX-2 will be presented in detail, with the goal of leading directly into a workshop discussion of its various features. Special emphasis will be placed on the overall optical configuration, ease of operation, optimization of analyzer performance, and best practice for detector selection.

APS Workshop 6
High-energy X-rays on Single Crystals: A Unique Capability at the APS

Location: Bldg. 402, Rm. E1200

Organizers: Alan I. Goldman (Iowa State U.) and Jonathan C. Lang (APS)

A key distinguishing feature of the Advanced Photon Source (APS) is the capability for high-energy scattering, which has been exploited for numerous applications including pair distribution function studies, high-pressure studies, and investigations of the mechanical behavior of materials. Coupled with the new generation of two-dimensional area detectors, high-energy diffraction studies of polycrystalline samples provide an important approach to structural measurements complementary to conventional x-ray and neutron diffraction measurements. The capabilities for high-energy single-crystal diffraction measurements at the APS, however, have only recently matured. The advantages of high-energy x-rays for diffraction studies have been widely discussed and were, for example, the topic of an APS sponsored workshop as early as 2001. Of particular importance, the use of high-energy x-rays ensures that the structure of the sample bulk, rather than near surface region, is probed and, because of the short wavelength (typically < 0.1 Å), the diffraction pattern is concentrated to smaller angles allowing the efficient use of area detectors and rapid data acquisition. Furthermore, the penetrating power of high-energy x-rays eases constraints on the use of ancillary equipment such as cryostats, pressure cells and magnets, which impose limitations on the angular access to the sample.

Over the past few years several groups working at the APS have developed techniques using high-energy x-rays to image both Bragg and diffuse scattering in reciprocal space, and applied these methods to a variety of phenomena governed by complex atomic disorder, both in the form of point defects and the nanoscale self-organization e.g. in the form of stripes, phase separation, or dimerization, which result from the competition between interactions with incompatible order. Examples include the high temperature cuprate and iron pnictide superconductors, colossal magnetoresistance materials, relaxor ferroelectrics, as well as investigations of rotational disorder in molecular solids and intercalation compounds, adsorption in microporous frameworks, and quasicrystals. We seek to expand the community of users for these single crystal methods through a workshop that introduces the unique capabilities at the APS for high-energy x-ray single crystal investigations and, at the same time, explores the requirements and interests of future users.

1:30 – 1:45	Alan Goldman (Ames Laboratory and Iowa State University) *Overview and Goals of the Workshop*
1:45 – 2:15	Andreas Kreyssig (Ames Laboratory) *Imaging of Reciprocal-space Planes by a High-energy X-ray Precession Camera*
2:15 – 2:45	Markus Hücker (Brookhaven National Laboratory) *Competing Electronic States in Cuprate Superconductors*
2:45 – 3:15	Manuel Angst (Jülich Research Center, Germany) *Probing Charge-order–based Multiferroicity by High-energy X-rays*
3:15 – 3:30	Break

3:30 – 4:00 Richard Welberry (Australian National University)
Polar Nanoregions and Diffuse Scattering in Relaxor Ferroelectrics

4:00 – 4:30 Ray Osborn (Argonne National Laboratory)
Single-crystal Diffuse Scattering Using High-energy X-rays

4:30 – 5:00 Yu Wang (Michigan Technological University)
Three-dimensional Diffuse Scattering Study of Phase Transition Precursor Phenomenon Using In Situ High-energy X-ray Single-crystal Diffraction

5:00 – 5:30 Jonathan Lang (Advanced Photon Source)
Summary and Open Discussion

WK6

Imaging of Reciprocal-space Planes by a High-energy X-ray Precession Camera

A. Kreyssig, D. K. Pratt, M. Ramazanoglu, G. Tucker, D.S. Robinson, J.C. Lang, R.J. McQueeney, and A.I. Goldman

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

A key distinguishing feature of the APS is the capability for high-energy x-ray scattering, which has been exploited for numerous powder sample applications. The instrumentation for high-energy single-crystal diffraction measurements at the APS, however, remains underdeveloped. High-energy x-rays offer several advantages: (1) absorption effects are minimized and the entire bulk of the sample is probed and (2) a large range of reciprocal space can be imaged when used together with even a modestly sized area detector. We have developed a high-energy x-ray precession camera for imaging of reciprocal-space planes. This technique is highly suited to studies of Bragg and diffuse scattering with its flexibility in dynamic range, resolution, and scattering vector range. These capabilities have been demonstrated by studies of single crystals and quasicrystals.

WK6

Competing Electronic States in Cuprate Superconductors

M. Hücker

Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973

There is mounting evidence for proximity of the superconducting ground state in the cuprates to competing states with static spin and/or charge density modulations. We have applied high-energy single-crystal x-ray diffraction to identify the charge component of these states in a number of cuprates and non-superconducting nickelates. Many of these experiments were performed under extreme conditions such as high magnetic and electric fields as well as high pressure. In this talk I will highlight some examples, such as the charge stripe order in $La_{2-x}Ba_xCuO_4$ [1, 2] and $Nd_{2-x}Sr_xNiO_4$ [3] as well as the recently discovered charge density wave order in $YBa_2Cu_3O_{6+d}$ [4], and emphasize how high-energy x-rays have been beneficial for these studies.

The work at Brookhaven was supported by the Office of Basic Energy Sciences, Division of Materials Science and Engineering, U.S. Department of Energy, under Contract No. DE-AC02-98CH10886.

[1] M. Hücker, M. v. Zimmermann, Z.J. Xu, J.S. Wen, G.D. Gu, and J.M. Tranquada, *PRB*, **87**, 014501 (2013).

[2] M. Hücker, M.v. Zimmermann, M. Debessai, J. Schilling, J.M. Tranquada, and G. Gu, *PRL*, **104**, 057004 (2010).

[3] M. Hücker, M. v. Zimmermann, and G.D. Gu, *Phys. Rev. B*, **75**, R41103 (2007).

[4] E. Blackburn, J. Chang, M. Hücker, A.T. Holmes, N.B. Christensen, R. Liang, D.A. Bonn, W.N. Hardy, M. v. Zimmermann, E.M. Forgan, and S.M. Hayden, *PRL*, **110**, 137004 (2013).

WK6

Probing Charge-order-based Multiferroicity by High-energy X-rays

Manuel Angst

Peter Grünberg Institut und Jülich Centre for Neutron Science, JARA-FIT
Forschungszentrum Jülich GmbH, Jülich, Germany
Experimental Physics IVC, RWTH Aachen University, Aachen, Germany

Magnetoelectric multiferroics have a large applications potential and often involve complex phase competitions. Among possible mechanisms of multiferroicity, ferroelectricity originating from charge ordering is particularly intriguing because it potentially combines large electric polarizations with strong magnetoelectric coupling. However, example materials where this mechanism is experimentally indicated to occur are exceedingly rare and none is really understood. The prototypical example LuFe$_2$O$_4$ was believed to provide the "proof of principle" that this mechanism can work in real materials since ferroelectricity originating from Fe^{2+}/Fe^{3+} charge order was proposed in 2005 [1]. The proposal had been made due to indications of a polar state by dielectric and pyroelectric measurements, combined with a reasonable model of charge order based on the location of superstructure reflections. This charge-order model has not been completely verified though [2], and the spin-order has also been an open question. We combined x-ray and neutron diffraction, and circular dichroism, measurements that allowed i) the unambiguous determination of the charge order, also in external electric and magnetic fields [3], ii) the determination of the spin structures in two competing magnetic phases [4], and iii) the relation between these orderings [3]. In this presentation, particular emphasis will be given to the contribution of high-energy x-ray diffraction to these findings. The results reveal a very strong coupling between spin and charge order. Most importantly, the unambiguously determined arrangement of Fe^{2+} and Fe^{3+} ions, which is robust in electric fields, excludes any charger-order-based ferroelectricity, in accordance with our recent dielectric spectroscopy results [5] that attribute the original macroscopic indications of ferroelectricity to artifacts. The general implication is that a clear example material for the "ferroelectricity from charge order" mechanism has yet to be identified.

[1] N. Ikeda et al., *Nature*, **436**, 1136 (2005).

[2] M. Angst et al., *Phys. Rev. Lett.*, **101**, 227601 (2008).

[3] J. de Groot et al., *Phys. Rev. Lett.*, **108**, 187601 (2012).

[4] J. de Groot et al., *Phys. Rev. Lett.*, **108**, 037206 (2012).

[5] D. Niermann et al., *Phys. Rev. Lett.*, **109**, 016405 (2012).

WK6

Polar Nanoregions and Diffuse Scattering in Relaxor Ferroelectrics

Richard Welberry

Research School of Chemistry, Australian National University, Acton, Canberra, ACT, 0200, Australia

We present a fully atomistic model of polar nanoregions (PNRs) in the relaxor ferroelectric PbMg$_{1/3}$Nb$_{2/3}$O$_3$. Our molecular dynamics calculations [1] reproduce both the characteristic form of the neutron diffuse scattering distribution and its temperature dependence. A shell model was used with a modified version of a published interatomic potential that was based on *ab initio* calculations. The parameters of this potential were optimized for the present work to provide a better description of the O atom interactions, as these are particularly important for neutron scattering. At high temperatures the Pb ions are displaced from their mean site positions in a direction that has an isotropic distribution, but at low temperatures the distribution condenses into eight localized sites displaced from the average position along each of the eight possible $\langle 111 \rangle$ directions. At intermediate temperatures (300 K) the distribution is cuboidal with some preference for $\langle 111 \rangle$ displacements but with all possible displacement directions present. Longitudinal correlations between the displacements of Pb-Mg/Nb and Pb-O increase monotonically in magnitude as the temperature changes from 700 K to 10 K with the sign of the Pb-O correlation being negative. At low temperatures this increase in correlation results in polar nanoregions that are clearly visible in plots of the local structure, although the exact form of these domains is more difficult to visualize. We show that the form of these PNRs can be revealed by an examination of conditional displacement distributions at low temperatures. Therein strongly anisotropic cooperative displacement behaviour is found. Remnants of this correlation pattern persist at much higher temperatures, but progressively a relatively smaller proportion of the Pb ions appears to be taking part and there is a substantially larger random component. It seems likely that the onset of the characteristic structured diffuse scattering at around 400 K coincides with the appearance of this cooperative displacement behavior.

[1] M. Pasciak, T.R. Welberry, J. Kulda, M. Kempa, and J. Hlinka, *Phys. Rev. B*, **85**, 224109 (2012).

WK6

Single-crystal Diffuse Scattering Using High-energy X-rays

Ray Osborn[1], Stephan Rosenkranz[1], Karena Chapman[2], and Peter Chupas[2]

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Atomic disorder, both in the form of point defects and the nanoscale self-organization that often accompany them, plays an important role in the functional behavior of complex materials. Many phenomena in materials science are a consequence of disorder, such as colossal magnetoresistance, unconventional superconductivity, ferroelectric relaxor behavior, fast-ion conduction, and adsorption in intercalation compounds and microporous frameworks. While there are several techniques that are sensitive to the existence of disorder and provide insight into local site occupancies and atomic distortions, single-crystal diffuse scattering is the only technique that can be used to determine both the local distortions around a point defect and the self-assembly of these defects into nanoscale structures. However, there are formidable technical difficulties both in obtaining reliable diffuse scattering data and in using it to construct models of defect structures. New developments in detector technology and computational power promise to improve the efficiency and ease-of-use of the diffuse scattering technique. A new generation of fast area detectors can collect data at 20 Hz and have dynamic ranges of 10^6 and soon 10^7, allowing the combination of both Bragg peak and diffuse scattering intensities to produce real-space model-independent pair distribution functions, a three-dimensional analog of conventional PDFs. As part of the Argonne Grand Challenge on Data-Driven Science, data collected using the rotation method will be streamed to a "Software-as-a-Service" (SaaS) platform that can handle the large data volumes generated, providing real-time data reduction, manipulation, and visualization. The goal is to transform diffuse scattering from the domain of specialist groups to an essential tool for all materials scientists interested in functional properties generated by crystalline disorder.

WK6

Three-dimensional Diffuse Scattering Study of Phase Transition Precursor Phenomenon Using *In Situ* High-energy X-ray Single-crystal Diffraction

Yongmei M. Jin[1], Yang Ren[2], and Yu U. Wang[1]

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[2]X-Ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Phase transition precursor is an ubiquitous phenomenon that generally occurs in metals, alloys, and ceramics. Various anomalies have been observed in precursor and have remained long outstanding critical issues of phase transformations in crystalline solids. The unique capability at APS 11-ID-C enables a systematic study of this intriguing phenomenon in quantitative detail. In particular, the high-energy, high-flux x-rays together with two-dimensional area detector for rapid data acquisition make it possible to carry out three-dimensional (3D) diffuse scattering of bulk single crystals under *in situ* conditions. By partially blocking strong Bragg peaks, both Bragg reflection and diffuse scattering are simultaneously measured, which provides complementary information of the crystal lattice and lattice dynamics. Computational methods are used for quantitative data analysis. The technique is employed to study martensitic precursor in magnetic shape memory alloy Ni-Mn-Ga. The observed *in situ* 3D diffuse scattering reveals heterogeneous phonon domains in high-symmetry austenite phase in a wide temperature range before martensitic transformation, which exhibits highly anisotropic, hysteresis-free, reversible lattice responses to externally applied stress. Based on the experimental findings, we show that incomplete phonon softening leads to dynamic symmetry breaking of lattice vibrations in phase transition precursor, which naturally precedes the static symmetry breaking of crystal lattice in phase transition. The natural consequences of dynamic symmetry breaking manifest as various precursor "anomalies" that have been difficult to understand from traditional theory of phase transitions. Finally, our ongoing effort to integrate materials modeling and supercomputer simulation with high-energy x-ray single-crystal diffraction is briefly discussed, which would help fully exploit the unique capability at the APS.

APS Workshop 7
Resonant Inelastic X-ray Scattering (RIXS): Frontiers and Perspectives

Location:	Argonne Guest House, Conf. Rm. A
Organizers:	Mary Upton and Yang Ding (Advanced Photon Source)

The Resonant Inelastic X-ray Scattering (RIXS) program at the APS is one of the world-leading synchrotron radiation programs. It addresses a multitude of complex materials with novel phenomena of enormous scientific importance and great technological potential, such as unconventional superconductivity, colossal mageneto-resistance in manganites, multiferroics, and graphene. In order to push the envelope for this technique, leading to higher scientific impact and a more diverse user community, this workshop focuses on reviewing last year's breakthrough scientific discoveries achieved with unprecedented energy-resolution at APS, as well as prospecting and exploring emerging scientific opportunities for the upcoming new RIXS beam line and its expanded capabilities, including the improved energy resolution and special sample environments.

1:50 – 2:10	Welcome and Introductory Remarks
2:10 – 2:40	Young-June Kim (University of Toronto) *RIXS Investigation of Honeycomb Lattice Iridates*
2:40 – 3:10	Wei Ku (Brookhaven National Laboratory and State University of New York) *First-principles Method of Propagation of Tightly Bound Excitons: Exciton Band Structure of LiF and Verification with Inelastic X-ray Scattering*
3:10 – 3:40	Break
3:40 – 4:10	Victor Struzhkin (Carnegie Institution for Science) *RIXS Spectroscopy at High Pressure: Mott-Hubbard Gap and Spin Crossover Transition*
4:10 – 4:40	Stuart Calder (Oak Ridge National Laboratory) *Investigations of the Slater Metal-Insulator Transition in* $NaOsO_3$
4:40 – 5:10	Mark Dean (Brookhaven National Laboratory) *Novel Magnetic Interactions in Model Iridate,* Sr_3CuIrO_6*, and Possible Spin Liquid,* $Na_4Ir_3O_8$

WK 7
RIXS Investigation of Honeycomb Lattice Iridates

Young-June Kim
University of Toronto, Toronto, ON M5S 1A7, Canada

In iridates, competition between spin-orbit coupling, crystal field, and electronic correlation leads to exotic and complex new physics. A variety of exotic phases, ranging from a high-temperature superconductor to a topological (Weyl) semimetal, have been theoretically predicted for iridates. Resonant inelastic x-ray scattering (RIXS) has been playing an essential role in elucidating many electronic phases and excitation spectra of these phases. Honeycomb lattice iridates, such as Na_2IrO_3 and Li_2IrO_3, present particularly appealing experimental systems, since they allow a special type of bond-dependent magnetic interaction called Kitaev interaction to be realized. We present our comprehensive RIXS studies of these honeycomb lattice iridates in this talk. Crystal-field-split d-d excitations are resolved in the high-resolution RIXS spectra. In particular, the splitting due to non-cubic crystal fields, derived from the splitting of j_{eff}=3/2 states, is much smaller than the typical spin-orbit energy scale in iridates, validating the applicability of j_{eff} physics in A_2IrO_3. Low energy lattice and magnetic excitations observed in Na_2IrO_3 will be also discussed.

WK7

First-principles Method of Propagation of Tightly Bound Excitons: Exciton Band Structure of LiF and Verification with Inelastic X-ray Scattering

Chi-Cheng Lee[1, 2], Xiaoqian M. Chen[3], Yu Gan[3, 4], Chen-Lin Yeh[1, 5], H. C. Hsueh[5], Peter Abbamonte[3, 4], and Wei Ku[1, 6]

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[4] Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439
[5] Department of Physics, Tamkang University, Tamsui, Taipei 25137, Taiwan
[6] Physics Department, State University of New York, Stony Brook, NY 11790

We propose a simple first-principles method to describe the propagation of tightly bound excitons. By viewing the exciton as a composite object (an effective Frenkel exciton in Wannier orbitals), we define an exciton kinetic kernel to encapsulate the exciton propagation and decay for all binding energy. Applied to prototypical LiF, our approach produces three exciton bands, which we verified quantitatively via inelastic x-ray scattering. The proposed real-space picture is computationally inexpensive and thus enables study of the *full* exciton dynamics, even in the presence of surfaces and impurity scattering. It also provides intuitive understanding to facilitate practical exciton engineering in semiconductors, strongly correlated oxides, and their nanostructures.

WK7

RIXS Spectroscopy at High Pressure: Mott-Hubbard Gap and Spin Crossover Transition

Viktor Struzhkin[1], Jung-Ho Kim[2], Yuri Shvydko[2], Yu. Orlov[4], M.H. Upton[2], D. Casa[2], Alexander Gavriliuk[3], Sergey Ovchinnikov[4], and S. V. Sinogeikin[5]

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[3] Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia
[4] L.V. Kirensky Institute of Physics, Krasnoyarsk, Russia
[5] HPCAT, Carnegie Institution of Washington, 9700 South Cass Avenue, Argonne, IL 60439

We have collected first high-pressure Fe pre-edge resonant inelastic x-ray scattering (RIXS) spectra under pressure at the MERIX beamline (sector 30 at the Advanced Photon Source, Argonne National Laboratory). It has been suggested from the earlier optical absorption measurements that a spin-crossover transition in a $3d^5$ compound $FeBO_3$ starting at about 50 GPa is responsible for the dramatic reduction of the Mott-Hubbard energy gap in this material. Our measurements confirm this conclusion and provide further details on the interplay between multi-orbital effects and Mott physics in $FeBO_3$. Preliminary results of RIXS studies of $3d^6$ iron configuration in FeO will be reported.

WK7

Investigations of the Slater Metal-Insulator Transition in $NaOsO_3$

Stuart Calder

Oak Ridge National Laboratory, Oak Ridge, TN 37831

The metal-insulator transition (MIT) is one of the most dramatic manifestations of electron correlations in materials, enjoying interest both for its fundamental nature and technological application. Various mechanisms producing MITs have been extensively considered over the years, including the Mott (electron localization via Coulomb repulsion), Anderson (localization via disorder), and Peierls (localization via distortion of a periodic one-dimensional lattice). One additional route to a MIT proposed by Slater in 1951, in which long-range magnetic order in a three-dimensional system drives the MIT, has received relatively little attention, particularly from an experimental viewpoint. Using neutron and resonant x-ray scattering we have shown that the MIT in $NaOsO_3$ is coincident with the onset of long-range commensurate magnetic order at 410 K. Whilst candidate materials have been suggested, most notably another osmate $Cd_2Os_2O_7$, our experimental methodology allows the first definitive demonstration of the long-predicted Slater MIT. We discuss our results in light of recent work on 5d iridium systems that contrastingly have been predicted to host a $J_{eff}=½$ Mott spin-orbit insulating state. The subsequent increased interest in iridium oxides has utilized specific capabilities unique to resonant x-ray scattering. We show how resonant x-ray scattering can have an equally effective impact in the study of osmates.

WK7

Novel Magnetic Interactions in Model Iridate, Sr_3CuIrO_6, and Possible Spin Liquid, $Na_4Ir_3O_8$

Xuerong Liu, Mark P.M. Dean, and John P. Hill

Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973

In the iridium oxides, the strong spin-orbit coupling (SOC) of the 5d iridium electrons entangles the orbital and spin degrees of freedom, providing opportunities for exotic magnetic states. Much of the early work on these compounds assumed the strong SOC limit in which the SOC dominated all other energy scales in the problem. Here, we present resonant inelastic x-ray scattering (RIXS) studies of the orbital and magnetic excitations in Sr_3CuIrO_6 and $Na_4Ir_3O_8$. Sr_3CuIrO_6 is chosen as a model iridate with well-defined, localized Ir-states and small distortions to the shape of the IrO_6, typical of the iridate compounds studied in the literature. By measuring the orbital excitations of Sr_3CuIrO_6, we show that the crystal field (CF) energy is similar to, rather than much smaller than, the SOC. This result demonstrates that both degrees of freedom must be accounted for in realistic models of the iridates. Furthermore, the combined effect of the CF, SOC, and novel coupling the 5d Ir sites and 3d Cu sites, leads to a large 30-meV gap in the magnetic excitation spectrum, also in contrast to the predictions of the strong SOC limit. Finally, we also studied $Na_4Ir_3O_8$, which has a hyperkagome lattice, and is a candidate quantum spin liquid. Here, a low energy continuum is observed below the orbital excitations. RIXS polarization dependence and optical conductivity measurements performed on the same sample imply that these excitations are magnetic in origin, suggesting that this compound does in fact host a spin-liquid.

CNM Workshop 8
Nanostructured Carbon Materials for MEMS/NEMS and Nanoelectronics

Location: Bldg. 401, Rm. A5000

Organizers: Anirudha V. Sumant (Center for Nanoscale Materials) and
Horacio Espinosa (Northwestern University)

The purpose of this workshop is to bring together experts from academia, national labs, and industry to discuss the latest developments in the synthesis and characterization of nanostructured carbon materials, which are specifically geared toward the development of advanced micro/nanosystems and nanoelectronic devices.

The materials of interest include nano/ultrananocrystalline diamond, carbon nanotubes, and graphene. The Center for Nanoscale Materials at Argonne has expertise and state-of-the-art facilities in the synthesis, characterization, and fabrication of all of the above-mentioned carbon materials, as well as a strong research program in fundamental studies on various aspects of these materials. The exceptional physical, chemical, bio-medical, mechanical, electrical, thermal and optical properties offered by these materials are promising for the development of high-performance MEMS/NEMS and nanoelectronic devices in various technologically important areas. This workshop will include topics covering fundamental studies on synthesis, characterization, and new properties; theoretical and modeling studies to understand structure property relationship; and issues related to fabrication and integration at micro/nanoscale.

This workshop is expected to provide an excellent platform for academics, scientists, and students to exchange ideas, foster collaborations with user facilities at Argonne, and embark upon new challenges in nanoscience.

8:45 – 9:00	Welcome and Introductory Remarks *Anirudha Sumant (Argonne National Laboratory), Horacio Espinosa (Northwestern University)*
9:00 – 9:40	James Hone (Columbia University) *Graphene Mechanics and NEMS Applications*
9:40 – 10:20	Nikhil Koratkar (Rensselaer Polytechnic Institute) *Wetting Transparency of Graphene*
10:20 – 10:50	Break
10:50 – 11:30	James Hannon (IBM) *Carbon Nanotubes from Lab to Fab*
11:30 – 12:15	Adam Khan (AKHAN Technologies, Inc.) *Towards Achieving Efficient N-type Doping in Nanocrystalline Diamond*
12:15 – 1:50	Lunch
1:50 – 2:30	Merlijn van Spengen (Delft University of Technology, The Netherlands) *MEMS On-chip Tribometers and the Relevance of N-UNCD*
2:30 – 3:10	Federico Buja (Delft University of Technology, The Netherlands) *Fabrication and Actuation of Nitrogen-incorporated Ultrananocrystalline Diamond Thermal Actuator*

3:10 – 3:40	Break
3:40 – 4:20	Philip Feng (Case Western Reserve University) *Silicon Carbide Nanoelectromechanical Systems (SiC NEMS) for Logic Devices in Extreme Environments*
4:20 – 5:00	Izabela Szlufarska (University of Wisconsin-Madison) *Wear of Nanocrystalline Carbide Ceramics by Atomistic Simulations*

WK8

Graphene Mechanics and NEMS Applications

James Hone

Dept. of Mechanical Engineering, Columbia University, New York, NY 10027

This talk will review collaborative efforts in characterizing the mechanical properties of graphene and related two-dimensional materials and its application to nano-electromechanical devices (NEMS). To fully characterize mechanical properties, we combine experimental tests consisting of nano-indentation of freely suspended membranes with multiscale analysis that connects atomic-level density functional theory to nonlinear anisotropic continuum mechanics. These measurements have previously revealed that graphene is both ultrastiff and the strongest known material, with a strength that reflects the intrinsic breaking strength of the carbon lattice. We have more recently extended this technique to monolayer MoS_2 and to polycrystalline CVD-grown graphene. For NEMS applications, we have developed techniques that allow fast, highly sensitive electronic readout. We have used these techniques to study fundamental physics in the quantum Hall regime, which reveals novel coupling between mechanics and the thermodynamic ground state. On the applications side, we are using graphene NEMS for RF mechanical signal processing, including filters and voltage-controlled oscillators.

WK8

Wetting Transparency of Graphene

Nikhil Koratkar

Department of Mechanical, Aerospace and Nuclear Engineering, and the Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180

In my talk, I will show that a monolayer graphene coating does not significantly disrupt the intrinsic wetting behavior of surfaces where the substrate-water interaction is dictated by Van der Waals (i.e., non-bonding) forces and the underlying substrate is significantly more wettable than graphene. For such surfaces, the graphene remains transparent to the substrate wetting behavior and remains non-invasive to the substrate-water interface. We call this effect the wetting transparency of graphene. An increase in the number of graphene layers results in the contact angle transitioning gradually towards the bulk graphite value and with more than six layers resulting in the water contact angle identical to that of bulk graphite. Molecular dynamics simulations and continuum predictions (using the effective interface potential) indicate that graphene's wetting transparency is related to its extreme thinness, which only slightly perturbs the Van der Waals interaction of water to the underlying substrate.

The wetting transparency of graphene is however lost on super-hydrophilic surfaces where the wettability is dominated by short-range chemical bonding such as the hydrogen bonding networks that are typical of the water-glass interface. The wetting transparency effect is also lost on super-hydrophobic surfaces which are less wettable than graphene. I will also show how minimally invasive (i.e., ultra-sheer) graphene drapes can be used to minimize droplet pinning and contact angle hysteresis on nano-patterned (i.e., rough) surfaces leading to enhanced droplet mobility which is required for a number of applications in micro- and nano-fluidics.

J. Rafiee, X. Mi, H. Gullapalli, A. Thomas, F. Yavari, Y. Shi, P. Ajayan, and N. Koratkar, "Wetting transparency of graphene," *Nature Materials*, **11**, 217–222 (2012).

E. Singh , A.V. Thomas , R. Mukherjee , X. Mi , F. Houshmand , Y. Peles , Y. Shi , and N. Koratkar, "Graphene Drape Minimizes the Pinning and Hysteresis of Water Drops on Nanotextured Rough Surfaces," *ACS Nano*, DOI: 10.1021/nn400466t (2013).

WK8

Carbon Nanotubes from Lab to Fab

James Hannon

IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY 10598

It is now widely appreciated that electronic devices based on carbon nanotubes (CNTs) have the potential to outperform conventional silicon devices. As the challenges associated with scaling silicon technology mount, CNTs are being seriously considered as an alternative, or successor, to silicon in high-performance logic applications. However, in order to create a viable high-performance CNT technology, daunting and unique integration challenges must be overcome. These include isolation of semiconducting CNTs, selective placement of CNTs from solution, and passivation. In this talk I will describe recent progress, made at IBM and elsewhere, on solving these challenges. I will highlight the device performance requirements for a competitive CNT technology, which guides our integration strategy. Finally, I will discuss the areas where fundamental research is needed in order to improve device performance.

WK8

Towards Achieving Efficient N-type Doping in Nanocrystalline Diamond

A. H. Khan

AKHAN Technologies

Achieving technologically relevant N-type doping still remains among the final and most challenging problems in diamond materials research, preventing highly promising diamond electronic and optoelectronic device demonstrations. Phosphorus has been demonstrated experimentally to be a deep-level donor (485 meV to 600 meV) in diamond, however, the impurity incorporation in the diamond lattice has not been demonstrated without the simultaneous inclusion of graphitization induced void-like planar defects (e.g., crystalline pitting) known to severely limit the mobility and related characteristics of phosphorus-doped diamond. For n-type diamond semiconductor to become a realistic possibility, impurity incorporation must be achieved in the absence of a high degree of graphitic inclusions (i.e., in the absence of crystallographic degradation). We explore through modified ion implantation methodology, a novel approach to achieving a large concentration of phosphorus incorporation in the nanocrystalline diamond grain without the previously observed surface segregation that results into graphitic defects. We further explore the applicability of n-type conductivity in nanocrystalline diamond through fabrication of p^+-i-n diode on wafer scale. In the absence of the deleterious effects of crystalline scattering sites, we observe record performance characteristics such as high current density (10,048 A/cm^2 at 20 V bias), and high power handling capability (100 W/mm at room temperature) in nanocrystalline diamond thin films. We are further working with Argonne's low-temperature nanocrystalline diamond technology to fabricate complementary metal-oxide semiconductor-compatible p-n junction devices, which are expected to open new era in developing the next generation of high-performance nanoelectronics devices

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WK8

MEMS On-chip Tribometers and the Relevance of N-UNCD

W. Merlijn van Spengen[1, 2]

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[2] Falco Systems BV, 1083 BA Amsterdam, The Netherlands

Micro-electromechanical systems (MEMS) technology has proven to be successful in many fields. However, the spread of complex micromachines with contacting and sliding surfaces has been significantly hampered by the poor tribological properties of materials traditionally used. We have set up a comprehensive program to investigate the limitations of the traditional materials such as silicon, and provide alternatives such as hard metals and metal oxides and, indeed, UNCD.

We have developed MEMS on-chip tribometers with which we can do on-chip friction and wear tests to obtain dynamic friction loops, showing the details of the interaction between the surfaces. The displacement and force readout are performed either capacitively or optically and provide nm and nN resolution; in the near future this will be pm and pN. With this universal setup, we have extensively studied friction in silicon MEMS, including friction- and wear-reducing measures such as DLC (diamond-like carbon) coatings and the application of normal force modulation (dither). The latter enables us to reduce friction and stress the contacting surfaces only under impact, not shear. Federico Buja, also at the workshop, will present our latest results on the newly developed N-UNCD MEMS thermal actuators. In the current talk I will review these developments and how they fit in our continuing effort to provide the MEMS community with solutions “o the tribological issues that prevent the widespread use of contacting and sliding surfaces in MEMS “micromachines.’

WK8

Fabrication and Actuation of a Nitrogen-incorporated Ultrananocrystalline Diamond Thermal Actuator

Federico Buja[1], Anirudha V. Sumant[2], and W. Merlijn van Spengen[1]

[1]TU Delft, 3mE-PME-MNE, 2628CD Delft, The Netherlands
[2]Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

A fully nitrogen-incorporated ultrananocrystalline diamond (N-UNCD) electrothermal actuator has been fabricated and actuated for the first time to be used for developing diamond based on-chip tribometer. The tribological investigation of N-UNCD at micro-electromechanical system (MEMS) scale requires the development of a functional device with sliding contacts. Improvements have been made on the compensation of internal stress gradient with thicker N-UNCD films (above 3 μm), therefore little out-of-plane bending after the device release is noticed. A numerical simulation, design and complementary metal–oxide–semiconductor compatible micro-fabrication process have been carried out in order to build a Chevron-type actuator for sliding and friction testing. The actuation has been proven by means of optical microscopy based detection, with 10 nm resolution, showing 500 nm displacement. This opens up the possibility to fully explore the friction and wear properties of this outstanding material at the micro and nanoscale, and also development of new diamond-based MEMS device with precise control on the lateral displacement down to nanometer scale.

WK8

Silicon Carbide Nanoelectromechanical Systems (SiC NeMS) for Logic Devices in Extreme Environments

Philip Feng

Electrical Engineering, Case School of Engineering, Case Western Reserve University, Cleveland, OH 02139

Silicon carbide (SiC), an advanced polymorphic material of great technological importance, possesses a number of attractive characteristics including wide bandgap, transparency from visible to near infrared, large refractive index, excellent thermal conductivity, very high elastic modulus, and remarkable mechanical hardness and chemical inertness. These make SiC highly interesting and promising for a wide spectrum of critical applications, ranging from high-temperature electronics, to sensors enabled by micro/nanoelectromechanical systems (MEMS/NEMS), to photonics and quantum information processing. Today's harsh-environment electronics face similar challenges as conventional Si electronics do, including power consumption and device scaling. Collective and increasing leakage issues become more acute as transistors are scaled with smaller dimensions. Among a few candidates for alternative logic devices, nanoscale contact-mode logic switches (relays) have been actively explored. NEMS switches offer compelling advantages including ideally abrupt switching with minimal off-state leakage, suitable for extreme environments, and small footprints. In pursuing these advantages, however, challenges remain: (i) all the high-performance mechanical switches recently demonstrated are still well in the MEMS domain and are orders of magnitude larger in size/volume than today's mainstream transistors, and (ii) most of today's truly nanoscale mechanical switches still suffer from nanoscale contact issues and very short lifetimes.

In this talk, I will present our recent results in advancing SiC NEMS toward a scalable nanoelectromechanical logic technology. I will demonstrate some clear advantages of SiC for enabling NEMS logic switches with robust nanoscale contacts and long lifetimes (in contrast to many other NEMS switches we have explored). Our nanocantilever-based SiC switches have all (but the length) dimensions in nanoscale, featuring motional volumes that are 10^4-10^5 times smaller than today's high-performance MEMS switches. For the first time, we experimentally record the time evolution of robust SiC NEMS switching events in ambient air, for at least $>10^6$ cycles *without failure*, with high on/off ratios (~10^4), and with highly repeatable performance over days. I will also show SiC NEMS switches and basic logic gates operating at high temperatures (T≈500°C). I will then discuss our effort in exploring and understanding the properties of the nanoscale contacts in SiC NEMS.

WK8

Wear of Nanocrystalline Carbide Ceramics by Atomistic Simulations

Izabela Szlufarska

Materials Science and Engineering Department, University of Wisconsin-Madison, Madison, WI 53706

Ceramics show outstanding mechanical properties such as high strength and high hardness over a wide range of temperatures and are stable in harsh environments. However, the low fracture toughness of ceramics limits their practical utility, for instance, as wear-resistance coatings. There have been several reports of improving the fracture strength of ceramics by reducing the grain sizes to nanometer regime. At the same time, it has been suggested that use of nanoscale tools leads to ductile machining by suppressing fracture in these small-scale deformations. We will discuss two examples of our work in this area. First, we investigated deformation mechanisms in ultrananocrystalline diamond (UNCD) and demonstrated that in this material plasticity is located primarily in the grain boundary (GB) regions. We discovered that in the absence of dislocation plasticity, hardness and yield stress have a simple functional dependence on the stress required for GB sliding. Our results explain the experimentally observed trends in mechanical properties of UNCD with hydrogen content and demonstrate that phenomena from the field of nanoscale friction can be utilized to understand the deformation of NC materials. In the second example, we will report on our large-scale molecular dynamics (MD) simulations of wear in nanocrystalline (nc) SiC. These simulations were performed to understand the toughening mechanisms in the presence of GBs and the effect of grain size on plasticity in ceramics. Dislocation plasticity inside the grains, GB sliding and GB fracture have been identified as the deformation mechanisms active during wear in nc-SiC, whereas separate simulations of wear performed on single crystal SiC show only dislocation plasticity. We have quantified the contribution of each of these mechanisms to strain relaxation inside the deformation zone as a function of grain size and the depth of cut.

EMC Workshop 9
Characterizing Energy Materials: Today and Tomorrow

Location: Bldg. 402, Rm. E1100

Organizers: Carlos Alvarez (Northwestern University; morning) and
Yasuo Ito (Northern Illinois Univversity; afternoon)

In the research of energy storage systems, the direct observation and characterization of fundamental processes that control the behavior of these complex systems at the nano and micron length scales is necessary to explain the collective system performance. This workshop will focus on using advanced techniques in electron microscopy and spectroscopy to characterize energy materials. This session will include areas such as batteries; solid oxide fuel cells; and energy catalyst.

8:50 – 9:00	Introductory Remarks
9:00 – 9:40	Dean Miller (EMC, Argonne National Laboratory) *Exploring Electrochemistry in Li-ion Batteries through Single-Particle Measurements: A Platform for Multimodal and Operando Characterization*
9:40 – 10:10	Jun Lu (Argonne National Laboratory) In situ *Fabrication of Porous-carbon-supported* α*-*MnO_2 *Nanorods at Room Temperature: Application for Rechargeable Li-O2 Battery*
10:10 – 10:40	Kyle Yakal-Kremski (Northwestern University) *Microstructural and Performance Evolution of LSM-YSZ Composite Electrodes with Thermal Treatments and under Switched Current Loadings*
10:40 – 11:00	Break
11:00 – 11:40	John Cumings (University of Maryland) In situ *Transmission Electron Microscopy of Lithium Storage in Nanomaterials*
11:40 – 12:10	Arnaud Demortiere (Argonne National Laboratory) In situ *Optical and Structural Studies of CdSe/CdS/Au Heterostructures*
12:10 – 1:45	Lunch
1:45 – 4:00	EMC Capabilities for the Future / Annual EMC Users Meeting

WK9

Exploring Electrochemistry in Li-ion Batteries through Single-Particle Measurements: A Platform for Multimodal and Operando Characterization

Jun Lu[1], Yan Qin[1], Peng Du[1], Zonghai Chen[1], Yang Ren[2], Tianpin Wu[1], Jeffery T. Miller[1], Jianguo Wen[3], Dean J. Miller[3], Zhengcheng Zhang[1], and Khalil Amine[1]

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[3] Electron Microscopy Center, Material Science Division, Argonne National Laboratory, Argonne, IL 60439

Energy dense and environmentally friendly, the lithium-air battery is one of the most attractive emerging energy storage systems. A fully developed and optimally packed Li-air battery could exceed specific energy of 2000 Wh/kg, which is more than twice as high as other battery types, either primary or secondary. One of the biggest hurdles for rechargeable lithium-O_2 battery is the large overpotential during charge and discharge, which depends on the nature of catalysts applied and their loading onto a high-surface-area cathode. Finding a catalyst that can facilitate the ORR/OER process, thereby improving the cycle efficiency of Li-air batteries, as reported in this paper based on systematic experimental results, is strongly required in the field. Herein, we applied a wet-chemistry approach to synthesize porous carbon supported α-MnO_2 nanorods at ambient temperature as an electrocatalyst for rechargeable Li-O_2 cells. By means of our unique synthetic approach, MnO_2 can be uniformly dispersed onto the surface of carbon support, while the porous structure and surface area of carbon are still well preserved. As a consequence, the as-prepared catalysts demonstrated good electrochemical behavior, with a capacity of ~1400 mAh/g (carbon + electrocatalyst) under a current density of 100 mA/g (carbon + electrocatalyst) during the initial discharge. The charge potential was significantly reduced, to 3.5-3.7 V, compared with most of the reported data, which are above 4.0 V. The mechanism of the capacity fade with cycling was also investigated by analyzing the cathode at different states of discharge/charge by using x-ray photoelectron spectroscopy.

WK9

Microstructural and Performance Evolution of LSM-YSZ Composite Electrodes with Thermal Treatments and under Switched Current Loadings

Kyle J. Yakal-Kremski

Northwestern University, Materials Science and Engineering, Evanston, IL 60208-3108

Solid oxide cells (SOCs) are versatile, fuel-flexible devices capable of both electricity generation and energy storage. To make SOCs viable for commercial applications, stable operation is desired over time spans of >40,000 hours at temperatures ~800-1000°C. $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$-$Zr_{0.84}Y_{0.16}O_2$ (LSM-YSZ) electrodes have been studied to determine the changes due to thermal treatment and a novel current-switching condition.

High-temperature anneals have been carried out on LSM-YSZ symmetrical cells to simulate thermal ageing after long times at operating temperatures in condensed times. Annealing of optimally fired cathodes led to polarization resistance increases of ~15% after 1000°C for 96 hours, and ~30% after 1100°C for 96 hours, as measured by electrochemical impedance spectroscopy. Additional cathodes fired at lower than optimal temperatures were also annealed. Although initial cell resistances are higher, annealing shows a regime of performance improvement. Focused ion beam scanning electron microscope (FIB-SEM) tomography was employed to gather three-dimensional microstructural data such as phase volume percent, specific surface area, and triple-phase boundary density. After 1000°C, 96 hours annealing of the optimal cathode, densification and an increase in average LSM particle size were observed, as quantified by both a pore phase volume percent decrease of 20% and a LSM specific surface area decrease of 26%.

LSM-YSZ symmetrical cells were also subjected to high current, up to 1.5 Acm^{-2}, over periods of ~1000 hours. The direction of polarization was switched periodically so that each electrode experienced the same time in both fuel cell and electrolysis mode. Initial tests using Ag current collectors showed Ag agglomeration near the electrode/electrolyte interface, as quantified by FIB-SEM. Further investigations have been carried out using porous LSM pellets as pressure contacts to eliminate Ag. Stable operation was observed for a current density of 0.5 Acm^{-2}, while after operation at 1.5 Acm^{-2}, resistances increased ~40%–140%, depending on the cycle period length. SEM investigations have shown extensive delamination of the electrode from the electrolyte for 1.5-Acm^{-2} operation, with cracks mostly propagating through the electrode side of the interface.

WK9

In Situ Transmission Electron Microscopy of Lithium Storage in Nanomaterials

John Cumings

University of Maryland, College Park, MD 20742

I will present an overview of the techniques available for imaging various nanomaterials by transmission electron microscopy (TEM) during their chemical reaction with lithium *in situ* during the imaging process. This overview will include work conducted as part of the Energy Frontier Research Center, Nanostructures for Electrical Energy Storage, supported by the Department of Energy. Following the overview, I will focus on recent results on lithium storage in silicon nanostructures and nano-heterostructures. Silicon has long been sought as a potential anode material for lithium ion batteries, due to its high capacity for lithium storage, about ten times higher than conventional graphite anodes. Nanostructured silicon stands poised to resolve the pulverization problems that have hindered the application of bulk silicon as battery anodes, and I will present new results on controlled silicon composite nanostructures that advance the science of lithium storage at the nanoscale and provide hope for future applications.

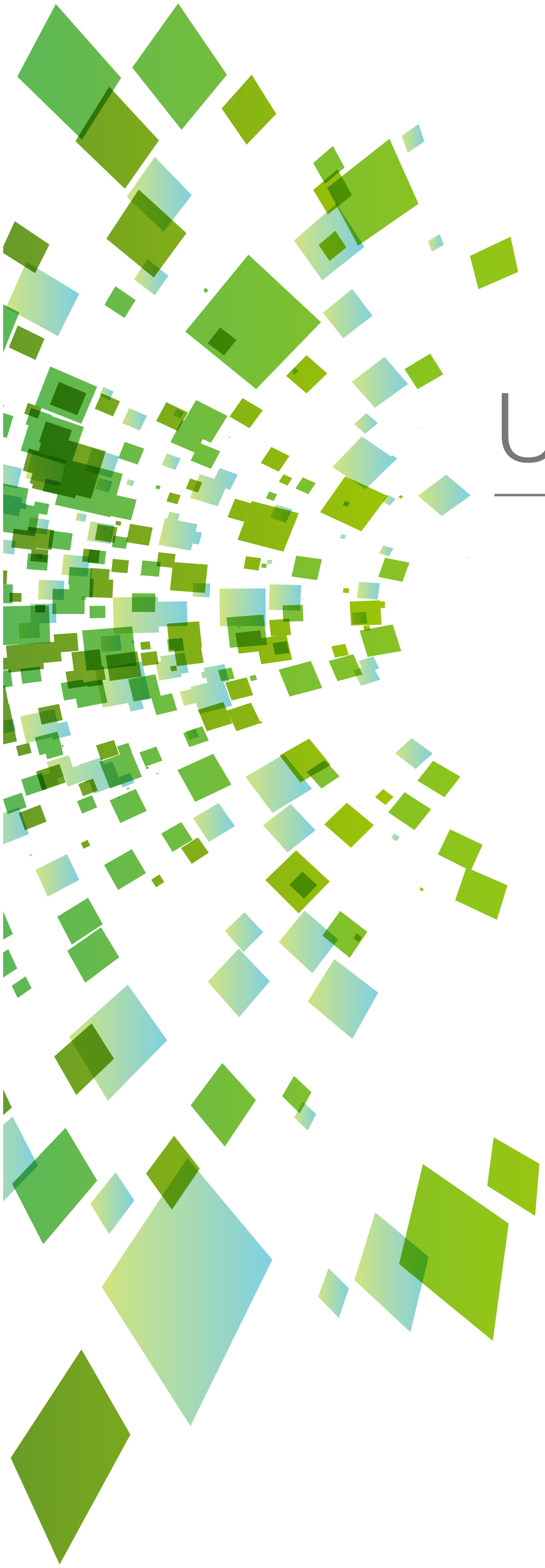
WK9

In Situ Optical and Structural Studies of CdSe/CdS/Au Heterostructures

Arnaud Demortiere

Argonne National Laboratory, Argonne, IL 60439

We report here detailed *in situ* studies of nucleation and growth of Au on CdSe/CdS nanorods using synchrotron small-angle x-ray scattering technique, time-resolved spectroscopy. We examine structural and optical properties of CdSe/CdS/Au heterostructures formed under ultraviolet (UV) illumination. We compare the results for CdSe/CdS/Au heterostructures with the results of control experiments on CdSe/CdS nanorods exposed to gold precursor under conditions when no such heterostructures are formed (no UV illumination). Our data indicate similar photoluminescence (PL) quenching and PL decay profiles in both types of samples. We show that the photoluminescence quenching in semiconductor/metal heterostructures is consistent with rapid hole trapping by gold-sulfur sites at the surface of semiconductor nanoparticles (NPs). This predominant quenching process takes place on fast (few picoseconds or less) timescales regardless of the presence or absence of the Au domains on CdSe/CdS semiconductor. This work suggests that exposure of semiconductor NPs to metal ions can play a significant role electronically and that structural characterization of hybrid semiconductor-metal materials does not convey the material behavior. We expect that the kinetic of PL quenching of semiconductor NPs exposed to different types of metal ions can be utilized in their detection. On the other hand, we study the structural and morphological evolution of CdSe/CdS/Au heterostructures under electron beam using transmission electron spectroscopy/scanning transmission electron spectroscopy characterizations.



2013
Users Meeting

SATELLITE WORKSHOPS

Thursday, May 9

Satellite Workshop 10
User Facilities for Industry 101

Location: Bldg. 401, Rm. A5000

Organizers: Andreas Roelofs (Center for Nanoscale Materials), Jyotsana Lal (Advanced Photon Source), Katie Carrado Gregar (Center for Nanoscale Materials), and Susan Strasser (Advanced Photon Source)

The Advanced Photon Source (APS), the Center for Nanoscale Materials (CNM) and the Electron Microscopy Center (EMC) at Argonne National Laboratory invite industrial scientists and engineers to attend a one-day workshop to learn more about Argonne National Laboratory and the capabilities/techniques available for use by industry. This workshop will showcase several successful industrial user experiments, as well as explain the different ways in which industrial scientists can work at Argonne or with Argonne scientists. Examples of how to write a successful user proposal and collaborate with user facility staff will be highlighted. Representatives from the participating user facilities as well as from Argonne's Technology Development and Commercialization (TDC) Department will be available to conduct one-on-one discussions with individuals regarding the feasibility of research ideas, proprietary research opportunities, etc.

The workshop will conclude with tours of the different user facilities and give participants the opportunity to interact directly with scientists at the different facilities.

9:00 – 9:30	Eric Isaacs (Argonne National Laboratory) *Introduction to Argonne*
9:30 – 9:45	Brian Stephenson (APS, Argonne National Laboratory) *Introduction to APS*
9:45 – 10:00	Andreas Roelofs (CNM, Argonne National Laboratory) *Introduction to CNM*
10:00 – 10:30	Olav Hellwig (HGST, a Western Digital Company) *Future Trends in Magnetic Recording Media*
10:30 – 10:45	Break
10:45 – 11:05	Gyorgy Snell (Takeda San Diego) *From High Throughput to High Difficulty: The Evolution of Protein Crystallography for Drug Discovery*
11:05 – 11:25	Brian Landes (Dow Chemical Company) *Sustainability? Not without New Capabilities in Measurement Science*
11:25 – 11:45	Adam Khan (AKHAN Technologies) *Towards the Diamond Age of Microelectronics*

11:45 – 12:00	Open Forum for Q&A
12:00 – 1:30	No-host Lunch
1:30 – 1:50	Deborah Clayton (Argonne National Laboratory) *Working with Argonne: Nuts & Bolts*
1:50 – 2:10	Susan Strasser (APS, Argonne National Laboratory) *Working with APS: Nuts & Bolts*
2:10 – 2:30	Katie Carrado Gregar (CNM, Argonne National Laboratory) *Working with CNM: Nuts & Bolts*
2:30 – 3:30	Facility Tours: APS or CNM (parallel tours)
3:30	One-on-One Discussions with Scientific Staff

WK10

Future Trends in Magnetic Recording Media

Olav Hellwig

HGST, a Western Digital Company, San Jose, CA 95135

In my talk, I will give an introduction to today's non-volatile re-writable data storage landscape consisting of flash memory, hard disk drives (HDD), and tape. I will highlight the importance that rotatable storage in the form of HDDs will also maintain in the future and introduce possible technologies, such as heat assisted magnetic recording (HAMR) and bit patterned recording (BPR) [1, 2] that will drive technology beyond the currently used perpendicular magnetic recording (PMR) regime [3, 4] and therefore allow reaching area densities in the range of 5-10 Tb/in^2.

In order to develop and control such new technologies, it is necessary to exploit advanced characterization techniques and tools that provide information about the nanoscale magnetic structure of new head devices and recording media. Covering a variety of studies related to advanced PMR and BPR technology [5–9], I will highlight as an example for newly developed advanced characterization techniques the use of resonant soft x-ray scattering and imaging techniques that allow probing element-specific magnetism on the nanoscale and thus gaining unique insight into the complex layered structures and their functionality in modern recording media.

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[2] Y. Shiroishi, K. Fukuda, I. Tagawa, H. Iwasaki, S. Takenoiri, H. Tanaka, H. Mutoh, and N. Yoshikawa, *IEEE Trans. Mag.*, **45**, 3816 (2009).

[3] I.R. McFadyen, E.E. Fullerton, and M.J. Carey, *MRS BULLETIN*, **31**, 379 (2006).

[4] S.N. Piramanayagam, *J. Appl. Phys.*, **102**, 011301 (2007).

[5] O. Hellwig, J.B. Kortright, D.T. Margulies, B. Lengsfield, and E.E. Fullerton, *Appl. Phys. Lett.*, **80**, 1234 (2002).

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[8] B. Pfau, C.M. Günther, E. Guehrs, T. Hauet, E. Dobisz, D. Kercher, H. Yang, L. Vinh, X. Xu, D. Yaney, R.L. Rick, S. Eisebitt, and O. Hellwig, *Appl. Phys. Lett.*, **99**, 062502 (2011).

[9] Tianhan Wang et al., *Phys. Rev. Lett.*, **108**, 267403 (2012).

WK10

From High Throughput to High Difficulty: The Evolution of Protein Crystallography for Drug Discovery

Gyorgy Snell

Takeda San Diego, San Diego, CA 92121

Structure-based drug design (SBDD) has been used with increasing success during the past decade for the discovery of potent and selective molecules to target various diseases. Protein crystallography carried out at synchrotron beamlines is the main SBDD tool used today. The various automation tools developed at the height of the structural genomics efforts helped also to establish high-throughput crystallography for drug discovery efforts, enabling the structure determination of large numbers of protein-ligand co-complex structures. During this talk some of the recent technical breakthroughs in x-ray and beamline technologies will be reviewed, such as microfocus beams and advanced software tools, which are benefitting the pharmaceutical industry to tackle drug targets with increasing difficulties. An SBDD case study will be also presented.

WK10

Sustainability? Not without New Capabilities in Measurement Science

Brian Landes

The Dow Chemical Company, Core R&D, Analytical Sciences, Midland, MI 48642

The concept of sustainability first emerged in the early 1970's but it exploded onto the global arena in 1987 with the Brundtland Report [1], in which sustainable development is defined as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs." The concept can be clearly described on the macro level using objects such as windmills or solar panels, and on the atomic level in describing specific reaction pathways to increase battery efficiencies, or developing model structures that remove impurities from water. The challenges—and thus, the opportunities—lie in the realm in between these two extremes. To design and implement truly sustainable technologies in the arenas of energy capture, energy storage, water filtration, and lightweighting demands the ability to measure the nature and dynamics of complex interactions between atoms, molecules, surfaces, and interfaces that occur in actual end-use environments. This requires the development of new methods to acquire data on "as-used" systems and devices. This talk will describe, by example, the use of these *in situ* experiments in both sustainable energy and materials research. We will also discuss challenges in measurement science that will be necessary to overcome to produce economically viable "sustainable" technologies.

[1] World Commission on Environment and Development (1987). Our Common Future. Oxford: Oxford University Press. ISBN 019282080X
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Satellite Workshop 11
Introduction to the GSAS-II Crystallographic Analysis System

Location: Bldg. 401, Rm. A1100

Organizers: Robert B. Von Dreele and Brian H. Toby (APS)

The workshop will introduce the attendees to the use of the new GSAS-II software package for the reduction, solution and refinement of crystallographic data, with particular emphasis on powder diffraction data. All software needed to install and run the software is freely available. Attendees will be required to bring their own laptops with the software already downloaded. The workshop will be targeted toward individuals with some experience with Rietveld analysis and to experienced single-crystal crystallographers with some knowledge of powder diffraction.

Background

The GSAS-II software suite will be the eventual replacement for GSAS and its associated graphical user interface (GUI) package, EXPGUI, which are likely the most widely used crystallography software package for materials crystallography, particularly for neutron and synchrotron powder diffraction (Rietveld) fitting, but GSAS also see use for neutron single-crystal analysis and combined x-ray single crystal/neutron powder diffraction analysis. As one measure of their importance, GSAS and EXPGUI together have received >7,000 citations and continue to be cited many hundreds of times annually.

The GSAS-II package has much wider goals than GSAS. Although over time its capabilities will continue to advance, the GSAS-II package already has capabilities needed for all aspects of powder diffraction crystallographic analysis, including area detector data reduction, indexing, and structure solution by charge flipping, in addition to the refinement and Fourier map analysis capabilities that duplicate GSAS features. GSAS-II can be used for analysis of constant-wavelength x-ray and neutron powder data, as well as x-ray and neutron single-crystal data. Oak Ridge National Laboratory has indicated an interest in driving the adaptation for time-of-flight neutrons. GSAS-II is a completely modern code, written almost completely in Python and designed with a sophisticated GUI and with advanced visualization features integrated. GSAS-II is open source and is freely distributed. GSAS-II has recently been made available to the public, with the understanding that new capabilities are being added and bugs addressed on a continuing basis.

Because GSAS-II includes an area detector calibration and integration module, the software may be of interest within the APS where powder diffraction is used for calibration of area detector placement, or where radial integration is used.

Program

The target audience for this workshop will be individuals who have at least some experience with Rietveld analysis and experienced single-crystal crystallographers who have not performed powder diffraction experiments, but have at least some familiarity with the technique. However, attendees wishing to use GSAS-II only for beam line data processing will have no difficultly following the first section of the course. Attendees should bring their own laptops (Windows, Mac and Linux are all supported) and should install GSAS-II prior to the workshop. Help will be provided at the workshop to help install the software for anyone who has had trouble.

The format of the course will be to alternate between short overview lectures, demonstrations of the program and hands-on exercises. Examples of some of the exercises can be seen from the tutorial present on the GSAS-II web site, https://subversion.xor.aps.anl.gov/trac/pyGSAS.

8:00 – 9:00	Coffee, tea and software installation support
9:00 – 9:45	An overview of GSAS-II capabilities
9:45 – 10:00	Area detector data reduction demo
10:00 – 10:20	Break
10:20 – 11:00	Self-paced exercise 1: Area detector data calibration and reduction
11:00 – 11:20	Autoindexing, charge-flipping and Fourier demo
11:20 – 12:00	Self-paced exercise 2: Autoindexing, structure solution & completion
12:00 – 1:30	Lunch
1:30 – 2:15	Self-paced exercise 2: Continued
2:15 – 2:45	Introduction to GSAS-II refinement capabilities and Rietveld demo
2:45 – 3:30	Self-paced exercise 3: Rietveld refinement exercise
3:30 – 3:50	Break
3:50 – 4:10	Overview of restraints and constraints
4:10 – 4:30	Planned future developments for GSAS-II
4:30 – 4:50	Participant feedback on potential improvements, development priorities and other perceived needs

Satellite Workshop 12
Workshop on Next-Generation Fast Orbit Feedback Systems for Storage Rings

Location:	Argonne Guest House, Conf. Rm. A
Organizers:	Glenn Decker (Advanced Photon Source) and Om Singh (NSLS-II)

With the advent of modern field-programmable gate arrays (FPGAs), orbit control system capabilities at synchrotron light sources can be pushed beyond their present performance limits to provide a level of enhanced beam stability never before achieved with such systems. In addition to increasing system update rates to the range of 10 to 20 kHz, fast data networking protocols allow interfaces to diverse sets of diagnostics and actuators. This includes not only standard rf beam position monitor (BPM) inputs, but in addition x-ray BPMs, beam size and tilt monitors. Outputs to fast steering correctors, low-level rf phase and amplitude controls, and fast focusing magnets are similarly possible. Implementation of feed forward systems for conventional hybrid insertion devices, electromagnetic devices with switchable polarity, APPLE-II devices and others have become critical to modern light source performance and could be significantly enhanced by modern FPGA components.

The objectives of the workshop are two-fold, including feedback system theory and simulation on the one hand, and modern fpga capability and implementation on the other. Bringing together the accelerator physicists with experts in FPGA technology is expected to benefit both fields significantly. The two conspicuous new initiatives on the horizon are NSLS-II at Brookhaven and the APS upgrade at Argonne. The collective wisdom of those responsible for presently operating light sources is sought to guide the design of new systems and upgrades and to identify potential pitfalls.

8:30 – 8:45	Glenn Decker (APS, Argonne National Laboratory) *Welcome*
8:45 – 9:45	Till Straumann (SSRL) *Design, Commissioning, and Operational Experience with the SPEAR-3 Orbit Feedback Systems*
9:45 – 10:15	Open Forum
10:15 – 10:30	Break
10:30 – 11:30	Yuke Tian (Brookhaven National Laboratory) *NSLS-II Feedback System Design, Implementation, and Algorithms*
11:30 – 12:00	Richard Farnsworth *Overview of Operational Fast Orbit Feedback Systems around the World*
12:00 – 1:00	Lunch
1:00 – 2:00	Glenn Decker (APS, Argonne National Laboratory) *Design Process for the Advanced Photon Source Fast Orbit Feedback System Upgrade*
2:00 – 2:30	Guided Discussion *Enumeration of questions to be addressed by a feedback simulator to inform feedback system design*

2:30 – 3:30	Open Discussion
3:30 – 4:30	John Carwardine (APS, Argonne National Laboratory) *Global Orbit Feedback Using Correctors of Different Bandwidths*
4:30 – 5:00	Open Discussion

Satellite Workshop 13
Time-resolved X-ray Science at BioCARS: Past, Present, and Future

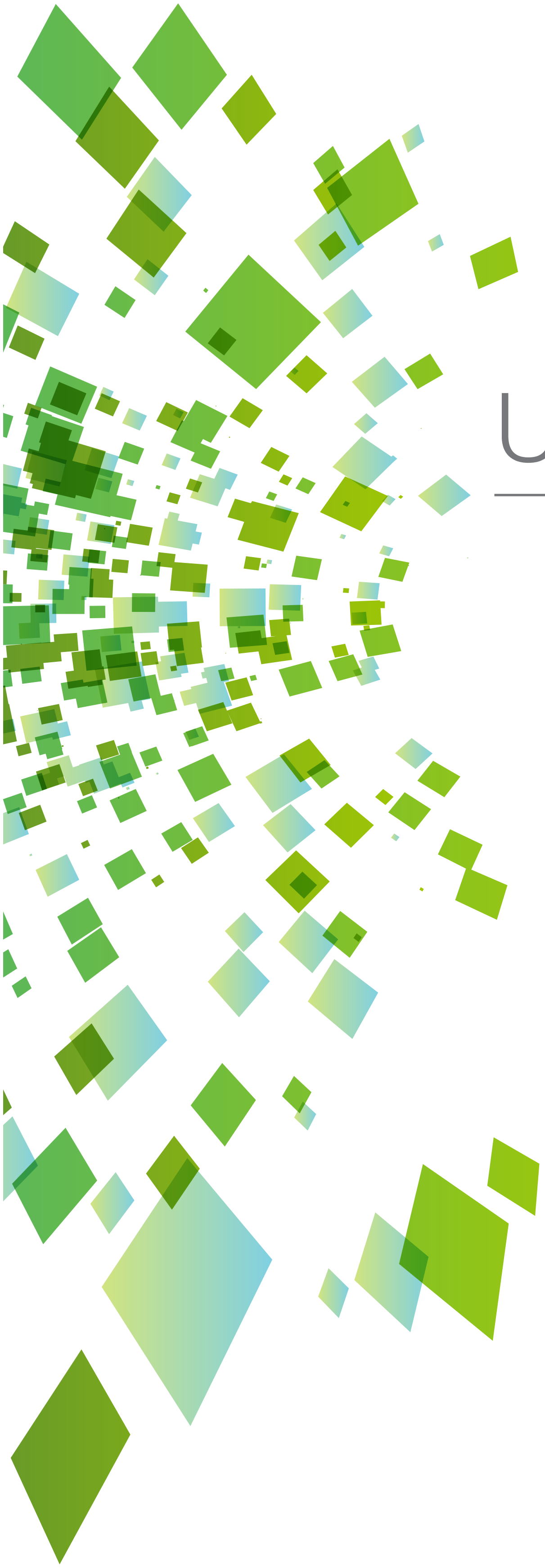
Location: Bldg. 402, Auditorium

Organizers: Robert Henning (CARS, University of Chicago), Eric Dufresne (Advanced Photon Source), Vukica Srajer (CARS, University of Chicago), and Philip Anfinrud (NIH)

The last major upgrade to the BioCARS 14ID beamline, completed in 2008, produced unprecedented time-resolved capabilities that have been exploited in many areas of X-ray science spanning biology, chemistry and physics. An APS-funded upgrade aims to further expand the capabilities of the 14ID beamline for the Physical Sciences. This workshop will bring together practitioners of time-resolved X-ray science to (1) discuss current capabilities and use of 14ID, and (2) discuss future challenges, needs and opportunities provided by the APS Upgrade to this diverse scientific community.

8:45 – 8:50	Keith Moffat (The University of Chicago/BioCARS) *Introduction*
8:50 – 9:15	Robert Henning (The University of Chicago/BioCARS) *BioCARS Time-resolved X-ray Science: Infrastructure*
9:15 – 9:40	Philip Anfinrud (NIH) *Time-resolved Laue Crystallography and Solution Scattering of Proteins*
9:40 – 10:05	Philip Coppens (University of Buffalo) *Time-Resolved Studies of Phosphorescence and Electron-Transfer in Chemical Complexes*
10:05 – 10:25	Break
10:25 – 10:50	Bertold Kraessig (APS, Argonne National Laboratory) *Diffractive Imaging of Laser-aligned Molecules*
10:50 – 11:15	Yulia Pushkar (Purdue University) *Time-resolved XES for Analysis of Fast Electron Transfer Processes*
11:15 – 11:40	Steve Durbin (Purdue University) *Induced Optical Transparency and X-ray/Optical Interactions in GaAs*
11:40 – 1:15	Lunch
1:15 – 1:40	Marius Schmidt (University of Wisconsin–Milwaukee) *5-Dimensional Macromolecular Crystallography*
1:40 – 2:05	Xiaojing Yang (The University of Chicago *Bacteriophytochromes: A Challenging Case for Time-resolved Crystallographic Investigation*
2:05 – 2:30	Eric Dufresne (APS, Argonne National Laboratory) *Current APS-U/BioCARS Upgrade Plans*
2:30 – 2:55	Break

2:55 – 3:20	Louis Emery (APS, Argonne National Laboratory)--invited *Fill Patterns for Time-resolved X-ray Science at APS*
3:20 – 3:45	Peter Eng (The University of Chicago/GSECARS) *K-B Focusing Optics*
3:45 – 4:15	Panel discussion with speakers: *Improving BioCARS Time-resolved Capabilities*



2013
Users Meeting

POSTER INDEX

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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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.

S-1		Time-resolved X-ray Absorption Studies of a Chromium-titanium-oxide-based Cathode Material for Lithium Ion Batteries
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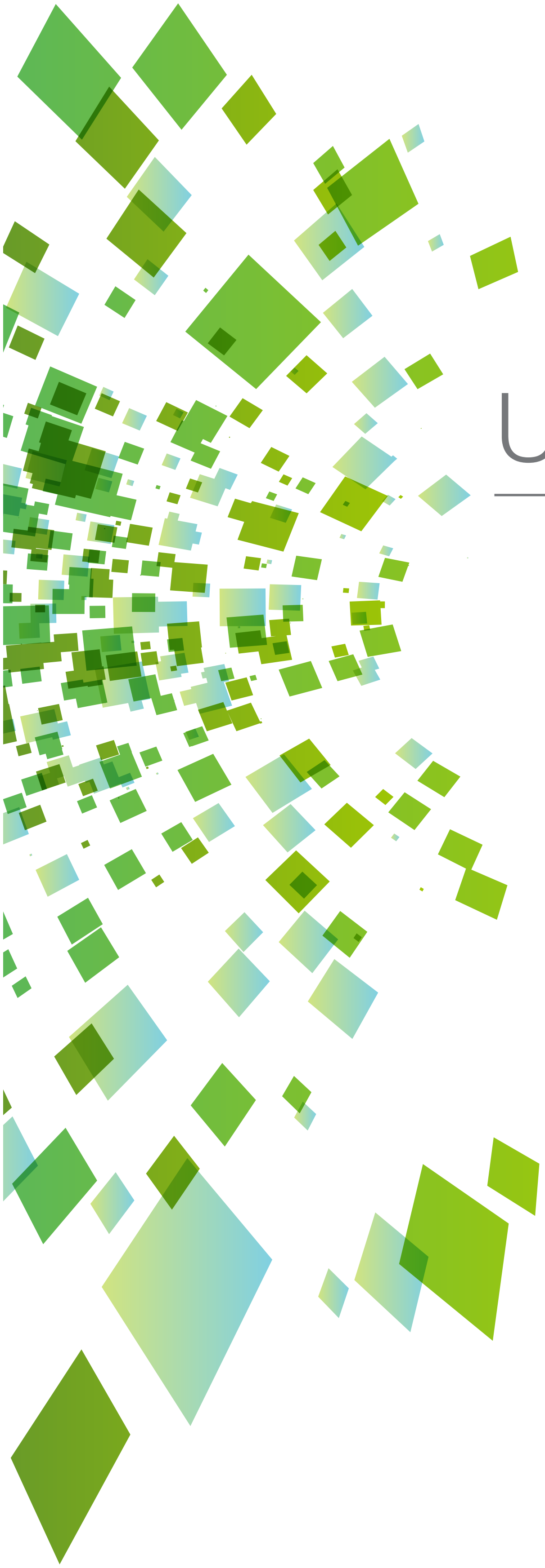
S-6		Identifying Protein Crystals Using Known Structures



2013
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POSTER ABSTRACTS

Biology

A-1

X-ray Diffraction and Microscopy Study of Non-enzymatic Decomposition of Collagen Fibers by a Biglycan Antibody and a Plausible Mechanism for Rheumatoid Arthritis

Olga Antipova, Raul Barrea, Thomas C. Irving, and Joseph P.R.O. Orgel

Biophysics Collaborative Access Team (BioCAT) and Pritzker Institute of Biomedical Science and Engineering, Illinois Institute of Technology, Chicago, IL 60616

Rheumatoid arthritis (RA) is a systemic autoimmune inflammatory and destructive joint disorder that affects tens of millions of people worldwide. Normal healthy joints maintain a balance between the synthesis of extracellular matrix molecules and the proteolytic degradation of damaged ones. In the case of RA, this balance is shifted towards matrix destruction due to increased production of cleavage enzymes and the presence of (autoimmune) immunoglobulins resulting from an inflammation induced immune response. Herein we demonstrate that a polyclonal antibody against the proteoglycan biglycan causes tissue destruction that may be analogous to that of RA affected tissues. The effect of the antibody is more potent than harsh chemical and/or enzymatic treatments designed to mimic arthritis-like fibril depolymerization. In RA cases, the immune response to inflammation processes causes synovial fibroblasts, monocytes and macrophages to produce cytokines and secrete matrix remodeling enzymes, whereas B cells are stimulated to produce immunoglobulins. The specific antigen that causes the RA immune response has not yet been identified, although possible candidates have been proposed, including collagen types I and II, and proteoglycans such as biglycan. We speculate that the initiation of RA associated tissue destruction in vivo may involve a similar non-enzymatic decomposition of collagen fibrils via the immunoglobulins themselves that we observe here *ex vivo*.

A-2

Update on SONICC Implementation at GM/CA at APS

Michael Becker[1], Christopher M. Dettmar[2], Jeremy T. Madden[2], Scott J. Toth[2], Justin A. Newman[2], Sergey Stepanov[1], Robert A. Oglesbee[2], Hartmut Hedderich[2], R. Michael Everly[2], Oleg Makarov[1], Shenglan Xu[1], Dale Ferguson[1], Vadim Cherezov[3], Susan Buchanan[4], Robert Fischetti[1], Garth J. Simpson[2]

[1] GM/CA at Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439
[2] Department of Chemistry, Purdue University, West Lafayette, IN 47907
[3] Department of Molecular Biology, The Scripps Research Institute, La Jolla, CA 92037
[4] Laboratory of Molecular Biology, NIDDK, National Institutes of Health, Bethesda, MD 20914

Second-order nonlinear optical imaging of chiral crystals (SONICC) based on femtosecond laser scanning microscopy has been implemented at the GM/CA undulator beamline 23ID-B at APS for rapid localization and centering of protein crystals. The technique is based on infrared laser light impinging on non-centrosymmetric crystals of proteins, which selectively may yield a frequency-doubled, visible signal generated by the anharmonic response of the electron cloud of the protein to the laser field. One aim of this method is to locate small crystals grown in opaque crystallization media for centering in x-ray beams of only a few microns or less in cross-section. The optical system implemented at the beamline includes "trans" and "epi" detection of second harmonic generation (SHG) signals. In addition, scanning visible laser light across the sample and detecting two-photon excited ultraviolet fluorescence (TPE-UVF) provides complementary contrast based on the native fluorescence of proteins. Experiments with membrane-protein crystals grown in mesophase indicate good agreement between SHG and x-ray diffraction raster in identifying locations of small crystals, exhibiting substantial time savings with SONICC. Different factors that influence imaging signals and the likelihood of successfully locating and accurately positioning a crystal via SONICC will be discussed. An update on progress towards offering a user-friendly system to general users will also be provided.

A-3

Protein Structural Dynamics in Solution Unveiled Via 100-ps Time-resolved X-ray Scattering

Hyun Sun Cho[1], Naranbaatar Dashdorj[1], Friedrich Schotte[1], Timothy Graber[2], Robert Henning[2], and Philip Anfinrud[1]

[1] Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, MD 20892-0520
[2] Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637

We have developed a time-resolved x-ray scattering diffractometer capable of probing structural dynamics of proteins in solution with 100-ps time resolution. This diffractometer, developed on the 14-ID-B BioCARS (Consortium for Advanced Radiation Sources) beamline at the Advanced

Photon Source, records x-ray scattering snapshots over a broad range of q spanning 0.02–2.5 Å^{-1}, thereby providing simultaneous coverage of the small-angle x-ray scattering (SAXS) and wide-angle x-ray scattering (WAXS) regions. To demonstrate its capabilities, we have tracked structural changes in myoglobin as it undergoes a photolysis-induced transition from its carbon monoxy form (MbCO) to its deoxy form (Mb). Though the differences between the MbCO and Mb crystal structures are small (rmsd <0.2 Å), time-resolved x-ray scattering differences recorded over eight decades of time from 100 ps to 10 ms are rich in structure, illustrating the sensitivity of this technique. A strong, negative-going feature in the SAXS region appears promptly and corresponds to a sudden >22 Å^3 volume expansion of the protein. The ensuing conformational relaxation causes the protein to contract to a volume that is only ~2 Å^3 larger than MbCO within ~10 ns. On the timescale for CO escape from the primary docking site, another change in the SAXS/WAXS fingerprint appears, demonstrating sensitivity to the location of the dissociated CO. Global analysis of the SAXS/WAXS patterns recovered time-independent scattering fingerprints for four intermediate states of Mb. These SAXS/WAXS fingerprints provide stringent constraints for putative models of conformational states and structural transitions between them.

A-4

X-ray Fluorescence Imaging and Metalloproteomics: Tying Images of Metals in Cells to the Proteins that Bind Them

Lydia Finney

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

Metals like copper, zinc and iron are important nutrients to all life. Their special properties that make them so useful to us in things like batteries and catalysts also make them useful to living organisms. Using hard x-ray fluorescence microprobes at the Advanced Photon Source, we have been able to see, often for the first time, where the metals themselves are inside cells and tissues. Yet, many of the images we acquire lead us to new questions. Are these metals required for the activity of proteins? Which proteins are binding which metals inside the cell? With over a third of all proteins thought to bind metals, knowing which metals are bound and how that binding changes in response to the environment could have big implications. For instance, the mismanagement of metals is involved in many diseases, including Lou Gehrig's disease, Wilson and Menkes disease, and possibly even Alzheimer's disease. Metals are also an environmental toxin, such as hexavalent chromium, and they are used in drugs, like the platinum in cisplatin that treats prostate cancer. In another vein, hexavalent uranium is an environmental contaminant of concern at several U.S. Department of Energy sites. The metal-binding proteins in microbes, such as those in the genus *Shewanella*, which can reduce uranium mobility in groundwater, play a major role in the beneficial activity of these organisms—and knowing which metal is in which protein at a given point in time could lead to new insights into how they do their work. We have developed a new tool to investigate this, combining native two-dimensional (2D) gel electrophoresis and x-ray fluorescence imaging, to quantitatively measure the amount of sulfur, iron, zinc, and other metals at every point of the 2D separation of proteins. By coupling this with mass-spectrometry, we have identified a novel protein (PA5217) as a zinc-binding protein in P. aeruginosa. Our finding highlights how this method not only determines changes in metal occupancy, but also identifies the associated protein.

A-5

Distribution of MIBG and MIBG-Fe@Ti Nanoconjugates in Neuroblastoma

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Neuroblastoma is a pediatric cancer accounting for 15% of all cancer related deaths in children. Metaiodobenzylguanidine (MIBG), a compound labeled with a radioisotope of iodine (I-121 or I-123), localizes specifically to neural crest tumors and is used in the treatment and diagnosis of neuroblastoma. While the use of MIBG as both a treatment and diagnostic tool have been demonstrated, questions surrounding its distribution in neuroblastoma cells and issues of off-target radiotoxicity remain. This study examines the issue of intracellular MIBG distribution in neuroblastoma and methods of reducing the amount of MIBG necessary to induce a therapeutic response through the conjugation of MIBG to iron oxide core-titanium dioxide shell nanocomposites (Fe@Ti). These nanocomposites (2–6 nm diameter) consist of a paramagnetic iron oxide core, lending itself as a contrast agent for magnetic resonance imaging, and a TiO_2 shell which acts as both a semiconductor, which generates reactive oxygen species (ROS) in response to ionizing radiation, as well as an anchor for the binding of potential targeting and therapeutic moieties. MIBG conjugation can serve as a method of targeting Fe@Ti nanocomposites to neuroblastomas and act as a radiosensitizer activated by MIBG. A second conjugation of a uniquely developed nuclear targeting peptide can be used for subcellular targeting of entire nanocomplexes to the nucleus.

Neuroblastoma cells SK-N-AS and SK-N-DZ were treated with MIBG, Fe@Ti nanocomposites, or MIBG-Fe@Ti nanoconjugates. Cellular distribution was then characterized through x-ray fluorescence microscopy performed at Argonne National Lab. In cells treated only with MIBG, iodine (as a marker for MIBG) localized exclusively in the cytoplasm of both cell lines and was excluded from the nucleus. In cells treated with MIBG-Fe@Ti nanoconjugates, Ti, Fe, and I signals (indicative for MIBG-nanoconjugates) were found to localize in the cytoplasm but their distribution was punctuate, suggesting endosomal localization. These results confirm that while MIBG is taken up by neuroblastomas, their cytoplasmic localization and their exclusion from the nucleus limits their effectiveness as a radiotherapeutic. Thus, the conjugation of a nuclear targeting peptide to these nanoconjugates holds promise in enhancing the tumor killing effects of MIBG, which may help minimize off-target radiation exposure to pediatric patients.

A-6

Investigating Biofilm Structure Using X-ray Microtomography and Gratings-based Phase Contrast

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Direct examination of natural and engineered environments has revealed that the majority of microorganisms in these systems live in structured communities termed biofilms. Understanding how biofilms function and interact with inorganic substrates such as metal ions and mineral surfaces connects the molecular-scale biogeochemical processes to those at the microorganism-level and provides insight to how microorganisms influence larger, pore-scale biogeochemical processes. To gain this understanding, fundamental capabilities for enhanced visualization, compositional analysis, and functional characterization of biofilms are needed. For pore-scale and community-scale analysis (100's of nm to 10's of microns), a variety of surface tools are available. However, understanding biofilm structure in complex three-dimensional environments is considerably more difficult. X-ray microtomography can reveal a biofilm's internal structure, but obtaining sufficient contrast to image low-Z biological material against a higher-Z substrate makes detecting biofilms difficult. Here we present results imaging *Shewanella oneidensis* biofilms on multiple substrates, using the x-ray microtomography system at sector 2-BM of the Advanced Photon Source, at energies ranging from 13–18 keV and spatial scales of 0.7 and 1.4 µm/pixel. We examine the use of contrast agents, such as Os, to enhance biofilm internal structure and allow for the segmentation of reconstructed datasets. We also present results using a Talbot interferometer to provide phase and scatter contrast information in addition to absorption, and discuss practical considerations surrounding the design and use of such a system for this application. Finally, we will compare and evaluate the relative utility of these different approaches for revealing biofilm structure. We anticipate that these measurements would serve both as a test of high resolution grating interferometry, and to form the basis for a new technique for understanding the function of microbial communities.

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A-7

Data Collection Strategy and Data Processing in JBluIce-EPICS

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GM/CA@APS beamline control software JBluIce-EPICS has been equipped with data collection strategy based on the Web-Ice scripts and with data reduction based on XDS. The Web-Ice C-shell scripts that run LABELIT, MOSFLM, and BEST were ported into JBluIce-EPICS. The results are displayed on the Strategy sub tab of the JBluIce Collect tab and can be conveniently exported to a data collection run. Selection of a lower symmetry space group triggers a strategy recalculation and automatic update of the results on the tab.

In JBluIce-EPICS data is processed “in parallel” to data collection using either fast_dp, a data reduction software developed at Diamond Light Source or an in-house developed pipeline of software packages XDS, POINTLESS, AIMLESS, or SCALA and TRUNCATE. The data quality parameters are displayed in the Analysis tab. Inside of JBluIce-EPICS, a variety of data analysis approaches are necessary to accommodate a wide range of experimental designs in data acquisition (e.g., inverse beam, vector/raster mode data collection etc.). Both strategy and data processing scripts are directly executed by JBluIce-EPICS through distributed resource management software, Grid Engine. Details of the above software pipelines, different approaches to data analysis, and integration into JBluIce-EPICS will be discussed.

A-8

The MDS (Multiple-Data Set) Data Collection Strategy: Implications to Dose Reduction

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The Multiple-DataSet (MDS) [1] data collection strategy was examined to determine if the method could be used to produce SAD data sets capable of phasing the structure with a lower x-ray dose. The tests were carried out using data collected on zinc-free Insulin crystals on beamline 22-ID (SER-CAT). In each experiment, a standard data set (e.g., 1° images exposed for 3 sec) was collected followed by the collection of N low-exposure data sets collected using 1/Nth exposures (e.g., three data sets, 1° images exposed for 1 sec) to keep the total radiation dose the same in all cases.

The anomalous signal was analyzed and a comparison was made between the standard data set and the merged low-exposure data set by MDS. The study, as expected, showed that the anomalous signal (as defined by the R_{as} index [2] and peak heights of sulfurs from Bijvoet difference Fourier maps) for the merged low-exposure (MDS) data set was significantly higher compared to the signal observed for the standard data set. The analysis was then repeated merging fewer low-exposure data sets (e.g., N-1, N-2) and the anomalous signal in these cases was found to be comparable or higher than that observed for the standard set. This implies that, by using the MDS strategy, a crystal can be exposed to a lower radiation dose and still provide sufficient anomalous signal for phasing. Thus, the MDS strategy may offer a better data collection option for radiation sensitive crystals and crystals with a lower symmetry, since it may provide enough data to solve the structure before significant radiation decay occurs.

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A-9

Watching a Signaling Protein Function in Real Time Via 100 ps Time-resolved Laue Crystallography

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To understand how signaling proteins function, it is crucial to know the time-ordered sequence of events that lead to the signaling state. We recently developed on the BioCARS 14-ID-B beamline at the Advanced Photon Source the infrastructure required to characterize structural changes in protein crystals with near-atomic spatial resolution and 150 ps time resolution, and we have used this capability to track the reversible photocycle of photoactive yellow protein (PYP) following trans-to-cis photoisomerization of its p-coumaric acid (pCA) chromophore over ten decades of time. The first of four major intermediates characterized in this study is highly contorted, with the pCA carbonyl rotated nearly 90° out of the plane of the phenolate. A hydrogen bond between the pCA carbonyl and the Cys69 backbone constrains the chromophore in this unusual twisted conformation. Density functional theory calculations confirm that this structure is chemically plausible and corresponds to a strained cis intermediate. This novel structure is short lived (~600 ps), has not been observed in prior cryo-crystallography experiments, and is the progenitor of intermediates characterized in previous nanosecond time-resolved Laue crystallography studies. The structural transitions unveiled during the PYP photocycle include trans/cis isomerization, the breaking and making of hydrogen bonds, formation/relaxation of strain, and gated water penetration into the interior of the protein. This mechanistically detailed, near-atomic resolution description of the complete PYP photocycle provides a framework for understanding signal transduction in proteins, and for assessing and validating theoretical/computational approaches in protein biophysics.

A-10

Aging Results in Copper Accumulations in GFAP-positive Cells in the Subventricular Zone

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Despite their increasing prevalence in society, diseases of aging occur by poorly understood mechanisms. To study one possible source of age-related neurodegeneration, we employ x-ray fluorescence (XRF) microscopy on thin (10-30 micron) samples of brain tissue, allowing *in situ* histological analysis. Previous lower resolution techniques have reported an increase in mean Cu concentrations in rodent brains. Our work with XRF microscopy, combined with immunohistochemistry, demonstrates for the first time that a major source of this increase is highly localized, dense Cu accumulations in astrocytes in the subventricular zone. It is shown that while the mean Cu concentration in the cortex remains essentially constant, concentrations in the subventricular zone grow consistently from ages 3 to

36 weeks, increasing by nearly a factor of four. The growth is well described as monomolecular growth, suggesting a single dominant accumulation mechanism. Analysis of Cu accumulations shows that the mean concentration above baseline levels grows linearly through the ages studied, implicating an unyielding mechanism that correlates strongly with diminishing neurogenic activity along the ventricle (by the Ki67 proliferation marker). We speculate that while Cu sequestration may be necessary for neural development at early ages, the mechanism by which Cu accumulates in the astrocytes is never "turned off," leading to extreme concentrations with old age that give rise to oxidative stress and play a key role in aging disorders. The bound form of Cu is still under investigation. However, preliminary studies using micro-XANES suggest that Cu is bound in the form of a Cu(I) multimetallic Cu-S cluster. A consistently observed [S]/[Cu] = 1.14 ± 0.16 is consistent with the assignment of Cu metallothionein (I,II), though more work is needed to confirm the bound form of the Cu in accumulations.

A-11

Development of *In Situ* Time-resolved XES for Studying Co Catalysis

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Our long-term goal is to develop a robust, easy to set up and sensitive detection system for time-resolved studies of changes in Co oxidation states and electronic structure. Co atoms are essential components of many catalytic systems including hydrogen producing and water oxidizing catalysts employed in sunlight-to-fuel conversion schemes. In these catalysts reactive intermediates are short lived (ns to ms time window) and must be produced and studied *in situ* by techniques with adequate time resolution. While time-resolved x-ray absorption spectroscopy is currently well established time-resolved x-ray emission spectroscopy (XES) (including time-resolved resonant inelastic x-ray scattering) can provide complementary and often more detailed information on the changes in electronic structure of the Co ion.

A dispersive mini-XES spectrometer designed for high energy-resolution study of Co catalysts is under development. The design of the spectrometer along with select Co-involved catalysts for initial testing and characterization will be presented. The catalysts include synthesized Co(II)-O-Ti(IV) light-absorbing units that exhibit long-lived (microseconds) metal-to-metal charge-transfer states, as well as a cobaloxime catalyst. Future plans using fast time-resolved XES with laser pump/x-ray probe to study short-lived intermediate states will also be presented.

Chemistry

A-12

Disentangling Simultaneous Photoreaction Channels with Combined Time-resolved X-ray Absorption and Emission Spectroscopies

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Time-resolved x-ray absorption spectroscopy (XAS) is a mature technique, which allows to follow structural dynamics of molecules [1]. Its element specificity, sensitivity to both local bonding, and the oxidation state of an absorbing atom are powerful when studying liquid phase chemical reactions. We studied a photoinduced complex reaction in Fe-based transition metal compound, which branches in to simultaneous ligand photodetachment and the photoionization of the central Fe atom up on laser excitation. We investigated aqueous $Fe^{II}(CN)_6$ solution following flash photolysis with UV laser light, which forms two photoproducts: $Fe^{II}(CN)_5$ and $Fe^{III}(CN)_6$ [2]. Picosecond-resolved XAS measurements after 266 nm excitation show both products with 3.5% and 15% for $Fe^{II}(CN)_5$ and $Fe^{III}(CN)_6$, respectively. Furthermore, the transient extended x-ray absorption fine structure measurements at 355 nm should clarify the existence of a hypothetical photoaquated $Fe(CN)_5$ complex. Time-resolved x-ray emission spectroscopy was used as an additional x-ray tool to look selectively at the valance-to-core and K_β emission lines of the central Fe atom. The status of these recent results will be presented and the current interpretation discussed.

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A-13

Intermediate X-ray Catalysis Research at Advanced Photon Source Beamline 9-BM

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It is well known that XAFS (x-ray absorption fine structure) is a useful "workhorse" technique for characterizing supported 3d, 4d, and 5d transition metal catalysts. *In situ* characterization of many catalytic materials involving carefully controlled gas treatment and elevated temperatures is necessary but often not trivial, especially in the intermediate-energy x-ray regime (~2.1–4 keV), where such measurements can be complicated due to absorption by cell components, the reaction gases themselves, air surrounding the reaction cell, and a host of other reasons. The intermediate-energy x-ray regime is where the L-edges of 4d metals, such as palladium, lie.

A specially designed catalysis reaction cell was used at the Advanced Photon Source beamline 9-BM for acquiring the intermediate-energy x-ray absorption near-edge structure (XANES) of bimetallic palladium catalysts while heating and with gas treatment from the Pd LIII and LII edges, at approximately 3.2 keV. The XANES edge position, the height of the "white line" peak, and the shape of the peak display significant changes with alloy formation and CO adsorption. This in turn shows that the Pd L-edge XANES are very sensitive to changes in the d-band density-of-states and can be used to derive rich information about how a supported Pd, or other 4d transition metal catalyst, behaves when under reaction conditions or upon alloy formation.

A14

Structural and Functional Characterization of Amorphous Metal-oxide Water-splitting Catalysts Using High-energy X-ray Scattering Combined with Pair Distribution Function Analysis

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We are investigating opportunities to use high-energy x-ray scattering (HEXS) and pair distribution function (PDF) analysis, and to combine these approaches with atomic-structure-based modeling as a means to achieve structure and function resolution at the atomic scale for electrolytically deposited, thin-film, amorphous metal-oxides. Amorphous thin-film metal-oxide water-splitting catalysts are of growing, wide-spread interest for development as catalysts for photochemical device applications. Our prior work has demonstrated the use of the HEXS-PDF approach to resolve the structure of "molecularly dimensioned" metal-oxide domains in amorphous cobalt-oxide and iridium-oxide water-splitting catalyst *ex situ* powders. In this presentation, we report on two new developments: first, the demonstration of the structure resolution of amorphous metal-oxide structure for thin films (≤0.5 μm), *in situ*, on electrode supports, and second, the on-going development of structure refinement techniques using Markov-chain Monte Carlo model-selection algorithms.

A-15

In Situ Extraction of Oil from Green River Oil Shale

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Green River oil shale represents a large resource of hydrocarbons. The United States Geological Service estimated the total in-place resource potential at 1.44 trillion barrels (2011). Oil shale is a nanocomposite material in which layers of organic material (kerogen) are interdispersed and chemically bonded to natural occurring mineral layers. These layers were formed as sediment from blue-green algae deposited during the Eocene (56–34 million years ago) when large lakes existed in five basins within what is now Utah, Wyoming, and Colorado. A key challenge in oil shale development lies in the size and complexity of the organic kerogen substituent. Oil shale cannot be extracted from the ground because kerogen is not soluble in any organic solvent. Furthermore, the lack of solubility has hampered detailed structural characterization. Past attempts for utilizing this resource envisioned mining followed by retorting at temperatures high enough to rupture C-C bonds. The environmental and energy requirements of such an approach are prohibitive. Accordingly, one goal of this project is to develop catalytic methods to convert kerogen into oil and high-value products under conditions that are sufficiently mild that they can be conducted *in situ* underground. The lack of a clear understanding of the functional groups and chemical linkages with the kerogen macromolecular structure slows the catalysis development. Therefore, a second concurrent goal is the structural characterization of kerogen. X-ray scattering provides powerfully approaches for characterizing these complex nanocomposites and guides the development of chemical degradation techniques. The products from the chemical degradation studies are analyzed by convention GC-MS and spectroscopic methods. The third goal is to develop a detailed molecular model of kerogen which can facilitate this study. The model is based on the characterization part of the project. The structures generated match the experimental data for the ratio of aliphatic to aromatic carbon; the amounts of oxygen, nitrogen, and sulfur; the average chain lengths for links; and the average number of links per core. The model is used to understand and predict Green River oil shale reactivity.

A-16

Effects of Electronic and Nuclear Interactions on the Excited-state Properties and Structural Dynamics of Copper(I) Diimine Complexes

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Due to their strong visible light absorption and ability to donate electrons in light-induced ET processes, copper diimines present a cheap and effective alternative to expensive ruthenium polypyridyl complexes in dye-sensitized solar cells. However, these copper complexes are inhibited by intricate, structure-dependent ultrafast dynamics, such as solvent ligation and Jahn-Teller distortions. X-ray transient absorption spectroscopy and time-dependent density functional theory were used to measure the structural and electronic dynamics of phenyl-substituted copper diimine complexes upon photoexcitation into the metal-to-ligand charge transfer state. Significant nuclear reorganization was measured, including a decrease in the flattening angle between the imine ligands and rotation of the phenyls, and correlated to the redistribution of the transferred charge. These dynamics relate directly to the potential performance of these copper complexes in photochemical applications; hopefully, these discoveries will lead to the development of copper-based systems that are optimized for solar energy conversion devices.

A-17

Electronic and Spectroscopic Characterization of Water-exchange Oxidation on Mononuclear Halogenated Ru(II) Complex

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Photosynthetic water oxidation is a fundamental process in the biosphere that results in the sunlight-driven formation of O_2 from water. Biological photosynthesis encompasses a series of complicated processes involving several transition states and intermediates that scientists continue to investigate. Mimicking this reaction in a man-made device will allow for sunlight-to-chemical energy conversion, with water providing electrons and protons for the formation of oxygen and reduced chemicals. About 30 years ago, Meyer and coworkers reported the first ruthenium-based catalyst for water oxidation, known as the "blue dimer" [1]. This catalyst may be considered as an artificial analog of the oxygen-evolving complex (OEC) in Photosystem II (PS II) [2]. Recently it has been demonstrated that single-site Ru and Ir catalysts are also active in water oxidation [3, 4]. These single-site catalysts are attractive model compounds for both experimental and theoretical studies of mechanism of water oxidation and show improved catalytic activity compared to "blue dimer". A better understanding of this mechanism and identification of the rate-limiting steps could pave the way to light-driven generation of molecular hydrogen by water splitting.

Water exchange on a mononuclear Ru(II) complex, $[Ru(II)(bpy)(tpy)Cl]^+$ (bpy = 2,2'-bipyridine, tpy = 2,2'; 6',2"-terpyridine) to give the corresponding $[Ru^{III}(L)(4\text{-pic})_2(OH_2)]^{2+}$ species as active catalyst was characterized by X-band electron paramagnetic resonance (EPR), x-ray absorption near-edge structure (XANES) at Cl and Ru K-edge as well as extended x-ray absorption fine structure (EXAFS) at Ru K-edge. When Ce(IV) is added to Ru(II) Cl complex, EPR spectra corresponding to that of $[Ru^{III}(L)(4\text{-pic})_2(OH_2)]^{2+}$ is obtained and a considerable decrease of 68% Ru-Cl interaction is observed in both Ru L-edge XANES and Ru-Cl distance at Ru K-edge EXAFS.

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A-18

Li_xFePO_4 (x = ~0.41): A New Lithium Iron(II, III) Phosphate Synthesized Via Li^+-ion Exchange under Hydrothermal Condition: A New Class of a Cathode Material for Lithium Ion Battery

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In the search for new cathode materials for lithium-ion battery applications, a new lithium iron phosphate that exhibits facile Li^+ ion transport and possibly superior electrochemical properties has been synthesized via employing previously demonstrated experimental procedures [1]. The new phase is a mixed valent lithium iron (II, III) compound, Li_xFePO_4 ($x \approx \sim 0.41$). It was acquired via the Li^+-ion exchange reaction of a newly discovered rubidium iron (II, III) phosphate, Rb_xFePO_4 under mild hydrothermal conditions. Single crystals of the latter were synthesized using high-temperature flux methods. The x-ray single crystal structure reveals a three-dimensional framework that consists of a fused Fe–O–Fe framework as well as interconnected channels where the rubidium ions reside. The polycrystalline sample of Rb_xFePO_4 for ion-exchange can be conveniently synthesized by heating a stoichiometric mixture of Rb_2CO_3, FeO, Fe_2O_3, and P_4O_{10}, with the molar ratio of $2x$:$4x$:(2-$2x$):1, at high temperature (~850°C) and sample purity was proved using high-resolution powder diffraction in 11-BM in Advanced Photon Source. It is essential to mention that Li_xFePO_4 exhibits an unrelated structure to that of the olivine-type $LiFePO_4$, the state-of-the-art cathode material first discovered by Goodenough and coworkers in 1997 [2]. Lithium content of the ion exchange sample was proved using high-resolution neutron powder diffraction, BT-1 Center for Neutron Research, National Institute of Standards and Technology.

In this presentation I would like to talk about the synthesis of Li_xFePO_4 and its property characterization such as x-ray and neutron powder diffraction, electronic properties, thermal stability, spectroscopic studies, and Li ion battery studies.

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A-19

Stepwise Evolution 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, or colloidal crystals, could in principle be used to create designer materials with unique properties useful in material synthesis, optics, biomedicine, energy, and catalysis. Nanoparticle superlattices can be assembled using a variety of entropic, depletion, electrostatic, or biorecognition forces and further, provide a convenient model system for studying crystal growth. DNA is a particularly attractive ligand for the programmable assembly of nanoparticles, as synthetically tunable variations in nucleotide structure allow for precise engineering of the nanoparticle hydrodynamic radius and coordination environment with nanometer scale precision. These factors, in turn, dictate the crystallographic structure, symmetry and lattice parameters 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 nanoparticle building blocks functionalized with DNA 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. This is a unique approach since prior studies involving superlattice assembly typically rely on repulsive interactions between particles to dictate structure, and those that rely on attractive forces (e.g., ionic systems) still maintain repulsive particle-substrate interactions.

A-20

Excited-state Structural Dynamics of Zn-substituted Hemoproteins and Model Compounds Detected by Transient and Steady-state XAS

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Long-range electron transfer is a critical process in redox-active biological systems. Zinc-substituted hemoproteins have long been used to deduce the kinetic mechanisms of photoinitiated inter-protein electron transfer and, using electron paramagnetic resonance to study their Jahn-Teller (JT) unstable triplet states, to give insight into how proteins may stabilize certain conformations of bound porphyrins to tune the electron transfer characteristics of their active sites. Both free Zn porphyrins' and Zn hemoproteins' lower excited states are subject to distortion along porphyrin b_{1g} and b_{2g} JT-active modes, though the degree of this distortion depends on the amount of structural perturbation exerted on the porphyrin by the protein environment.

As a point of comparison to actual protein systems, we have measured structural changes in the excited states of Zn tetraphenyl porphyrin (ZnTPP) and Zn protoporphyrin IX (ZnPPIX) in a 5-coordinate complex with 1-methyl imidazole to mimic axial ligation by a histidine in myoglobin using transient x-ray absorption spectroscopy. We have also measured steady state K-edge x-ray absorption spectroscopy of a metastable triplet excited state population in Zn-substituted myoglobin and cytochrome c at liquid He temperature. In both time-resolved and steady-state experiments, a small contraction of the porphyrin ring is observed on excitation. Changes in the extended x-ray absorption fine structure on continuous illumination with a xenon lamp appear much more prominent than in the free porphyrin. This may indicate a JT distortion is responsible for this contraction because the degree of distortion along a JT active mode is expected to be larger in the substituted hemoproteins due to interaction between the porphyrin and heme pocket.

A-21

Towards Powder X-ray Diffraction with PPM Limits of Detection for Active Pharmaceutical Ingredients with Integrated Nonlinear Optical Instrumentation

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Many analytical methods can be used to characterize active pharmaceutical ingredients (APIs), such as x-ray diffraction (XRD), Raman, IR-spectroscopy, solid-state NMR, differential scanning calorimetry, transmission and scanning electron microscopy. However, these methods typically exhibit detection limits above 1%, which can complicate analysis of materials with low crystal loadings.

Second harmonic generation (SHG) microscopy in combination with two-photon excited ultraviolet fluorescence (TPE-UVF) is an attractive alternative for the determination of percent crystallinity of a sample. In previous studies, calibration curves were prepared to quantitatively assess the viability of SHG-based crystallinity detection, and were found to be in good agreement with typical techniques such as powder x-ray diffraction. However, SHG provides little direct structural information about the crystal lattice/composition.

Limits of detection for benchtop x-ray diffractometers are on the order of a few percent. However, the incorporation of a nonlinear optical instrument, combining SHG, TPE-UVF, with a synchrotron x-ray source, allows for the potential to substantially decrease XRD limits of detection. In preliminary work, pharmaceutical samples with a 0.01% w/w API loading were examined, resulting in strong agreement with SHG and x-ray raster scanned diffraction. Combining mini-beam collimation of the synchrotron beam with area detection of the diffracted x-rays has the potential to identify crystal forms at ppm or ppb levels.

A-22

Mapping Electronic and Structural Changes upon Ultrafast Charge Separation in RuCo Supramolecular Complexes

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Photoinduced functionality exhibited by natural or rationally designed supramolecular complexes is very often triggered via ultrafast electron transfer accompanied by structural rearrangements. From artificial photosynthesis to molecular electronics, many fields of modern research increasingly rely on a detailed understanding of these basic processes. One common goal, requiring combined experimental and theoretical effort, aims at unraveling the various electronic and geometric factors that govern the rates of electron transfer within series of tailored molecular architectures to eventually promote long-lived charge separation or efficient charge transport.

We have employed transient x-ray absorption spectroscopy (TXAS) at sector 11-ID-D at the APS (Argonne National laboratory) to investigate the reversible photocycle occurring within several prototypical molecular dyads that consist of a Ru moiety as the photosensitizer and electron donor, and a Co moiety as the electron acceptor, with or without any electronic delocalization in their ground state. The changes in structural parameters have been extracted from the transient spectra by using fitting procedures based on quantitative XANES analysis.

This work, which can be readily generalized to a wide variety of multichromophoric assemblies, demonstrates the strength of multi-edge TXAS for tracking coupled changes in oxidation and coordination on their intrinsic time scale.

Condensed Matter Physics

A-23

Physical Properties and Magnetic Structure of CeCuBi2 Intermetallic Compound

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In this work, single crystals of $CeCuBi_2$ intermetallic compound were investigated by means of temperature dependent magnetic susceptibility, pressure dependent electrical resistivity, heat-capacity, ^{63}Cu nuclear magnetic resonance and magnetic x-ray diffraction experiments. Our single crystals of $CeCuBi_2$ shows an antiferromagnetic ordering at T_N~16 K which is higher than the values previously reported for Cu-deficient samples. The magnetic properties of $CeCuBi_2$ is consistent with an Ising antiferromagnet and the magnetization data at low temperatures reveal the existence a spin-flop transition when the field is applied along the *c*-axis. (H_c ~5–6 T and T=2 K; AFM to FM interlayers). The x-ray resonant diffraction data below T_N reveal a commensurate antiferromagnetic structure with propagation vector $\tau = (0\ 0\ ½)$ and the Ce moments oriented along the c-axis. The combined analysis of the heat capacity, pressure dependent resistivity and temperature dependent ^{63}Cu suggest that $CeCuBi_2$ shows a weak heavy fermion behavior with the 4*f* electrons of Ce^{3+} being strongly localized. We discuss our data taken into account the tetragonal crystalline electrical field (CEF) and the anisotropic magnetic interaction between the Ce^{3+} ions in this compound.

A-24

X-ray Magnetic Circular Dichroism Study of Induced Pt Magnetic Moment in Pt/$Y_3Fe_5O_{12}$ Bilayers

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The generation, manipulation, and detection of spin currents are essential to spintronics. Platinum (Pt) has been widely used in experimental study of pure spin current phenomena, including the spin Hall effect, inverse spin Hall effect, spin Seebeck effect, spin Hall switching, spin Hall induced ferromagnetic resonances, and spin pumping, etc. Thin Pt films on $Y_3Fe_5O_{12}$ (yttrium iron garnet =YIG) show ferromagnetic-like transport properties, which may impact the functionality of Pt in spin current detection, but do not provide direct quantitative information on the Pt magnetization. We report x-ray magnetic circular dichroism measurements of YIG/Pt(1.5 nm), showing an average Pt moment of 0.054 μB at 300 K and 0.076 μB at 20 K. This observation indicates strong proximity effects and induced magnetic ordering in Pt on magnetic insulators and their contribution to the spin-related measurements should not be neglected.

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A-25

Tuning Spin-Orbit and Exchange Interactions in Sr_2IrO_4 with Ru and Rh Doping

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Sr_2IrO_4 is a spin-orbit interaction (SOI) driven insulating “weak” ferromagnet. Whether the nature of this insulating gap is of the Mott-Hubbard or Slater type has been the subject of ongoing debate. In sharp contrast to Sr_2IrO_4, which is an insulator, Sr_2RhO_4 is a paramagnetic metal and Sr_2RuO_4 is a *p*-wave superconductor. Although, both Rh and Ru doping in the 5*d*-based Sr_2IrO_4 drive the system paramagnetic metallic, the insulating state is more robust for Rh doping. It has been proposed that the weaker SOI in the 4*d*-based Rh and Ru is related to the closing of the insulating gap. Whereas Rh ($4d^5$) is isoelectronic to Ir ($5d^5$), Ru ($4d^4$) has one less electron and therefore, fills the t_{2g} band with holes driving the system metallic at lower concentrations compared to Rh ($4d^5$).

In order to probe the electronic state in pure and doped Sr_2IrO_4, we carried out x-ray absorption near edge structure (XANES) and x-ray magnetic circular dichroism (XMCD) measurements at Ir $L_{2,3}$ edges. The white line intensity ratio L_3/L_2 (branching ratio), which relates to the expectation value of $\langle \mathbf{L.S} \rangle$ is found to be independent of both Rh and Ru doping. In contrast, XANES measurements in $Sr_2Ir_{1-x}(Rh, Ru)_xO_4$ ($0 \le x \le 1$) at Ru and Rh $L_{2,3}$ edges show that while the branching ratio for Ru decreases dramatically with x, the Rh branching ratio stays constant over the entire doping region. Also, the oxygen K edge measurements do not show any significant spectral weight shift with Rh doping. These results indicate absence of hole doping into oxygen 2*p* states and the picture where the 5*d* spin-orbit interaction is quenched with Rh doping is not valid.

A-26

Synchrotron Radiation Studies of Rapidly Evolving Self-assembled Nanoparticle Langmuir Films

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Nanoparticle Langmuir films self-assembled on a liquid sub-phase represent a class of systems that is of great interest for studies of phase transitions in quasi-two-dimensional systems, chemical self-assembly, surfactant behavior, and biologically relevant monolayers and membranes. We utilize grazing-incidence x-ray off-specular (GIXOS) scattering to study elastic properties, structure, and surface fluctuating modes of these systems. We present here a comparison between the GIXOS and the x-ray reflectivity (XR) measurements, where XR is conventionally used to provide structural information of samples along the surface-normal direction. We further present a detailed analysis of GIXOS data from the self-assembled nanoparticle films and describe how we use it to obtain quantitative, angstrom-resolution details of the electron density profile normal to the surface, complementary to that obtained with XR. Additionally, GIXOS provides us with improved temporal resolution that allows us to directly study the evolution dynamics of self-assembled nanoparticle films in response to lateral compression.

A-27

Local Structure, Stripe Pinning, and Superconductivity in the High-pressure HTT phase of $La_{1.875}Ba_{0.125}CuO_4$

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The strong T_c suppression in $La_{1-x}Ba_xCuO_4$ at x=1/8 ($LBCO_{1/8}$) is widely believed to be related to formation of static stripes, at least partially driven by a strong electron-lattice coupling in a low-temperature tetragonal (LTT) phase [1]. A recent high-pressure experiment appears to challenge this view, as static stripe order (charge order, or CO) was observed to persist to pressures higher than that required to induce the LTT-to-HTT transition [2]; however, the presence of local distorted domains (LTT or LTO) of same correlation length as CO was also reported, suggesting the presence of quenched buckling disorder. Thus, the character and evolution of the local structure across the LTT-HTT transition appears to be relevant.

To study the relationship between local structure and electronic interactions, concomitant low-temperature La K-edge polarized XAFS and diffraction measurements were performed in $LBCO_{1/8}$ single crystals at high pressure. The diffraction data confirm the pressure-induced LTT-HTT transition, with persistent CO and distorted local domains. Furthermore, the concomitant collapse of such local domains is observed above 3.5 GPa, proving their intrinsic relationship. XAFS results show the persistence of local LTT tilts at high pressure, demonstrating that the distorted local domains have LTT symmetry. This result suggests a significant order-disorder component to this pressure-induced phase transition, whereby the local LTT tilts remain present in the local scale but disorder over long range resulting in HTT symmetry is seen by diffraction. Despite this persistence, the local LTT tilt is continuously reduced under pressure, which is proposed to directly influence both the small dTc/dP and the suppressed maximum $T_c(P)$ (~18 K, versus ~ 33 K when $x \neq 1/8$) observed in this compound [3]. Finally, this work strongly suggests that both CO and superconductivity are intrinsically related to the local, rather than long-range, order in $LBCO_{1/8}$.

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A-28

Probing Ultrafast Responses in Antiferromagnetic NiO with Time-resolved X-ray Diffraction Techniques

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Ultrafast experiments on NiO have recently attracted much attention due to the possibility to optically control antiferromagnetism in picosecond timescales. Also, by pumping with near-infrared femtosecond pulses, coherent excitation of terahertz waves have been demonstrated to occur due to impulsive excitation of magnons. Time-resolved x-ray diffraction experiments can directly probe the lattice dynamics and the magnetic domain distribution due to magnetostriction effects. In this work we present preliminary results of time-resolved x-ray magnetic scattering and dynamics of magnetic domains of single crystals of NiO optically pumped with femtosecond pulses at sector 7-ID-C at the APS.

A-29

Anharmonicity Studies with Nuclear Resonant Inelastic X-ray Scattering

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The interpretation of non-resonant inelastic x-ray scattering (NRIXS) measurements has been done mostly in the context of quasi-harmonic approximation. Phonon density of states and dynamic properties like mean kinetic energy and mean force constant can be derived. Going beyond the harmonic lattice model, we show that the anharmonic terms in the lattice potential can be measured. This opens up the NRIXS method to study anharmonicities in materials. Given any specific model of lattice potentials, one can calculate the moments of a would-be measured NRIXS spectrum. This may be used to restrict and adjust models of lattice potentials. We will present new results and re-analysis of some previous ones in light of this anharmonic consideration.

A-30

Fast CCD Area Detector for X-ray Speckle Visibility Spectroscopy Measurements from the Diffusion of Concentrated Alpha Crystallin Suspensions

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We present speckle visibility spectroscopy (SVS) measurements of protein diffusion in concentrated suspensions of alpha crystallin, a major protein found in the mammalian eye lens with the help of a prototype fast CCD area detector that has been optimized for coherent x-ray measurements.

The CCD detector is collaboration between the Advanced Photon Source at Argonne National Laboratory, the Advanced Light Source at Lawrence Berkeley National Laboratory (LBNL). Our group at Northern Illinois University is the first to use it for soft condensed matter coherent x-ray scattering studies and simultaneously optimize and characterize the detector for enhanced performance. The detector uses a custom LBNL-designed CCD, with 480 × 480 pixels and 96 outputs, giving a nearly column parallel and therefore a very fast (200 fps) readout.

With the help of SVS, we have pushed for faster dynamics measurements at the single-photon limit and show its promise for coherent x-ray scattering in the flux/photon limited situations.

A-31

Interfacial Bonding and Structure of Bi_2Te_3 Topological Insulator Films on Si(111) Determined by Surface X-ray Scattering

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Interfacial topological states are a key element of interest for topological insulator thin films, and their properties can depend sensitively on the atomic bonding configuration. We employ *in situ* non-resonant and resonant surface x-ray scattering to study the interfacial and internal structure of a prototypical topological film system: Bi_2Te_3 grown on Si(111). The results reveal a Te-dominated buffer layer, a large interfacial spacing, and a slightly relaxed and partially strained bottom quintuple layer of an otherwise properly stacked bulk-like Bi_2Te_3 film. The presence of the buffer layer indicates a nontrivial process of interface formation and a mechanism for decoupling between the topological film and the Si(111) substrate.

A-32

Full Partial Structure Factor Determination of Y_2O_3 and Ho_2O_3 Liquids at 2600°C

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The full set of partial pair distribution functions for R_2O_3 liquids at 2600°C (where R= Y or Ho) were measured by combining aerodynamic levitation with neutron diffraction, high-energy x-ray diffraction, and isomorphic substitution. Average R-R, R-O and O-O coordination numbers of 11.7(4), 5.5(2), and 8.5(3), and respective separation distances of 3.58(2), 2.22(2), and 3.14(4)Å were obtained from the corresponding pair distribution functions. Partial charge Buckingham and Morse potential molecular dynamics models are found to accurately predict the coordination numbers and distortion of the nearest neighbor R-O and R-R interactions. However, the first peak in the simulated O-O distributions are broader than the measurements, indicating a much more well-defined edge-shared connectivity persists in the melt than predicted. Moreover, this relatively sharp O-O peak appears to be ubiquitous for most oxide liquids and glasses. The method of yttria-holmia substitution with x-ray pair distribution function measurements used here, has potential to provide rare earth element specific structural insight into many important materials containing yttria or its isomorphous lanthanides (Ho_2O_3, Er_2O_3).

A-33

Structural and Magnetic Dynamics in Epitaxial $La_{0.7}Sr_{0.3}MnO_3$ Films

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$La_{0.7}Sr_{0.3}MnO_3$ (LSMO) is a well-studied prototype perovskite material with half-metallic and ferromagnetic properties above room temperature with large potential for spitronic applications. In contrast to the thorough investigation of the equilibrium properties of this material, its dynamical response under ultrashort optical impulses is not well understood.

Here, we present our experimental results correlating the ultrafast spin dynamics above and below the Curie point with the simultaneous structural changes induced with fs lasers in epitaxial LSMO films. The laser fluence dependency of the spin and structural dynamics is captured using complimentary magneto-optical and time-resolved x-ray diffraction measurements. The variable temperature (at equilibrium) studies of the film structure are compared with results on laser-induced structural changes on the ps timescale. We find that the observed evolution of ultrafast structural dynamics can be used to better understand the fs-ps transient magnetic anisotropy changes in the LSMO films. Additionally, with the use of an external magnetic field, we could probe magneto-acoustic and magneto-thermal transients on the ps to ns timescale in this correlated electron material.

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A-34

Study of Time- and Potential-dependent Changes in Room-temperature Ionic Liquid Structure at Epitaxial Graphene Interface

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Room temperature ionic liquids (RTIL) are promising electrolytes for electrochemical supercapacitors due to their wide electrochemical stability range, low volatility, and high capacitance. On the other hand, carbon electrodes are already used widely as electrodes in supercapacitors. Therefore, a molecular level understanding of the RTIL/graphene interface during charging and discharging processes is necessary to design the next generation electrochemical energy storage devices. We used *in situ* real-time x-ray reflectivity to determine the change in electric double-layer structure of imidazolium-based [Tf2N$^-$] ionic liquids on the epitaxial graphene interface with the applied potential, and compared the results with the simultaneously collected cyclic voltammetry data at different scan rates. X-ray reflectivity data were also obtained at a series of fixed potentials to investigate the similarities and differences between the dynamic and static structures at the interface.

A-35

Termination and Hydration of Ultramafic Mineral Surface: Forsterite (010)

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The weathering and hydrous alteration processes of ultramafic rocks (serpentinization) attract much attention recently for the attribution to abiotic hydrocarbon generation in near-surface region of the planet. These processes exert significant effects on the Earth's atmosphere and the micro- and meso-ecological systems in Earth's surface and subsurface. Atomic-level characterization of the interface between water and mineral surface, which plays crucial roles in mineral weathering and dissolution processes, is highly demanded to better describe the processes in molecular scale. We use *in situ* high-resolution x-ray reflectivity to examine the natural forsteritic olivine (010) in aqueous condition. By modeling the electron density profile in surface normal direction and fitting the measured data with least-square method, the atomic structures of hydrated mineral surfaces are depicted. We found, for alumina-polished forsterite surface under acidic environment, a homogeneous termination with about half of the magnesium depleted and replaced with water species. In contrast, a silica-polished forsterite under basic condition does not show such homogenous surface, for which the morphological difference from the alumina-polished surface is confirmed by *ex situ* atomic force microscopy measurements. These results provide a reference of hydrated molecular structure of olivine surface for comparison with even more interesting high pressure and high temperature study in the future.

A-36

Effect of Gold Nanoparticles on the Structure of a Phospholipid Monolayer

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Interfacing nanomaterials with biological systems has become an area of intense interest: Nanoparticles have recently been used in various biological applications including drug delivery, sensors, and biological tags. The development of nanoparticles for these applications requires understanding of the biocompatibility of these materials. This project studies a composite system of DPPC, a pulmonary lipid surfactant, mixed with gold nanoparticles ligated with dodecanthiol. Phospholipids are found to self-assemble on the air/water interface and have been used as models for biological membranes. We use liquid surface x-ray scattering techniques, along with atomic force microscopy and optical microscopy to understand how the gold nanoparticles integrate with the lipid film and affect the ordering and packing of DPPC in these systems.

A-37

Coherent Scattering Study of Striped Polarization Nanodomains in a $PbTiO_3/SrTiO_3$ Superlattice

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Ferroelectric materials are characterized by large, switchable remnant polarization, which can exist in thin films with thicknesses of even a few atomic layers. In thin layers of ferroelectric materials, the remnant polarization can spontaneously form a striped nanodomain pattern in order to minimize the electrostatic energy. The ferroelectric $PbTiO_3$ layers of $PbTiO_3/SrTiO_3$ superlattices are electrically decoupled from each other by intermediary dielectric $SrTiO_3$ layers and form polarization nanodomains similar to what would be observed in $PbTiO_3$ ultra-thin films. These nanodomains lead to important properties, including electromechanical clamping between the neighboring domains and different domain wall dynamics in ferroelectric and dielectric layers in response to an applied electric field. We have studied the nanodomain structures of a $PbTiO_3/SrTiO_3$ superlattice using coherent x-ray scattering. The degree of transverse coherence of the focused x-ray beam produced by zone plate optics was improved by illuminating the zone plate through a horizontal slit. The visibility of the speckles is maximized when the width of the slit matches the transverse coherence length of the x-ray source. The coherent x-ray scattering pattern exhibits a diffuse scattering satellite arising from the domain structure. The domain satellite has a speckle pattern that is reproducible and static at room temperature, up to durations limited by the beamline stability. The intensity scattered into the reciprocal space volume occupied by an individual speckle varies by 70% as the beam is moved across the sample, while the integrated intensity of the entire scattering satellite is constant. Variations of the domain structure occur within the spot size of the focused x-ray and there is no long-range order in the domain pattern. The variation of the spatial statistics of the domain structures can be characterized by evaluating the correlation function between the speckle patterns taken at different spots on the sample surface.

A-38

Strain Effect on Mn K-edge XANES of $Pr_{0.67}Sr_{0.33}MnO_3$ Thin Film

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Perovskite manganite is a strongly correlated electronic material system with many interesting and promising properties, such as colossal magnetoresistance (CMR) and high spin polarization. However, a high magnetic field of the order of a tesla is required to get a large CMR effect; also, the effect occurs near the phase transition temperature and thus occurs over a narrow temperature range. Because of the strong coupling between the electron and the phonon, strain is an effective method to tailor the material properties. $Pr_{1-x}Sr_xMnO_3$ is a system with a high Curie temperature and a rich phase diagram as a function of the hole concentration $\boldsymbol{x}$. In this work, we grew 12 nm $Pr_{0.67}Sr_{0.33}MnO_3$ thin films using pulsed laser deposition on (001)$SrTiO_3$, (110)$NdGaO_3$, and (001)$LaAlO_3$ single-crystal substrates. The lattice mismatch between the substrate and $Pr_{0.67}Sr_{0.33}MnO_3$ could be exploited to form films with various in-plane tensile strain, no strain, and compressive strain. X-ray diffraction and resistance-temperature curves were measured to study the crystal structure and transport properties. We utilized the polarized x-ray absorption near edge structure (XANES) technique at sector 20-ID-B to study the strain effects on the Mn K-edge XANES. The strain and transport properties were investigated.

A-39

Ultrahigh Compressibility and Anomalous Elastic Characteristics in Glass Carbon: Implication for High-energy-absorbing Materials

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Glass carbon, hybrid of graphite and fullerene components, presents amazing high volume compression ratios of ~70% to 5 GPa and ~60% at 10 GPa, identified by *in situ* high-pressure photographic technology. The origin is traced back to structural and elastic analyses obtained from recent integration of multi-angle energy-dispersive x-ray diffraction and ultrasonic elastic wave velocity measurements in a Paris-Edinburgh cell of HPCAT. It can be concluded that the interlayer compression in glass carbon is insufficient to explain so high a volume compression and there necessarily involves the deformation of its internal fullerene balls. This can also be responsible for the anomalous change of elastic modulus (bulk, shear, and Young's modulus) under pressure: negative modulus derivative is continued to 2 GPa, and then reversed to positive value under higher pressure. Combined with molecular dynamics simulations, a strategy is proposed for designing controllable elastic or plastic compression deformation via the size and quantity change of fullerene components in energy-absorbing carbon materials.

Environmental & Geology

A-40

Rb Adsorption at the Quartz(101)-Water Interface and Development of a High P/T Cell for *In Situ* X-ray Reflectivity Measurements

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Quartz is an abundant and ubiquitous rock-forming mineral in Earth's continental crust, and influences the chemistry of numerous aqueous systems [1]. The sorptive property of quartz changes the mobility of ions in water while its dissolution process controls long-term silica cycling through the earth system. The dissolution rate of quartz at near-neutral pH increases substantially in the presence of cations while the degree of enhancement depends on the choice of cation [2, 3]. However, the detailed understanding on the mechanism remains unclear mainly because of the lack of atomic-scale information on the processes to explain the complexity of the interface chemistry. Molecular-scale investigation of the quartz surface cation interaction is the first step in understanding this cation-induced mechanism. Here, we report on Rb^+ adsorption at the quartz(101)-water interface from 10 mM RbCl solution at pH 10 observed by using x-ray reflectivity (XR) and resonant anomalous XR measurements. The best-fit model of the experimental data suggests that Rb^+ adsorbs at an average height of 2.7 Å above the surface (defined as the average position of the two terminal oxygens), which may be a mixture of inner- and outer-sphere species. The total occupancies of these complexes is 0.19 Rb^+/A_{UC} (where the surface unit cell area is A_{UC} = 33 Å^2), implying a surface charge (at pH 10) of ~1 e- for 2 nm^2. We are expanding the scope of our investigation into the quartz dissolution mechanism by designing a new experimental cell capable of reaching ~200°C and 230 atm of pressure. This cell will enable us to explore a wider range of P/T conditions for quartz dissolution while still allowing us to perform x-ray reflectivity experiments *in situ*.

[1] Schulz, M.S. and A.F. White, *Geochim. Cosmochim. Acta*, 1999. **63**(3-4): p. 337.

[2] Dove, P.M. and D.A. Crerar, *Geochim. Cosmochim. Acta*, 1990. **54**(4): p. 955.

[3] Dove, P.M., *Geochim. Cosmochim. Acta*, 1999. **63**(22): p. 3715.

A-41

Analysis of Heavy Metal Concentrations in a Historic Collection of Bird Eggs

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When birds encounter metals in their environment, part of their physiological detoxification process is to excrete those metals as they form their eggs. Therefore, bird eggs have been used as a way of evaluating contamination in the environment. The majority of the numerous studies using egg contamination to track environmental contamination use destructive techniques on newly harvested eggs. The Jurica-Suchy Nature Museum at Benedictine University houses an extensive collection of eggs dating back to the late 1800's. These specimens have the potential to yield information about past environmental conditions, but it is unthinkable to destroy irreplaceable specimens for toxicological analyses. Additionally, since preservatives such as arsenic were historically used in natural history collections, contamination by the museum environment needs to be ruled out in any analysis of museum specimens.

Using a microcapillary analyzer on the x-ray detector and a focused x-ray beam, we were able to detect the fluorescence out of a limited volume of intact egg shell. This technique allowed us to analyze the metal concentrations within an egg's shell without destroying or damaging the museum specimens and excluding any surface contamination from the museum environment. We analyzed the metal content in 38 eggs from osprey, grebes, and common terns dating from the 1880s to the 1920s. We did not find the metal contaminants commonly found in contemporary eggs (cadmium, mercury, chromium, selenium), and we were able to exclude surface contamination from museum chemicals with our technique.

High Pressure

A-42

Bridging the Strain Rate Gap between Static and Dynamic High-pressure Experiments

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Generally, high-pressure experiments can be classified as being either static or dynamic. Static experiments are characterized by very low strain rates with no corresponding increase in temperature, whereas dynamic experiments are characterized by very high strain rates with a large increase in temperature. The strain rate gap between the two types of experiments is several orders of magnitude: strain rates are typically on the order of 10^{-2} s^{-1} or smaller for static experiments and 10^3 s^{-1} or greater for dynamic experiments. A number of recent advances in high-pressure techniques and apparatus have now made it possible to consider the generation, control, and measurement of intermediate strain rates which bridge the gap between these two types of experiments. Complementary advances in detector technology coupled with the unmatched brightness of a third-generation source like the APS make it possible to explore the dynamic processes that occur in materials during these rapid pressure increases. We present a number of apparatus, experimental techniques, methods of signal conditioning, and data reduction strategies developed at HPCAT over the last year which is being used to explore intermediate strain rates, together with the results of early experiments which promise to ultimately lead to bridging the strain rate gap between static and dynamic experiments.

A-43

Fast-temperature-readout Spectrometer for Atomic Dynamics Measurements

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In state-of-the-art extreme condition experiments, laser heating is combined with diamond-anvil cells to simulate the environment of Earth's deep interior. To determine the sample's temperature in such experiments, the common measurement utilizes an optical spectrometer coupled to a CCD to analyze the sample's emitted radiation. This method is often too slow to capture the sample's transient temperature fluctuations, which can be significant for materials near their melting points. To accurately capture this effect, we have developed a fast-temperature-readout (FasTeR) spectrometer in line with nuclear resonance scattering measurements under extreme conditions at sector 3-ID-B of the Advanced Photon Source at Argonne National Laboratory. Dedicated to determining the sample's temperature near its melting point, FasTeR consists of photomultiplier tubes and an optical dichroic filter array, and features a fast readout rate, high sensitivity, large dynamic range and well-constrained focus. In comparison with the conventional system, FasTeR increases the temperature readout rate by 1–2 orders of magnitude. FasTeR has been successfully combined with nuclear forward scattering measurements on a compressed iron-nickel alloy to determine the melting point by monitoring the dynamics of the atoms.

Instrumentation

A-44

Proposed Detector Development Initiatives for the APS Upgrade

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New, application-specific detectors are a key technology that will help enable the science of the APS Upgrade. Two detector developments are currently being planned: (1) CPix2 is a counting detector being planned for pump-probe beamlines. This detector features two counters per pixel in order to permit acquisition of a pump and probe image without readout dead time. Incorporating dual discriminators, this detector will enable separation of the fluorescence, Compton, and scattered signal. (2) FASPAX (Fermi-Argonne semiconducting pixel array x-ray detector) is a versatile integrating detector capable of acquiring 48 single-bunch images (a burst of images at 6.5 MHz). The detector will provide flexible dynamic range—from single photon sensitivity up to 105 photons/pulse/pixel. This detector will benefit high-flux applications such as the high-flux pump probe or Dynamic Compression Sector, but will also be appropriate wherever a high-frame-rate area detector is needed.

A-45

Demonstration of the Bionanoprobe: Cryogenic Hard X-ray Fluorescence Nanoprobe

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X-ray fluorescence (XRF) microscopy is one of the most sensitive imaging techniques to study trace elemental distributions in biological specimens. By using spatially coherent, highly brilliant x-rays as the excitation source and advanced x-ray optics, current synchrotron-based XRF microprobes at the Advanced Photon Source (APS) at Argonne National Laboratory reproducibly achieve a 150-nm spatial resolution on biomaterials. Conventional sample preparation methods usually involve dehydration, such as air-drying, freeze-drying, and critical-point-drying, which removes cellular water and may consequently cause structural collapse. Radiation-induced artifacts may also become an issue during repeated scans, particularly as the spatial resolution increases beyond the sub-micron scale. To allow imaging under hydrated "natural state" conditions, as well as to reduce structural radiation damage, we have developed a bionanoprobe (BNP), a hard x-ray fluorescence microscope with cryogenic capabilities, dedicated to studying trace elements in frozen-hydrated biological system. This instrument is the first microscope of its kind. The BNP is installed at an undulator beamline at the Life Science Collaborative Access Team (LS-CAT) at the Advanced Photon Source. It provides a spatial resolution of 30 nm for fluorescence imaging and high throughput. The cryo sample handling module and sample changing robot enable frozen samples to be well preserved at ~110 K while being examined in the BNP. In this presentation, we will describe the instrument design, quantify instrument performance, and report the first results obtained with the BNP from frozen-hydrated whole cells.

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A-46

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 to image nanoscale materials with chemical, electronic, and magnetic contrast [1]. Sub-nanometer-scale resolutions can be achieved by combining the chemical-specific information that high-brilliance x-ray radiation provides with the detailed atomic and electronic structure information that scanning tunneling microscopy offers. The current SXSTM instrumentation is designed as a lens-less microscope that can accept monochromatic radiation switched on and off by a 3 kHz chopper system. Utilizing this chopper system and a topographic filter, the SXSTM system can de-convolute the chemical signal from the topographic signal measured at the tip and allow for simultaneous measurement of both the chemical and topographic signals [2]. The SXSTM technique will enable fundamentally new methods of characterization and will potentially improve our understanding of physical phenomena at the nanoscale.

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-47

Dynamic Compression Science Capability at the Advanced Photon Source

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To address scientific discovery challenges related to the dynamic compression of condensed matter, Washington State University and the Advanced Photon Source have partnered to establish a first-of-a-kind capability at sector 35. The Dynamic Compression Sector

(DCS) at the APS will focus on time-resolved x-ray diffraction and imaging measurements in a broad range of materials subjected to rapid impulsive loading (~5 GPa to well above 100 GPa stresses and time-durations ranging from ~5 ns to a microsecond) in single-event experiments. A variety of dynamic compression drivers will provide the loading conditions of interest, and the x-ray measurements will be augmented by simultaneous continuum measurements (using laser interferometry).

The DCS facility layout, experimental capabilities, and proposed experiments will be described.

A-48

Second Harmonic Generation for Monitoring X-ray Damage

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X-ray diffraction is a powerful tool for determining the atomic resolution structure of proteins, accounting for ~89% of the structures in the World Wide Protein Data Bank. However, x-rays are not a gentile probe and can perturb the order within a protein crystal, which often limits resolution achievable. The exact mechanism of this damage is still under debate. Second harmonic generation (SHG), the frequency doubling of light, is a sensitive probe for asymmetric polarizability and high degrees of order. SHG has been shown to detect protein crystals with a high degree of contrast due to their intrinsic chiral nature and highly ordered crystal lattices. In this work, SHG has been shown to be a good monitor of x-ray-induced damage within crystals. Careful examination into the conditions under which SHG arises also gives new evidence for the mechanism of x-ray damage.

A-49

Application of Polycapillary Optics to X-ray Spectroscopy Using Diamond Anvil Cells

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Polycapillary optics can be useful both for focusing and detection of x-rays. They offer some extra advantages when used with diamond anvil cells (DACs). Polycapillary concentrating optics can provide the small beams needed for x-ray spectroscopy in DACs. The large divergence output beams can mitigate the diamond diffraction glitches often seen when performing extended x-ray absorption fine structure spectroscopy at high pressure. At lower energies some broadened Bragg glitches can remain, but enough are removed to make it easier to find a glitch-free diamond orientation. At higher energies the Bragg glitches are broadened to a smooth background that can be ignored. Examples will be shown for the Ge and Sb K-edges. On a bending magnet beamline, polycapillaries also provide a tremendous increase in flux as compared to K-B optics. Their main disadvantage is a short working distance that may not be compatible with all types of DACs. In detection applications, polycapillary collimating optics can be used to collect a large solid angle x-ray emission. The collimation is sufficient to provide high energy resolution when used with a backscattering analyzer. Typically the collection efficiency is similar to several spherically bent crystal analyzers, and the optic is also confocal providing rejection of the scattering from the diamonds and gasket.

A-50

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 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 five stripes were produced with film homogeneities < 0.2% as well as gradients.

Lastly, we will be showing the first Montel optics specially 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.

A-51

Coupling Altera FPGAs with Arcturus µC5282 Microcontrollers for Beamline Instrumentation

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Coupling the power and flexibility of Altera Field Programmable Gate Arrays (FPGA) with Arcturus µC5282 embedded microcontrollers provide a low cost solution for beamline instrumentation.

In this poster, we discuss various applications which bring together Altera Stratix FPGAs with embedded Arcturus µC5282 microcontrollers to implement instrumentation for timing and detector applications.

A-52

A 2nd Generation Interfacial X-ray Microscope

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Understanding and controlling physical and chemical processes occurring at the interface of materials is a central theme in many of today's scientific inquiries and technological advancements. Experimental investigations of interfaces have benefited from a large set of imaging techniques such as probe microscopy and electron microscopy. The aforementioned methods can routinely achieve resolution that spans the atomic to the nanometer scales and have greatly advanced our understanding of complex interfacial phenomena. Yet, numerous systems comprised of buried interfaces that are of immense significance remain out of the reach of these methods because of their lack of depth penetration capabilities or inoperability in extreme conditions of pressure and/or temperature.

Taking advantage of the penetration of x-rays and their insensitivity to the physical environment of the probed system, a first-generation interfacial x-ray microscope (IXM) was developed by P. Fenter [1-2] that combined the exquisite surface sensitivity of x-ray scattering and the imaging capabilities of transmission x-ray microscopy (TXM). The IXM was used to image the topography of solid/gas, solid/liquid, and solid/solid interfaces with sub-nanometer height sensitivity and an in-plane resolution of 130 nm. This unique instrument is currently being upgraded and commissioned at the APS (sector 33-ID-D) with the aim of achieving an in-plane resolution of 50 nm and reducing the acquisition time by an order of magnitude.

The 2nd generation interfacial x-ray microscope employs a tapered capillary as a condenser to generate a 10 × 10 μm^2 x-ray illumination spot on the surface of the sample. The capillary is mounted on a hexapod (PI) with six spatial degrees of freedom for the initial alignment of the optical axis of the capillary with the x-ray beam. Placed before the sample is an order sorting aperature (OSA) with a diameter of 100 µm that blocks the transmitted beam and other stray rays that do not focus at the sample position. The OSA is mounted on an ion chamber to monitor the incident photon flux. This serves to characterize the scattering strength of a system and to normalize the reflected signal allowing for the measurements of x-ray reflectivity with a minimal change in the setup. A Fresnel zone plate placed upstream from the sample acts as an objective lens to focus the reflected beam from the sample on the detector (CCD).

The microscope is mounted on a Kappa diffractometer that allows us to run the microscope in transmission mode (TXM) or in reflection mode (IXM) by changing the angle of incidence of the focused beam with respect to the sample and to track the image on the detector with a rotation arm. Imaging of a gold star test pattern revealed that the microscope has an in-plane resolution of 60 nm with a 13 × 13 μm^2 field of view. Future investigations will use the microscope to image *in situ* geochemical processes such as topography change due to mineral dissolution, as well as lithiation of cathodic materials and other interfacial processes.

This work is supported by the Geosciences Research Program of the Office of Basic Energy Sciences.

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A-53

Development of Next-generation X-ray Beam Position Monitor System for High-heat-load Undulator Front Ends at the Advanced Photon Source

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To provide more stable beam for users at the Advanced Photon Source (APS), a new-generation x-ray beam position monitor (XBPM) system for high-heat-load front ends has been developed, which contains four components for monitoring beam position and intensity: (1) XBPM #1, for orbit feedback control; (2) intensity monitor #1, to help alignment in the front end; (3) XBPM #2, for monitoring and logging the beam position at the exit mask; and (4) intensity monitor #2, for monitoring and logging the white beam flux leaving the front end. Intensity monitor #2 may also be used to aid beam alignment through the exit mask. We will present functional specification and design concept of each component and the latest test results of XBPM #1.

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A-54

Optics Testing at Beamline 1-BM

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Beamline 1-BM at the Advanced Photon Source has been reconfigured, in part for testing of synchrotron optics with both monochromatic and white beams. Monochromatic energies between 6 and 25 keV are available. Two primary agendas are topography and rocking curve analyses. Additionally, Talbot grating interferometry for measurement of wavefronts and microfocusing are being developed. Recent examples will include topography of sapphire and tests of Kirkpatrick-Baez mirrors. The layout of three stations will be presented.

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A-55

Detector Testing at 1-BM

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In the fall of 2012, a significant amount of beam time at 1-BM was designated for optics and detector testing. The allocation of significant beam on a dedicated beamline recognizes the importance of the work done by Optics and Detector Groups at APS. The detectors testing program will serve as a test-bed for new x-ray detectors and provide in-house calibration of beamline detectors at APS. The setup and results from early experiments done on count rate limitations of photomultiplier tubes and absolute flux calibrations of PIN diodes, ion chambers and photomultiplier tubes are detailed. Additionally, future plans for the Detector Group at 1-BM are included.

A-56

Integrated Nonlinear Optical Microscope and XRD Instrument for Rapid Crystal Centering on a Synchrotron Beamline

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A nonlinear optical (NLO) microscope, combining second-harmonic-generation (SHG) microscopy and two-photon excited ultraviolet fluorescence (TPE-UVF) imaging, has been integrated with a synchrotron x-ray diffraction (XRD) beamline for rapid screening, identification, and centering of protein crystals in the x-ray source. SHG, the frequency doubling of light, is a technique that is highly specific for non-centrosymmetric crystals, and is forbidden for cryoprotectants, protein aggregates, and most common salts. Due to the inherent chirality and resulting lack of symmetry, approximately 84% of protein crystals are predicted to be detected by SHG microscopy. As a compliment, TPE-UVF relies on the natural fluorescent properties of aromatic residues (primarily tryptophan) but has no dependence on crystallinity. TPE-UVF is particularly useful for locating protein crystals when the symmetry of the crystal forbids SHG, as well as distinguishing protein crystals from SHG active salts crystallized from the mother liquor. These NLO techniques are also capable of detecting crystals in the lipidic cubic phase (LCP), which are otherwise difficult to discern using conventional bright-field techniques.

A variety of proteins grown in LCP have been investigated and good agreement was observed between the crystal location within the loop for both the NLO images and conventional XRD raster images. The NLO instrument was able to obtain higher resolution images (2 μm spatial resolution) with faster image acquisition times (<10 s) compared to XRD raster scans (>5 μm spatial resolution and 3–60 min image acquisition times). Once fully developed, NLO microscopy may serve as the primary method for crystal centering, significantly increasing the sample throughput of synchrotron beamlines and eliminating damage caused by x-ray exposure during raster scanning.

A-57

APS Optical Slope Measuring System (OSMS)

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An optical slope measuring system (OSMS) was recently brought into operation at the Advanced Photon Source of the Argonne National Laboratory. This system is equipped with a precision autocollimator and a very accurate mirror-based pentaprism on a scanning stage and kept in an environment-controlled enclosure. This system has the capability for measuring precision optics with sub-microradian root mean square (rms) slope errors, which has been confirmed with a series of tests, including demonstrations of stability, reliability, and repeatability. Measurements of a flat mirror with slope error 0.2 mrad rms are presented that show that the variation of two sets of slope profile scans is less than 50 nrad, and the corresponding height error profile has less than 2 nm rms.

Lahsen Assoufid, Nathan Brown, Dan Crews, Joseph Sullivan, Mark Erdmann, Jun Qian, Pete Jemian, Valeriy V. Yashchuk, Peter Z. Takacs, Nikolay A. Artemiev, Daniel J. Merthe, Wayne R. McKinney, Frank Siewert, and Thomas Zeschke, "Development of a high-performance gantry system for a new generation of optical slope measuring profilers,", (Nov. 2012).

A-58

A Beamline for Picosecond Magnetization Dynamics at the APS

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Time-resolved magnetic spectroscopy in the picosecond time scale is ideally matched to dynamics in many materials where a close coupling among electronic, magnetic, and structural degrees of freedom leads to the emergence of novel phases with spectacular functional properties, such as magnetoelectronic and magnetoelastic behavior, unconventional superconductivity, and metal- insulator transitions. The ability to directly couple laser fields to specific structural and electronic excitations and follow their magnetic response with element, time, and spatial resolution offers a powerful way to understand the origins of material properties at a fundamental level. Access to this time scale in x-ray experiments has typically been through laser slicing, low-alpha operations, or free electron lasers. All of these offer pulse durations in the pico- or femtosecond regime, but at considerable cost in average flux or availability of the facility. The APS will construct a new short-pulse facility based on the bunch-deflection scheme proposed by Zholents [1], consisting of three beamlines, one of which is the short pulse soft x-ray spectroscopy (SPSXS) beamline.

The SPSXS beamline will cover the 200–2000 eV energy range using an APS bending magnet. It is designed to take full advantage of the new timing capability in the upgrade, in addition to providing circularly polarized radiation. Since the correlation between time and electron momentum is in the vertical plane, the monochromator disperses in the horizontal plane. The beamline is designed to maximize flux and preserve the time resolution by minimizing the number of optical components. The optical design allows (1) the the pulse duration to be varied from 1.5 to 100 ps full width at half maximum (FWHM) without affecting the energy resolution and (2) the resolution to be changed without affecting the pulse duration. More than 10^9 photons/s will reach the sample with a resolving power of 2000 and a pulse duration of ~2 ps for photon energies between 150 and 1750 eV. The spot size expected at the sample position will vary with pulse duration and exit slit opening. At 900 eV and at a resolving power of 2000, the spot will be ~10 × 10 μm^2 with a pulse duration of 2.3 ps FWHM.

[1] A. Zholents *et al., Nucl. Instrum. and Meth. A* **425**, 385 (1999).

A-59

Our Road Map for APS-designed Pixel Array X-ray Detectors

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Fabrication of APS pixel array x-ray detectors requires packaging custom sensors with application specific integrated circuit readouts. The timing is synchronized to the APS clocks and the resulting data must be passed to beamline computers. This poster will summarize our progress for several projects: avalanche photodiode arrays with nanosecond response times; pump-probe pixel arrays for 324, 24-bunch mode timing: two counters, two energy levels per pixel; and 24-bunch mode, 153 ns, strip detectors for radiography and x-ray photon correlation spectroscopy. We will also discuss our ongoing programs with scintillators for hard x-ray imaging applications.

A-60

Variable Q-range X-ray Scattering Chamber at 12-ID-B

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Built for the upgrade of sector 12-ID at the Advanced Photon Source, this device provides automated computer controlled Q-range changes for x-ray scattering experiments by varying the sample to detector distance within a large vacuum chamber. Eliminating the need to vent the system when changing camera lengths allows for quick and efficient change overs between experimental setups. The detector cannot operate in a vacuum environment, therefore it is housed within an air chamber open to atmospheric pressure. A large carbon window isolates the detector from vacuum while allowing high x-ray transmission. An array of motorized beam stops mounted directly upstream of the window protects the detector from the direct x-ray beam for various types of scattering experiments. A smaller detector protrudes into the lower front section for simultaneous wide-angle x-ray scattering data collection. A fully automated support structure aligns the vacuum chamber to the x-ray trajectory.

A-61

Synchrotron-based Metrology of Torsional MEMS Devices

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We present a method for characterizing single-crystal silicon torsional microelectromechanical systems (MEMS) devices based on Bragg x-ray diffraction. These devices oscillate at frequencies of tens of kHz and depending on the frequency can have various rotational amplitudes. This leads to the passage of x-rays only in short periods by diffracting only when the crystal is passing through the Bragg angle. The width of the rocking curve and the angular speed of the device determine the interval between times that crystal diffracts and associated pulse widths.

We use time-dependent Bragg diffraction to measure the pulse width, Δt_w , often on the order of nanoseconds in length, and gap between pulses, T_g, from which we determine these devices' operating characteristics, specifically, the oscillation amplitude of a fast-moving MEMS device and the minimum possible pulse width. Changing the angle about which the device oscillates compared to the Bragg peak ($\Delta\theta$) changes T_g. T_g along with device's oscillation frequency and Bragg acceptance width allows for the determination of the rotational amplitude. As a function of $\Delta\theta$, the difference in Δt_w between the theoretical and experimental values can be used to determine the dynamic deformation of an oscillating device. The method characterizes the device by following specific reflections, in this case Si (400), and we use this method to determine a device's dependence on operating frequency and drive voltage.

A-62

Modular Designs of K-B Mirror Mount System for X-ray Microfocusing at the Advanced Photon Source

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The Kirkpatrick-Baez (K-B) mirrors are sophisticated x-ray micro- and nano-focusing tools for synchrotron radiation applications. Prototypes of two modular x-ray K-B mirror mounting systems have been designed at the Advanced Photon Source, Argonne National Laboratory. These compact, cost-effective modular mirror mount systems are designed to meet challenging mechanical and optical specifications for producing high positioning resolution and stability for various scientific applications with focused hard x-ray beams down to the 100-nanometer scale.

The optomechanical design of the modular x-ray K-B mirror mount system as well as the preliminary test results of its precision positioning performance are presented in this paper.

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A-63

Hard X-ray Spectrographs with Resolution beyond 100 micro-eV

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Spectrographs take snapshots of photon spectra with array detectors by dispersing photons of different energies into distinct directions and spatial locations. Spectrographs require optics with a large angular dispersion rate as the key component. In visible light optics diffraction gratings are used for this purpose. In the hard x-ray regime, achieving large dispersion rates is a challenge. Here we show that multi-crystal, multi-Bragg-reflection arrangements feature cumulative angular dispersion rates almost two orders of magnitude larger than those attainable with a single Bragg reflection. As a result, the multi-crystal arrangements become potential dispersing elements of hard x-ray spectrographs. The hard x-ray spectrograph principles are demonstrated by imaging a spectrum of photons with a record high resolution of ~ 90 micro-eV in hard x-ray regime, using multi-crystal optics as dispersing element. The spectrographs can boost research using inelastic ultra-high-resolution x-ray spectroscopies with synchrotrons and seeded XFELs.

A-64

A Novel Angular-dispersive Monochromator for Ultra-high-energy-resolution Inelastic X-ray Scattering

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We report design, implementation, and performance of a novel x-ray monochromator for ultra-high-energy-resolution ($DE/E \sim 10^{-8}$) inelastic x-ray scattering spectroscopy using x-rays with photon energies $E \sim 9$ keV where most synchrotron sources deliver maximum brightness. The operating principle of the monochromator is based on the phenomenon of angular dispersion in Bragg back-diffraction [1]. This allows us to achieve a spectral bandwidth substantially smaller than the intrinsic energy bandwidths of Bragg reflections at such intermediate hard x-ray energies.

The optical scheme of the monochromator is a modification of a scheme reported earlier [2], where a silicon collimator/wavelength selector crystal was replaced with a 100 μm thick asymmetric type IIa diamond crystal. Along with the ultrasmall bandpass, this modification provides a three-fold increase in the aperture of the accepted beam, a reduction in the cumulative angular dispersion rate of x-rays emanating from the monochromator for better focusing on a sample, a sufficient angular acceptance matching the angular divergence of an undulator source (~10 μrad), and, an improved throughput due to low x-ray absorption in the thin diamond crystal. The measured spectral bandpass was approximately 0.25 meV and the spectral efficiency of the monochromator was ~ 50% with an aperture of 0.3×1.0 mm^2. The performance parameters of the monochromator are suitable for non-resonant inelastic x-ray spectroscopy with an energy resolution $DE < 1$ meV.

[1] Y.V. Shvyd'ko, M. Lerche, U. Kuetgens, H D. Ruter, A. Alatas, and *J. Zhao, Phys. Rev. Lett.* **97**, 235502 (2006).

[2] Y.V. Shvyd'ko, S. Stoupin, D. Shu, and R. Khachatryan, *Phys. Rev*. A **84**, 053823 (2011).

A-65

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 between beamlines, assists with hardware troubleshooting, and provides EPICS support. The next generation of detectors offered by the Detector Pool could include features such as thicker sensors, larger area coverage, and faster frame rates, and will depend on feedback from beamline staff and users.

A-66

Towards a Dedicated Bio-SAXS/WAXS Beamline at APS

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Solution x-ray scattering has become a major structural tool for biomacromolecular study since the early of 2000s due to the developments in data interpretation methods and technical advances in x-ray area detectors and synchrotron based sources. Consequentially, beam time requests on biomolecular solution x-ray scattering have been continuously increasing at APS. Currently, the APS operates three insertion device small-angle x-ray scattering (SAXS) beamlines: 5-ID, 12-ID, and 18-ID. However, all of these beamlines are shared with other techniques rather than bioSAXS/ wide-angle x-ray scattering (WAXS), such as grazing-incidence small-angle x-ray scattering, diffraction and spectroscopy. Moreover, both 5-ID and 18-ID are CAT beamlines that offer a limited amount of general user beamtime. In order to meet the need of bioSAXS/WAXS community, a dedicated, high-throughput bioSAXS/WAXS beamline has been proposed as a part of the current APS upgrade project. In this presentation, we will overview the current SAXS beamlines at APS and discuss about the early stage ideas of this proposed bioSAXS/WAXS beamline and its capabilities.

Materials Science

A-67

Carbon Fiber Microstructural Characterization Using Synchrotron Wide-Angle X-ray Diffraction

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Carbon fiber exhibits a unique combination of material properties, including high tensile strength and modulus, low weight, high temperature resistance, and low thermal expansion, that has made it an ideal choice as a structural component in light-weight composites for a wide range of applications from aerospace to sports equipment. The unique properties of this material are a direct consequence of its constituent oriented graphene-based microstructure, which is typically obtained commercially through controlled pyrolysis under tension of either polyacrylonitrile or mesophase pitch based precursor fiber. Measurement of the characteristics of this graphene-based microstructure, such as orientation, domain size, and interlayer spacing is thus critical to understanding structure-property-process relationships. This work will describe unique synchrotron-based wide-angle x-ray diffraction capability developed to enable (i) measurement of single carbon fiber filaments, and (ii) observation of microstructural evolution in real time and *in situ* during simultaneous fiber heating and tensioning.

A-68

Component-dependent Response of the Structure of Striped Nanodomains in Weakly Coupled Ferroelectric/Dielectric Superlattices

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Striped polarization nanodomains in ferroelectric/dielectric superlattices arise from the detailed interaction of the polarization, structure, and electronic boundary conditions. Depending on the composition of the ferroelectric and dielectric components, the polarization can be distributed unevenly across different layers. In weakly coupled $PbTiO_3/SrTiO_3$ superlattices, theoretical calculations have predicted that the magnitude of the polarization in dielectric layers is 30–50% of that in ferroelectric layers. This uneven distribution of polarization decouples dynamics of striped domains in each layer and can lead to a component-layer-dependent structural distortion of domains in applied electric fields. Domain x-ray diffraction patterns acquired using time-resolved x-ray microdiffraction agree with a model in which the dielectric layers show larger distortion of domains than the ferroelectric layers. Structural insight into the domains is provided by domain diffuse scattering satellites. The striped domains of a $PbTiO_3/SrTiO_3$ superlattice were transformed into a uniform polarization state at a nanosecond timescale under applied electric fields. The relative intensity of domain satellites changes by a factor of 1.5 during the transformation, indicating a detailed change in the domain structure. A kinematical x-ray simulation shows that the relative intensity changes of domain satellites is linked to a larger distortion of domains in dielectric $SrTiO_3$ layers. After the transformation of domains, the variation of the intensity of the superlattice structural reflections agrees with the existence of a larger piezoelectric distortion in $SrTiO_3$ layers than $PbTiO_3$ layers. Both the layer-dependent polarization switching and piezoelectric distortion are consistent with the initially weaker polarization in $SrTiO_3$ layers.

A-69

In Situ GISAXS Investigation of Pore Orientation Effects on the Thermal Transformation Mechanism in Mesoporous Titania Thin Films

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Titania thin films with vertically oriented cylindrical mesopores have numerous potential applications in photovoltaic cells, electrochemical devices, and photocatalytic technologies due to their accessible cylindrical straight pores, which provide well-defined short diffusion paths for reactants and charge carriers [1]. The Rankin group at the University of Kentucky has established a technique based on Pluronic P123 surfactant templating to synthesize titania thin films with hexagonally ordered cylindrical mesopores tilted orthogonal to the substrate [2]. Results from transmission electron microscopy and scanning electron microscopy indicate that this ideal structure have better thermal stability than the normal parallel films, although the mechanism of this mesostructural stability did not explored in details. This study addresses the effects of mesopore orientation on mesostructural stability and crystallization of titania thin films during calcination based on measurements with *in situ* grazing incidence small-angle x-ray scattering. Complementary supporting information is provided by *ex situ* transmission and electron microscopy. The orientation of the pores at the top surface is controlled by sandwiching another P123-modified glass slide on top of the titania thin film to completely orient the pores orthogonal to the pores in some samples. The results show that when the pores are oriented parallel to the substrate at the top surface (for unsandwiched films), the pore structure is stable upon calcination at 400°C, but that the structure is quickly lost due to crystallization throughout the film during calcination at 500°C. The films with pores oriented orthogonal to the substrate at the top surface (sandwiched films) retain their long-range pore order even after calcination at 500°C. The reasons for this difference are ascribed to greater resistance to anisotropic stress during heating of the orthogonally oriented pores and to titania crystallization nucleation at the top surface of the films with orthogonally oriented pores.

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A-70

Characteristics of an Adaptable Metal Waste Form Containing Technetium

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Multi-phase steel-based alloy waste forms have been developed to immobilize the metallic and technetium-bearing waste streams that may be generated during future reprocessing of used nuclear fuels and have demonstrated advantages for waste streams with components that are difficult to incorporate into alkali borosilicate glass. Production of a metal waste form with metallic wastes from molten-salt electrochemical processing (pyroprocessing) has been demonstrated for sodium-bonded metallic fuels and a similar waste form is expected to be suitable for waste streams from pyroprocessing of used oxide nuclear fuels. The metallic waste form is essentially a direct by-product of the pyroprocessing, and has inspired the development of general-purpose prototype metal waste forms for laboratory testing. Static corrosion tests on the prototype metal waste forms were done to determine the redox behavior of the radionuclides at and near the corrosion interface and their potential incorporation into alteration phases along with the oxidative dissolution and mass transport steps that may limit the release of radionuclides to the bulk water. X-ray absorption spectroscopy (XAS) was done to examine the surface of a metal waste form coupon that had been subjected to 200°C water vapor for 119 days of testing. XAS is a powerful method for determining oxidation states and structural-bonding environments of elements in solids, particularly within challenging radioactive specimens. The penetrating nature of x-rays makes them an ideal probe of specimens that may require levels of containment for safe handling. To this end, a special sample container has been fitted with x-ray windows configured for grazing angle and near-normal incidence and signal collection geometry for variable depth penetration of the signal, the most surface-sensitive geometry allowing sub-micrometer surface penetration. XAS measurements were made at the MRCAT beamline 10-ID at the Advanced Photon Source at Argonne. To achieve the required spectral resolution, we chose a bent-Laue analyzer with a bandwidth of about 150 eV, so that the K-α fluorescence peaks of the 4d-metals were well separated. These data place severe restrictions on the thickness of any surface oxide on the specimen examined, which appears to be less than 6 micrometers of molybdenum oxidized on the surface, while any iron and technetium in this altered layer would appear to be depleted or confined to an even thinner region. These data are presented with a discussion of the general corrosion behavior of the metal.

A-71

Small-angle X-ray Scattering from Multicomponent Borosilicate Glasses and Secondary Minerals

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Aluminoborosilicate glass remains the only waste form for high-level radioactive waste that is currently in production, and will likely be utilized in some form in a closed nuclear fuel cycle. Permanent disposal will require a fundamental understanding of the processes by which the glass dissolves and alters under long-term geological conditions in a disposal system. Glass, being a metastable state of matter, can lower its configurational free energy by transforming into other (usually crystalline) materials. For an alkali aluminoborosilicate glass, such as those considered for nuclear waste storage, contact with fluid water provides a mechanism for ionic and molecular transport, allowing structural rearrangements that lower free energy and introduce chemical potential gradients and ultimately lead to crystallization and phase separation. Licensing of a repository and waste form system will require extensive modeling of these phenomena to ensure compliance with required human health and environmental protection regulation. This modeling, in turn, is dependent upon a consistent theoretical understanding of glass/water interaction based upon experimental evidence.

There are several facets to this problem which are amenable to inquiry using small-angle x-ray scattering (SAXS) as a probe of short- and medium-range structure, especially when coupled with electron microscopy (scanning and transmission). Of particular interest are changes in density fluctuations as multicomponent glasses corrode. During early stages of interaction between glass and water, some components are leached out of the glass in a combined hydration/ion-exchange process that removes highly soluble components such as boron, lithium, sodium, potassium, etc. in exchange with water. Little is known about the structural changes in the surface of the glass during this process, as it is difficult to probe using electron microscopy. Later stages of alteration result in mineralization, and crystalline aluminosilicates and clay minerals start to precipitate or form by direct alteration of relict glass components after extensive hydration and ion exchange. While the mineralization of corroded glass has been extensively studied using microscopy, the use of SAXS allows quantitative analysis of nucleation sites, growth rates, and particle size distribution.

A-72

X-ray Irradiation-induced Colossal Resistance Change in Pt/TiO_2/Pt Cells

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Interaction between x-ray and matters has been drawing much attention due to its scientific interests as well as technological applications. In particular, synchrotron-based x-ray has been used as a powerful diagnostic tool to unveil nanoscale phenomena in functional materials. However, an understanding of how the functional materials respond to the brilliant x-ray is far from complete. Here we report the x-ray-induced colossal resistance change in 40-nm thick TiO_2 films sandwiched by Pt top and bottom electrodes. We observe that the resistance level is modulated in a few orders of magnitude by the intensity of impinging x-ray. In addition, this photovoltaic-like effect can trigger an irreversible resistance change by another few orders of magnitude. We will discuss the physical mechanism behind the emergent phenomenon.

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A-73

Quantification of Crumpling in Graphene Oxide and Other Sheet-like Structures

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Two-dimensional sheet-like nanostructures have garnered significant scientific interest in recent decades, particularly due to their inherent high specific surface areas (SSAs). Such large SSAs also result in an intrinsic tendency to crumple or fold based on surface interactions under ambient conditions. An understanding of the topological details of such structures has revealed various qualitative features driven by thermodynamics and interfacial chemistry. A scaling model based methodology will be presented which can be utilized to do quantitative analysis using small angle scattering data. A wide range of materials like graphene oxide, membrane layers as well exfoliated sheets of molybdenum oxide and tungsten oxide have been investigated to understand how such quantification may yield a general classification of such materials based on crumpling behavior.

A-74

XAFS Analysis on Atomic-layer-deposited Platinum on Polycrystalline Yttrium-stabilized Zirconium Oxide for Intermediate Temperature Solid Oxide Fuel Cell Application

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A key objective in future solid oxide fuel cells (SOFCs) is the reduction of its operating temperature below 500°C. This requires pin-hole-free, sub-micron electrolyte materials for efficient oxygen ion transport without electrical shorting and active redox catalysts on electrode surfaces. Both anode and cathode of the SOFC require high surface area porosity for fuel and oxidant gas transport to the triple phase boundary regions of the cell. To meet these needs, atomic layer deposition is utilized as a unique means of synthesizing both ultra-thin electrolyte layer and porous catalytic electrode on a silicon substrate structure. Here, the platinum metal serves as the redox catalyst and it is directly deposited onto thermally annealed yttrium-stabilized zirconium oxide (YSZ) electrolyte layer within the same atomic layer deposition (ALD) reactor. The ALD nucleation of Pt is significantly enhanced by the thermal annealing of the YSZ creating a mesoporous Pt film ideal for the SOFC application. In this investigation, the L_3 x-ray absorption of Pt at 11,563 eV is examined in fluorescence detection mode providing local bond and chemical state information of the resulting ALD Pt on YSZ under ambient air conditions as well as under reducing (4% H_2 in He at 350°C) and oxidizing (1% O_2 in He at 350°C) conditions.

The x-ray absorption near-edge structure analysis indicates the 2 nm-thick mesoporous ALD Pt on YSZ is about 35-40% oxidized as Pt(II) and 60-65% Pt(0) under either ambient air or oxidized conditions. All the oxidized Pt(II) appears to be on the surface of Pt as it is fully reduced to Pt(0) under gaseous reducing atmosphere. The extended x-ray absorption fine structure analysis indicates Pt-Pt and Pt-O bond distances in the Pt films to be typically 276 pm and 205 pm respectively with Pt-Pt and Pt-O nearest neighbor coordination to be around 11 and 1.8, respectively.

A-75

Structural Analysis and Transport Behavior of Doped Barium Calcium Niobates

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Solid oxide fuel cell (SOFC) is one of the most promising energy conversion devices, where cheap and easily transported hydrocarbon fuels (e.g., CH_4) can be electrochemically oxidized into electricity and heat with efficiency up to 90% [1]. The waste gases, which are rich in CO_2, can be safely sequestrated underground and subsequently chemically transformed back to fuels ($CO_2 \rightarrow CO/CH_4$) by electrolysis when renewable energy sources (solar/wind) are available [2]. Such "hydrocarbon economy" has unique advantages over the "hydrogen economy" in term of its superior energy capacity (≥8 times of H_2) and its utilization of existing infrastructures for economical delivery and storage [2]. However, one of the biggest hurdles for the commercialization of this technology is the stability of the functional catalysis; the active site of the state of the art Ni-YSZ anode is deactivated easily by ppm level H_2S and coke [1].

On the other hand, mixed conductive (O^{2-}, e^- and H^+) oxides are suggested as alternative anodes such that fluorite-based oxides (Ru/CeO_2, Cu/CeO_2, Ni/CeO_2) and simple perovskite-based oxides (Ni/BZCYYb, Sr_2MgMoO_6, $(La_{0.75}Sr_{0.25})_{0.9}Cr_{0.5}Mn_{0.5}O_{3-\delta}$) showed substantially high stability in H_2S (ppm level) contaminated hydrocarbon fuels [3–8]. In addition, the electrochemically active area is found to be well extended to more than 100 μm away from the triple phase boundary where the oxide ion, electron and fuel meet [9]. The impact of the usage of precious metals (e.g., Pt) on electrochemical activity is shown to be insignificant on mixed conductors [9]. Among the mixed conductive electrodes reported, double perovskite-type oxides are relatively less studied, which might be due to the complexity of the system [10–11]. Nonetheless, substitution on both 4a and 4b sites is viable by various cations to modify the physical and chemical properties. In current research, we are reporting our latest systematic study on the substitution of Fe, Mn, Co for Ca/Nb in barium calcium niobates (BCNs), an intermediate temperature (300–600°C) protonic conductor first studied by Nowick et al in 1994 [12]. For the first time, simple perovskite-type phases for the doped BCNs are stabilized. The transport behaviors and chemical stabilities of the two families of compounds will be discussed.

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A-76

In Situ Surface X-ray Diffraction Study of Ruddlesden-Popper Series Thin Film Growth

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The Ruddlesden-Popper series of $SrTiO_3$ and $LaNiO_3$ have attracted much attention as potential materials for solid-oxide fuel cell cathodes and thermoelectrics. To understand the fundamentals of this class of layered oxide thin films, we studied the growth of (001)-oriented Sr_2TiO_4 and La_2NiO_4 on $SrTiO_3$ substrates by using reactive molecular beam epitaxy with *in situ* surface x-ray diffraction at the Advanced Photon Source. For Sr_2TiO_4, the synthesis of the double-SrO layer followed by TiO_2 dynamically reconstructs back into the $SrTiO_3$ phase. Density functional theory confirms the layer stacking energetics favor the experimentally observed restructuring. In contrast with Sr_2TiO_4, the growth of La_2NiO_4 involves the stacking of polar LaO^+ and NiO_2^- layers. This raises the question of how polarity mismatch at the interface with the $SrTiO_3$ substrate will influence the growth process as well as how Nature dynamically handles compensation of the polar surface. A detail comparison of these two cases will be discussed.

A-77

Mesoscopic Membrane Morphology Regulated by Molecular Crystallization

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A grand challenge in self-assembly of multicomponent systems is to control the crystal symmetries and the resulting geometries of co-assembled molecular structures. We generate here crystalline ionic bilayers in a large variety of geometries, which resemble unusual cellular shell shapes, by mixing +3 and -1 ionic amphiphiles. To structurally characterize the co-assembly from the mesoscopic to nanometer scale, we combine electron microscopy with small- and wide-angle x-ray scattering. We use pH to control the degree of ionization of the amphiphiles and hence their intermolecular electrostatic interactions. At low and high pH, closed faceted vesicles with two-dimensional hexagonal molecular arrangements were observed, while at intermediate pH ribbons with rectangular-C packing of the amphiphiles were observed. Thus pH acts as a switch to control the morphology of the ionic bilayers via transitions in the crystalline lattice. This work promotes the design of nanocontainers for various applications and improves our understanding of the origin of polyhedral shells in nature.

A-78

Dynamics of the Competing Spin and Charge Orders in a Layered Manganite $LaSr_2Mn_2O_7$ under Femtosecond Optical Excitation

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We demonstrated a control of the competition between the antiferromagetic metallic phase and the charge- and orbital-ordered insulator phase at the reentrant phase boundary of a layered manganite, $LaSr_2Mn_2O_7$, using ultrafast optical excitation at a photon energy of 1.55 eV. Time-dependent evolution of the Jahn-Teller superlattice reflection, generally accepted as the indicator of the charge and orbital order formation, is measured at different laser fluences. The laser-induced net change in the Jahn-Teller reflection intensity shows a reversal of sign between early (~ 10 ns) and late (~160 ns) delays. The effect is consistent with a scenario that the laser excitation modulates the local competition between the metallic and the insulator phases.

A-79

Nanoscale *In Situ* Full-field Imaging, Fluorescence Microscopy and Nanotomography of Lead-free Solder Bonding

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Demand for high-performance portable electronics has forced the adoption of smaller and smaller integrated circuit packaging with characteristic length scales of only tens of nanometers. Increasingly, small size combined with the push to use environmentally friendly lead-free solders has made precision control of solder attachment and reflow extremely important. We have combined *in situ* nanoscale x-ray fluorescence microscopy, x-ray tomography, and full-field imaging to investigate the melting, solidification, and high-temperature annealing of 10-micron industrial SAC 305 (Sn 96.5wt%, Ag 3wt%, Cu .5wt%) solder balls bonded to copper coated tips. This work was preformed at sector 26 allowing for a 30 nm spatial resolution. This resolution allows for localization of the 3% Ag concentration of the solder relative to faults.

So far, solder bonding studies are usually carried out by annealing or aging the solder joint *ex situ*. This *post facto* analysis of the thickness of intermetallic compounds, void and fault formation is then used to justify solder

composition and reflow profiles. In contrast, our work combines multiple x-ray techniques to track the evolution and change in solder before, during and after reflow and annealing. This has the potential to provide new insights into nanoscale properties of environmentally friendly bonding for consumer electronics.

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A-80

Application of a Pilatus Area Detector to Simultaneous X-ray Diffraction and X-ray Absorption Spectroscopy Measurements

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X-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) are two main x-ray techniques in synchrotron radiation facilities that have been widely utilized in various experiments. A user often measures them one after another on a given sample in order to probe both structural and electronic properties. In this work, we present the application of Pilatus area detector to do XRD and XAS measurements simultaneously. For XRD, the momentum transfer in the specular diffraction was measured by fixing the angles of incoming and outgoing x-rays, while scanning the x-ray energy. By selecting of a region of interest in the Pilatus area detector, the outgoing angle of x-ray can be fixed; during the XRD energy scan, we take advantages of the rest of the area in Pilatus area detector to collect the x-ray fluorescence to do the XAS measurement simultaneously. The key point is to select the angle for the incoming x-ray, which can convert the energy range of x-rays for an XAS measurement to the required momentum transfer in the specular diffraction for XRD. By this unique approach, we demonstrate that the Mn K-edge x-ray absorption near-edge structure spectrum and XRD on thin film $Pr_{0.67}Sr_{0.33}MnO_3$ (002) peak and substrate $LaAlO_3$ (002) peak can be probed simultaneously in a single measurement. This method offers a few advantages. It provides high-resolution XRD due to the high-energy resolution of our monochromator. Since the sample remains static during the measurement, in pump-probe measurements it is easy to maintain the accurate overlap of the x-ray spot and a laser spot. This allows simultaneous high-precision time-resolved XRD and time-resolved XAS measurements.

A-81

Time-resolved *In Situ* X-ray Study of Homoepitaxial $SrTiO_3$ Growth Using Reactive Molecular-Beam Epitaxy

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Functional materials based on complex oxides in thin film form offer new and exciting strategies for meeting many of our outstanding energy challenges. Unfortunately, synthesis of such oxide films can be a major challenge even when utilizing reactive molecular-beam epitaxy (MBE), a powerful deposition technique that is often regarded to allow the construction of materials atomic plane by atomic plane. To understand the fundamental physics of oxide growth by reactive MBE, we have developed world's first reactive MBE system with *in situ* synchrotron x-ray scattering capability at the Advanced Photon Source. Here we present *in situ* surface x-ray scattering results of the homoepitaxial growth of $SrTiO_3$ thin films on (001)-oriented $SrTiO_3$ substrates. We measured the *in situ* x-ray specular reflectivity and surface diffuse x-ray scattering during co-deposition and shuttered-growth of Sr and Ti for $SrTiO_3$ homoepitaxy. The goal of this study was to have a direct comparison of shuttered growth vs. co-deposition to understand the nature of the distinctly different approaches. An area detector recorded both the specular x-ray scattering connected to out-of-plane atomic positions and the diffuse x-ray scattering associated with in-plane correlations at the same time. During growth of $SrTiO_3$ by co-deposition, where the fluxes of Sr and Ti are roughly equal, the specular intensity at the half-order position is at a minimum while the diffuse intensity is at a maximum. This is consistent with a two-dimensional island growth mode with unit-cell-high $SrTiO_3$ islands that nucleate/grow on the terraces and coalesce before the next layer starts. Interestingly, we observe that shuttered growth does not proceed by the nucleation and coalescence of single-layer-high SrO islands, followed by the same for TiO_2. Instead, the scattering indicates that the SrO grows as three-dimensional islands and then restructure into $SrTiO_3$ unit cells during the growth of the TiO_2 to form an atomically flat layer. This shows directly that the process of growth is quite distinct between the two approaches.

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A-82

Interrogating Mesoscopic Dynamics by Optical Pump, Hard X-ray Nanodiffraction Probe Techniques

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Mesoscopic science addresses problems at the length scales where the theory for individual microscopic objects fails to predict the phenomena that arise from the complex inter-object interactions. To fulfill the urgent need to interrogate mesoscopic dynamics in complex materials, we are developing a multi-wavelength optical pump, hard x-ray nanodiffraction probe capability at sector 7 of the Advanced Photon Source. This new capability measures the nonequilibrium dynamics of atomic structure at sub-micron length scales and sub-nanosecond time scales, paving a way to study rich mesoscopic phenomena in the time domain. The initial results have revealed that dynamics of the interaction of optically induced strain in a multiferrloic $BiFeO_3$ thin film upon above-band-gap optical excitation varies between structural mosaic blocks.

A-83

In Situ High-energy X-ray Diffraction Study of a New Class of Nanocomposite Materials with Superior Properties

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Designing and developing new materials with desired properties is always very important and also challenging. Composites made with nanoscale reinforcing materials are promising because the intrinsic properties of nanoreinforcement may be effectively harnessed. However, previous results are far below the expectation due to various reasons. Recently, we have successfully developed a new class of novel nanocomposites with superior mechanical properties, based on a concept of elastic and transforming strain coupling [1]. The new nanocomposite materials consist of metal nanowires homogeneously embedded in transforming shape memory alloys. By proper engineering the structure of the nanocomposites, they can exhibit exceptional properties like high strength with low modules and large elastic strain, which did not exist in a single bulk material before. They have great potential for applications in medical devices and other instruments. In order to understand the underlying mechanism for such superior properties, we need to investigate the atomic-scale structure evolution of the nanowires and shape-memory alloy during deformation, which is difficult for lab x-ray diffraction and other techniques. High-energy synchrotron x-rays have provided great opportunities for structural studies of multiple phases in complex materials under realistic condition and in real time. We have utilized such a powerful technique for *in situ* structural investigations of the nanocomposites during the process of loading/unloading. We found that the metal nanowires exhibit a large elastic strain over 6.5%, and a strong coupling between nanowires and shape-memory alloy matrix [1]. We uncovered the mechanism of the superelasticity of a novel stretchable coaxial NiTi-sheath/Cu-core composite with high strength and high conductivity [2]. We also discovered the origin of the superelastic memory effect in shape memory alloys [3]. The *in situ* observations of the structure evolution and phase transformation have provided the important structure-property information for the in-depth understanding of advanced nanocomposite materials.

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A-84

Structural Analysis of Indium Oxide films doped with Yttrium, Scandium, and Lanthanum

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Transparent oxide semiconductors (TOS)-based thin film transistors have been an attractive research area recently because of their potential use in next-generation flat-panel display systems. Traditional solution-based processing sol-gel method requires high annealing temperature. A new method called "combustion" was reported by the Professor Marks group at Northwestern University, which allows low-temperature synthesis while maintain good electronic properties. A series of Indium oxide films doped with different second cation species (La, Y, Sc) has been deposited on fused quartz substrate and annealed at two different temperatures (250° and 300°). Preliminary x-ray diffraction pattern of these "combustion" synthesized indicated that the larger the cation ionic radii, the more amorphous the films would be. It would be interesting to observe the local structures of these atoms. Therefore, x-ray absorption fine structure measurements have been conducted at sector 5 at APS to reveal the local structures of these amorphous TOS films.

A-85

A Versatile Surface/Interface X-ray Experimental Platform for Advanced Materials Synthesis and Complex Processes in Variable Environments at 12-ID-D of Advanced Photon Source

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A multifaceted experimental platform for *in situ* and real-time surface/interface x-ray studies has been developed and implemented recently at the end station (D-hutch) of sector 12-ID at the Advanced Photon Source. Driven by scientific scopes and technical specifications of various user groups, a modular instrument mounting system which allows for the rapid changeover of different growth chambers, process cells, and sample manipulators has been built to conduct multiple surface/interface x-ray experiments with a single mechanical interface to a standard six-circle diffractometer. The conceptual logics, custom designs, and fulfillment of such experimental stage will be presented briefly in the poster. As flowing, the versatility and capabilities of this platform will be demonstrated with a few full-fledging or ongoing user research projects, such as *in situ* structural determination of polar/non-polar surfaces of various perovskite substrates, and real time growth studies of off-axis magnetron sputter deposition of epitaxial oxide heterostructures, and *in operando* studies of model catalysts and studies of oxygen exchange processes in oxide thin films under controlled electrical and chemical boundary conditions.

A-86

Lens-less Imaging of Atomic Surface Structures Via Ptychography

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We demonstrate by numerical simulation that atomic structures on single-crystal surfaces can be reconstructed using the len-sless ptychography coherent x-ray diffraction imaging (or ptychography CDI). The phase contrast from atomic height variation can be maximized at the anti-Bragg condition. We also show experimentally that real platinum (001) surfaces with atomic steps can be reconstructed, which opens many opportunities, such as *in situ* monitoring of atomic surface structures of single-crystal catalysts in extreme conditions, thin film growth, and nanoscience applications.

Nanoscience & Nanotechnology

A-87

Voltage Tuning of Two-dimensional Nanoparticle Superlattices at an Electrified Liquid/Liquid Interface

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Nanoparticle superlattices have applications in plasmonics, electro-voltaic devices, catalysis, and chemical sensing. Although numerous chemical and physical routes have been developed for preparing nanoparticle superlattices, it is hard to tune their structure after fabrication. We use x-ray surface scattering at ChemMatCARS APS sector 15-ID to demonstrate voltage tuning of a charged nanoparticle superlattice. The superlattice is formed at the interface between two immiscible electrolyte solutions. Tuning the electric potential difference across the interface varies the lattice parameters and the interfacial depth of the nanoparticles. Preliminary atomistic molecular dynamics simulations on a single charged nanoparticle at the liquid/liquid interface suggest that the depth variation is due to the stronger affinity of counter ions present in the lower permittivity phase. These observations provide new insight into understanding nanoparticle interactions at electrolyte interfaces.

A-88

Stimulus-responsive Superlattice Assembled and Tuned by Polymer

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Tailoring the interaction between nanoparticles is crucial for controlling the self-assembly. Among many types of interactions, the depletion interaction that arises by adding polymers in the solution of nanoparticles has recently been of interest. We found that when the polymer is rigid it can induce an assembly through not only the depletion but also the mechanism that is to maximize the free volume entropy of the system. These two mechanisms yield a nanorod's superlattice with a wide range of lattice parameters from one up to five times its diameter, which so far hasn't been achieved with mechanisms other than the DNA interaction. In addition, by tuning external stimulus like temperature, the lattice parameter of superlattice can be reversibly controlled; it can expand or contract with increasing temperature depending on the type of polymer selected. We believe this study reported here will have broad and significant impact on the studies of self-assembly process and materials development.

A-89

Probing Large-wavevector Phonons in Two-dimensional Nanostructures Using X-ray Thermal Diffuse Scattering

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Vibrational phenomena play an important role in the thermal and electronic properties of nanoscale systems, particularly in technologically important systems like silicon- and silicon-germanium-based nano- and thermoelectrics. Large wave-vector phonons in silicon nanostructures dominate the thermal conductivity and affect electron mobility through intervalley scattering of conduction electrons. Improved fundamental understanding of vibrational phenomena is crucial in enabling the engineering of these properties in nanoscale systems. These technologically important large wave-vector modes have eluded experimental observation in nanoscale systems due to the sample size restrictions of conventional bulk characterization techniques such as inelastic neutron or x-ray scattering. Optical techniques capable of measuring vibrations in these small systems suffer from a fundamental mismatch between visible photon momentum and phonon wave-vector. As a result, experimental measurements have probed only the small wave-vector modes near the center of the Brillouin zone.

Synchrotron thermal diffuse x-ray scattering (TDS) is sensitive to thermally populated phonon modes with wave vectors spanning the entire Brillouin zone. This technique allows measurement of previously unobserved large wave-vector modes in nanoscale systems. 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. The experiments yield information about the population and dispersion of acoustic phonons in silicon nanomembranes throughout the entire brillouin zone, in samples with thicknesses of 97 and 21 nm, and in high-symmetry directions, in samples as thin as 4 nm. The first measurements of phonons in Si-SiGe-Si trilayer structures are also performed. Deviations consistent with a modified phonon occupation resulting from the finite size effects applicable to low-energy acoustic modes in nanoscale structures are observed.

A-90

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

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Traditional scanning probe microscopes with angstrom-scale resolution provide in-depth understanding of surface states and interactions. The combination of low-temperature scanning tunneling microscopy (LT-STM) and synchrotron-based x-rays is capable of analyzing chemical interactions, magnetic spin states, and electronic properties on surface at high spatial resolution. Here, we will present the ongoing development of an LT-SXSTM, which is LT-STM with synchrotron x-ray capability. This new system is based upon two prototype instruments, which have been designed and built in our group [1, 2]. The new system features a low-noise, high-stability compact STM and a liquid helium flow cryostat mounted on a stage with four degrees of freedom. In addition, finite element heat transfer simulations were performed to validate thermal shielding and isolation of the STM design.

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A-91

Time-resolved EXAFS and XANES Analysis of Pt Nanoparticle Synthesis at the Atomic Cluster to Nanocrystal Transition

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We have recently discovered a previously unknown Pt structure that exhibits substantially enhanced electrocatalytic oxygen reduction reaction (ORR) [1] and ethanol oxidation reaction (EOR) [2] activity relative to state-of-the-art commercial systems. This new Pt structure exists as a tightly packed but non-crystallographic assembly of atoms that bridges the transition from atomic clusters to single-crystal nanoparticles. Such a novel arrangement of Pt atoms presents an opportunity for new research across a range of fields including magnetics [3], electrocatalysis [1, 4, 5], optics [6, 7], and selectivity in gas-phase synthesis [8]. The synthesis technique we have developed to produce this transitional structure has been shown to yield fine discrimination of particle sizes with small standard deviations and permits systematic, well controlled alteration of bulk atomic structure (as observed using HAADF-STEM). We have recently used these well-defined nanoparticles to demonstrate that the enhanced ORR catalytic activity in this size region on Pt-only catalyst is due to the high density of stepped surface active sites. We are currently extending this synthesis technique to non-Pt metals that have been shown to enhance several different electrochemical, surface-sensitive reactions including ORR, EOR, and vanadium oxidation/reduction. Control over nanoparticle size and structure for Pt depends upon the formation of an initial complex with $SnCl_3^-$ ligands [9]. Here we demonstrate the formation of different Pt-$SnCl_3^-$ complexes and their destruction during Pt reduction, particle nucleation, and growth as a prelude to investigating other metals. The need for this information is common to all nanoparticle synthesis methods but has only recently begun to be addressed through experiment using time-resolved, *in situ* x-ray absorption spectroscopy (XAS) data [10-13].

The paucity of *in situ* data is due to two experimental requirements: 1) a reproducible synthesis scheme that produces monodisperse particles with sufficiently slow nucleation and growth to separate the stages of particle evolution; and 2) an *in situ* monitoring method that does not alter the growth mechanisms [13-15]. Instead, laborious trial-and-error experiments have previously been used to determine optimum synthesis conditions for a given nanoparticle shape, size, and distribution. Time-resolved examination of evolving metal coordination and oxidation state for greater mechanistic insight can be facilitated by synthesis methods with more gradual but distinct particle nucleation and growth steps. In this study, we present a detailed analysis of XAS data obtained during the autocatalytic reduction of a Pt-Sn complex in aqueous solution to form stable, monodisperse nanoparticle suspensions without the use of organic surfactant. We here show the evolution of Pt valence and coordination from an initial complex and correlate this with specific growth phases previously identified using time-resolved, *in situ* SAXS/WAXS measurements [9]. We show the generation of critical nuclei as hypothesized by LaMer [16] from absorption data. Our results suggest that particle size control is achieved through non-specific $SnCl_2$ ligand binding. This work provides fundamental correlations between synthesis conditions, growth mechanisms, initial complex geometry, particle size, metal coordination, metal valence, number density, and polydispersity that may be extended to other catalytic materials of interest.

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A-92

Magnetic-field-induced Assembly of Core-shell Magnetic Nanostructures by Ultrasmall X-ray Scattering (USAXS) and Transmission Electron Microscopy

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Magnetic-field-assisted self-assembly of clusters of silica/magnetite core-shell magnetic nanoparticles have been studied using the USAXS technique. The self-assembly in the colloidal form of these hybrid nanostructured clusters is found to be dependent on the strength of external magnetic field. *In situ* characterization of colloidal suspension of these nanoparticles under uniform magnetic field was performed in two directions, namely orthogonal and parallel direction to the x-ray beam. It is observed that dipolar chains of magnetic nano-entities arranged themselves into two-dimensional magnetic sheets. The investigation of core-shell nanoparticles using scattering techniques, Transmission electron microscopy and subsequent structure factor calculation suggest that the lattice parameters of a super lattice can be tuned by changing the strength of external magnetic field.

A-93

Development of a Fast Strip Readout X-ray Detector

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This project aims at designing a fast linear strip x-ray detector optimized for x-ray photon correlation spectroscopy measurements. This detector will provide readout 1000 times faster than current strip or area detectors and 256 times more solid angle than equivalent point detector systems. Twenty-four bunch mode, 153 ns camera readout will be achieved by coupling every pixel to its own lower level discriminator circuit using an application specific integrated circuit (ASIC), and through real-time data compression using circuit board digital logic. The ASIC will be fabricated in AMI Semiconductor's 0.5μm C5 process. The custom silicon sensor will be fabricated at Northern Illinois University's Microelectronics Research and Development facility.

A-94

Use of the Bionanoprobe to Track the Subcellular Distribution of EGFR-targeted Fe_3O_4@TiO_2 Nanoparticles

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The epidermal growth factor receptor (EGFR) is overexpressed in several epithelial-derived cancers and plays an important role in tumorigenesis. Our goal is to utilize the nuclear translocation of EGFR to deliver DNA-cleaving Fe_3O_4 core-TiO_2 shell (Fe_3O_4@TiO_2) nanoparticles (NPs) to the nucleus of EGFR-expressing cancer cells. We have conjugated epidermal growth factor (EGF)-derived peptides to the surface of 6–7 nm Fe_3O_4@TiO_2 NPs to create EGFR-targeted NPs (B-loop NPs) and showed that these NPs can bind EGFR as well as the nuclear transport protein importin-β. We determined by flow cytometry that these EGFR-binding NPs are internalized better than NPs carrying a scrambled control peptide (Scrambled NPs). In order to track the subcellular distribution of EGFR-targeted NPs we used the Bionanoprobe at sector 21-ID-D to obtain high-resolution x-ray fluorescence maps of Ti and Fe within cells. The cryogenic capabilities of the Bionanoprobe allowed us to scan frozen-hydrated cells that retain their three-dimensional conformation. Furthermore, we were able to rotate cells over a range of 144 degrees on the Bionanoprobe. These Bionanoprobe derived x-ray fluorescence microscopy images of cells treated with B-loop NPs or Scrambled NPs showed that only B-loop NPs localized to the nucleus of EGFR-expressing HeLa cells. Lastly, we determined using a Comet Assay that cells treated with nuclear-localizing B-loop NPs generated significantly more double-stranded DNA breaks than cells treated with Scrambled NPs after exposure to ultraviolet irradiation. Therefore by using a single EGFR-binding ligand to achieve both cellular and nuclear delivery this targeting strategy could allow for the delivery of genotoxic drugs or NPs to the most aggressive and drug-resistant EGFR-expressing cancer cells.

Other

A-95

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

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Large-scale implementation of manmade 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 ($2H_2O \rightarrow O_2 + 4e^- + 4H^+$) in photosystem II (the trans-membrane metalloprotein complex responsible for splitting water in the photosynthetic process) requires a catalyst, the oxygen-evolving complex (OEC) Mn_4Ca cluster. Characterization of sub-millisecond reactive intermediates in this system is central to understanding the catalysis involved in water splitting. We present results from two different x-ray spectroscopy techniques.

1. *X-ray emission spectroscopy* (XES) is an informative technique for the analysis of the oxidation and spin states of the Mn center, as well as its ligand environment. [1] Following the progression of x-ray–induced damage by Mn Kβ x-ray emission spectroscopy, we demonstrate the feasibility of collecting room-temperature (RT) data on the electronic structure of the S-states of photosystem II. Two different beam structures were tested during

these measurements: continuous monochromatic beam (at 20-ID), and pulsed pink beam (22 μs pulse width, at 14-ID). The dosage/damage relation for continuous beam measurements matches preliminary RT models well; [2] the XES spectral shape obtained at RT and low T are similar, indicating that no significant charge redistribution is happening within the OEC upon freezing photosystem II. [3] The determined damage threshold (~100 ms for continuous monochromatic beam; ~100 μs in pulsed pink beam mode) is sufficient for the analysis of electron dynamics and the catalytic mechanism. The reported timeframes are expected to be representative of other metalloproteins. In addition, we present preliminary time-resolved Kβ emission laser pump, x-ray probe experiments conducted in pulsed pink beam mode (in which the pump phase advances the catalytic cycle to the subsequent S-states: S_2, S_3 and S_4).

2. *X-ray absorption spectroscopy* (XAS) is also sensitive to the oxidation state of Mn (x-ray absorption near edge structure [XANES]), but in addition, can provide structural information such as bond lengths and ligand identities from directly around the Mn atoms (x-ray absorption fine structure [EXAFS]). We present results indicating the RT structure of photosystem II in comparison to those at LT. In addition, EXAFS was performed on S_2, S_3, and S_4/S_0 samples frozen on millisecond timescales in the hopes of catching short-lived intermediate states.

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A-96

Reducing Complexity: Applying Non-negative Matrix Analysis to X-ray Spectromicroscopy

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In x-ray spectromicroscopy, the problem of resolving a sample of mixed chemical states into individual components is of interest in fields from biochemistry to environmental science. Analytical methods such as principal component analysis (PCA) and cluster analysis have been used to resolve components, but produce unphysical regions of negative sample thickness. To counter this, we employ the method of non-negative matrix approximation (NNMA), which factors the optical density of the sample into its chemical components and thicknesses, constraining both to be non-negative. Compared to PCA and cluster analysis, NNMA is able to result in more accurate identification of states within the sample We also show that the addition of constraints (such as sparseness of the thickness matrix) to the NNMA algorithm further improves performance.

A-97

Characterization of Ultrananocrystalline Diamond Zone Plates with Comparison to Simulation

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Characterizing hard x-ray focusing optics is a vital step during optics development to establish the performance characteristics of the optic. Zone plates are diffractive optics capable of focusing x-rays to the scale of the outer most zone width, which can be less than 100 nm using lithographic fabrication techniques. Hard x-ray zone plates commonly behave as phase zone plates where the zones apply a phase shift to the incoming beam to add in phase at the same foci as the transparent zones. Focusing efficiency of phase zone plates is a function of the zone thickness, material, and energy [1], and the thickness will most likely be greater than 1 μm for peak efficiency. The combination of thick zones with a small zone width leads to high-aspect-ratio structures requiring advanced material and techniques for fabrication. In this research, ultrananocrystalline diamond (UNCD) was used as an electroplating mold material. The fabrication process involves electron beam lithographic patterning of a mask material that is used during pattern transfer into the UNCD [2]. The resulting mold is then filled with electroplated Au creating a phase zone plate with alternating Au and UNCD zones. The fabrication method was chosen to increase focusing efficiency for sub-100 nm resolution zone plates but the efficiency and resolution must be measured. Characterization data of the fabricated zone plates will be presented and compared with simulated zone plate models. Resolution was measured using an overlay technique while efficiency was measured by comparing intensity of focused light to illuminating intensity. The simulation used was a free-space propagation technique using the Helmholtz transform to speed up calculation [3]. The simulated spot size and efficiency will be compared with calculated resolution and measured efficiency. Application of fabricated zone plates and possible future work will be discussed as well.

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Polymers

A-98

Investigating Morphology in Ion Exchange Membranes under Changing Environmental and Strain Conditions Via *In Situ* SAXS

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Our team has developed a specialty in probing the morphology changes ion exchange membranes undergo during water absorption via *in situ* small-angle x-ray scattering (SAXS). The unique capabilities of the synchrotron at the

Advanced Photon Source in sector 12 allow us to perform x-ray scattering using a custom-built oven to control temperature and relative humidity conditions. A number of novel proton and anion exchange membranes systems have been studied yielding several publications. This poster will highlight some of the work done with perfluorinated sulfonic acid ionomers (PFSAs) [1], polystyrene-block-poly(vinyl benzyl trimethylammonium) anion exchange membranes [2], and polyethylene-block-poly(vinyl benzyl trimethylammonium) anion exchange membranes. In addition to humidity studies, our group has recently used SAXS to investigate structure change under extensional strain using a Sentmanat extensional rheometer. Our group has proven structural change in ionomers under varying water content and strain can be explored and quantified using x-ray scattering. The experimental work is in conjunction with theory work to elucidate the mechanism for ion transport.

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A-99

Experimental and Simulation Study of Agglomeration Dynamics in Thermo-sensitive Polymers across the Lower Critical Solution Temperature

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Stimuli-sensitive linear polymers can respond to surrounding environmental changes such as electric field, pH, temperature, light, and ion concentration, which can lead to change in their conformations. Poly(N-isopropylacrylamide) (PNIPAM), a classical thermo-sensitive polymer, has a lower critical solution temperature (LCST) at ~32°C. PNIPAM are soluble in water and they exhibit phase transition behavior below the LCST. If the concentration of PNIPAM is >1 ppm then polymer chains undergoing coil-to-globule transition above the LCST will aggregate to yield a stable colloidal dispersion. Experimentally, a narrow size distribution of spherical particles has been observed when a dilute PNIPAM solution was heated above the LCST. The size of the mesoglobules was found to be unaffected by the molecular weight (MW).

We present result of our preliminary investigation of the mechanism of agglomeration in detail by combining real-time, *in situ* small-angle x-ray scattering (SAXS) measurements with atomistic simulations of the polymer collapse and mesoglobule formation. We have performed out SAX experiments at the Advanced Photon Source at Argonne National Laboratory to study the aggregates at quasi-equilibrium states and their formation process with kinetic measurements. We used pulsed IR-laser to heat the aqueous polymer-sample locally and simultaneously probe the change in size of polymer at the same spot. The laser heating time and x-ray acquisition were synchronized with synchrotron x-ray bunches. We have also performed atomistic molecular dynamics (MD) simulations of the PNIPAM-water system to study the mechanism and dynamics of agglomeration of the oligomers of PNIPAM both below and above the LCST. The effect of the temperature on the nature of aggregates formed and conformation of the PNIPAM chains were also studied using MD simulations. The simulations were carried out below and above the LCST, namely at 278 and 310 K. Simulated trajectories were analyzed for structural and dynamical properties of both PNIPAM and water. The atomic trajectories and agglomerate morphologies obtained from MD simulations were used to compare with SAXS experimental results. These simulated SAXS curves compared with the experimentally obtained curves to validate the conformations and morphology from MD simulation and further to understand the process of agglomeration of PNIPAM chains at different temperature.

Technique

A-100

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 small-angle x-ray scattering (SAXS), small-angle neutron scattering, electron or optical microscopy, tomography, etc. In this context, the Bonse-Hart type ultra-small-angle x-ray scattering (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 wide-angle x-ray scattering (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 eight minutes. The talk will present the technical design and capabilities of this instrument, as well as scientific examples taking advantage of this unique instrumentation.

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A-101

Generation of Acoustic Pulses from a Photo-acoustic Transducer Measured by Time-resolved X-ray Diffraction

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The phonon Bragg switch is a potentially efficient and inexpensive method of generating picosecond x-rays from third-generation hard x-ray synchrotron sources [1]. This method uses a high-wavevector coherent phonon to modulate the intensity of a hard x-ray beam on a picosecond timescale, making it possible to significantly enhance the time resolution of third-generation sources. In this work, we aim to generate an acoustic phonon Bragg switch of hard x-ray radiation by directly printing a high-wavevector metallic grating onto a crystalline substrate. This method has recently been used to generate an acoustic phonon switch of ultraviolet radiation [2] as well as generating high-wavevector coherent optical phonons in bismuth films [3].

As a preliminary step of building and characterizing the acoustic phonon hard x-ray switch, we have investigated the generation of acoustic pulses from thin gold films on crystalline substrates, using time-resolved x-ray diffraction. We utilize synchrotron x-ray pulses to observe strain generated by optical excitation of a gold film on a (111) germanium substrate. The resulting optical pump/x-ray probe spectra reveal that the spatiotemporal structure of the acoustic pulse is bipolar with acoustic wave-vectors up to inverse of the film thickness [4]. Future experiments at the APS will investigate the realization of the acoustic phonon Bragg switch for time-resolved x-ray studies.

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A-102

Characterization of X-ray Optics and Beam Wave Front Using Single-grating, High-speed Interferometry

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We present the x-ray grating interferometry measurements performed with a single-grating spatial harmonic imaging technique. Application of this technique for grating interferometry measurement enables data acquisition at relatively high speed compared to other grating interferometry measurement modes. The measurements were performed using both one-dimensional and two-dimensional gratings at the 1-BM-B beamline of the APS. We will present the measurement of the coherence property of the monochromatic x-ray beam passing through the beamline optics and the Si double-crystal monochromator. The important application of this technique would be for high-speed wave-front sensing and correction (adaptive optics).

Use of the Advanced Photon Source and Center for Nanoscale Materials, Office of Science User Facilities 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.

A-103

tomoRecon: High-speed Tomography Reconstruction on Workstations Using Multi-threading

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Computers have changed remarkably in just the last two to three years. Memory is now very inexpensive, as little as $10/GB or less than $1000 for 96 GB. Computers with eight or 12 cores are now inexpensive, starting at less than $3,000. This means that affordable workstations are in principle now capable of processing large tomography datasets. But for the most part, tomography reconstruction software has not changed to take advantage of these new capabilities. Most installations use clusters of Linux machines, spreading the work over computers running multiple processes. It is significantly simpler and cheaper to run a single process that spreads the job over multiple threads running on multiple cores.

tomoRecon is a new multi-threaded library for such tomography data reconstruction. It consists of only 545 lines of C++ code, on top of the ~800 lines in the Gridrec reconstruction code. The performance using tomoRecon on a single modern workstation significantly exceeds dedicated clusters currently in use at synchrotron beamlines. For example, tomoRecon running on a single Windows 7 workstation that costs about $6,000 is can reconstruct a [2048, 2048, 1500] tomography data set in two minutes, which is 20-times faster than the $70,000 Linux cluster used at beamline 2-BM.

tomoRecon is available on web for anyone to use. The home page is http://cars9.uchicago.edu/software/epics/tomoRecon.html. The documentation is available at http://cars9.uchicago.edu/software/epics/tomoReconDoc.html.

A-104

Addressing the Data Challenge in X-ray Microscopy: Towards Unsupervised Analysis

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X-ray fluorescence microscopy is a powerful technique to map and quantify trace element distributions in biological specimens. It is perfectly placed to map nanoparticles and nanovectors within cells at high spatial resolution. Advances in instrumentation, such as faster detectors, better optics, and improved data acquisition strategies are fundamentally changing the way experiments can be carried out, giving us the ability to more completely interrogate samples at higher spatial resolution, higher throughput, and better sensitivity.

Yet one thing is still missing: the next generation of data analysis and visualization tools for multidimensional microscopy that can interpret data, identify and classify objects within datasets, visualize trends across datasets and instruments, and ultimately enable researchers to reason with abstraction of data instead of just with images. We will present first steps we have taken towards increased automation in data analysis. Specifically, we developed an unsupervised framework to locate, identify, and distinguish cells based on their individual elemental content derived from x-ray fluorescence datasets. We start by thresholding pixels into foreground/background components based on their elemental content, and then obtain an initial guess of the cells based on segmentation of the foreground pixels. We then use a generalized likelihood ratio test to improve the cell configurations and to refine these putative cell areas with respect to the multiple elemental distributions simultaneously. One of the strengths of this algorithm is its ability to identify and distinguish even overlapping objects. We will demonstrate the approach on a three-cell type test dataset we acquired at beamline 2-ID-E of the APS. In this dataset, we identified around 320 cells with several regions of strong overlap. In addition, we will also show the robustness of this framework with respect to variations of input parameters.

A-105

Advances in 3D X-ray Microdiffraction at Sector 34

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Beamline 34-ID-E of the Advance Photon Source provides a submicron-sized (<500 nm) x-ray beam through K-B mirror focusing. The availability of both monochromatic and polychromatic (7–30 keV) beams allows a wide variety of structural analysis in crystalline materials, with three-dimensional (3D) spatial resolution provided by scanning a calibrated differential aperture. Recent advances feature the implementation of slew-scanning capability for efficient data collection during depth-profile scanning. The much-enhanced data acquisition rate (>500%) allows 3D mapping of material microstructures over larger volumes and shorter time periods.

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A-106

Investigating Silver-ion-exchanged Zeolites Using Simultaneous Pair Distribution Function and Infrared Spectroscopy Techniques

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Noble metal silver in multiple forms of silver species including cationic Ag^+, $Ag_n^{\delta+}$ clusters, supported Ag nanoparticles, and Ag_2O [1–4] has shown important catalytic activity promoted by H_2 [5]. Zeolites do not only provide the well-defined pores and channels to control and isolate specific Ag species, but their surface chemistry and the extent of ion-exchange also impact activity and selectivity [6]. In the current case, a recent study [7] has quantitatively delineated the structures and kinetics of Ag species during reduction using pair distribution function (PDF) methods. However, total x-ray scattering has no intrinsic sensitivity to molecular functionality. Therefore, combining this x-ray method with diffuse reflection infrared Fourier transformed spectroscopy (DRIFTS) will provide comprehensive structural information and surface chemistry evolution for silver-ion-exchanged zeolites upon dehydration and reduction. Combination of simultaneous PDF and DRIFTS techniques can provide both structural information for the solid state of heterogeneous catalysts and surface functional group information for surface chemistry.

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Upgrade

A-107

The Short-pulse X-ray Imaging and Microscopy (SPXIM) Beamline

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The short-pulse x-ray imaging and microscopy (SPXIM) beamline is one of the two hard x-ray beamlines that will take full advantage of the short pulse x-ray source in the Advanced Photon Source (APS) Upgrade. It is a new beamline that will offer two instruments: a time-dispersed diffractometer and a nanoprobe/microscope.

A horizontally diffracting double-crystal monochromator, which includes a sagittally focusing second crystal, will collect most of the photons generated when the chirped electron beam traverses the undulator. A Kirkpatrick-Baez mirror system after the monochromator will deliver to the sample a beam that has an approximately linear correlation between time and vertical beam angle. The expected time resolution of the whole system is 2.6 ps at 10 keV, and the total flux expected at the sample position is 5.7×10^{12} photons/s with a horizontal and vertical spot size respectively of 33 μm by 14 μm full width at half maximum. This new beamline will enable novel time-dispersed diffraction experiments on small samples using the full repetition rate of the APS. It will instrumented with a diffractometer and high-resolution detector to resolve spatially the time-angle correlation. Sample excitation will be provided by a versatile suite of femtosecond laser excitation sources with up to 6.5 MHz repetition rate (x1300 from existing repetition rate), with wavelengths from 0.2–20 microns. The laser infrastructure will also deliver laser beams to the short-pulse x-ray scattering and spectroscopy beamline.

The second instrument will use the optical aperture set by zone plate optics to deliver a short x-ray pulse on a time-resolved nanodiffraction set up excited by the high-repetition rate lasers. The small vertical source size of SPXIM on 6-ID (15 μm RMS) enables sub-100 nm focusing, with 2.6 ps time duration. Both instruments will provide unique capabilities at a third-generation synchrotron for the study of complex materials and nanoscale devices on time scales relevant to today's technology.

A-108

The Short-Pulse X-ray Scattering and Spectroscopy (SPXSS) Beamline

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The short-pulse x-ray scattering and spectroscopy (SPXSS) beamline is an upgrade of the existing 7-ID beamline using the slitted beam from the time-angle correlated x-rays generated by the short-pulse x-ray RF crab-cavities. It will provide hard x-rays from 5–35 keV with a variable pulse duration controlled with a vertical slit down to 2 ps (a factor 40 less than today). A choice of two monochromators will provide energy bandwidths of 0.01 and 1%. An x-ray chopper opening at the ring revolution frequency (272 kHz) allows one to change the repetition rate for samples that do not recover in 153 ns. New Kirkpatrick-Baez mirror optics capable of producing ~5 microns x-ray spot sizes with a monochromatic beam will be used. An upgraded diffractometer in 7-ID-C and two pixel array detectors will enable a suite of x-ray diffraction, scattering, and spectroscopy techniques for an oversubscribed beamline often time-resolution limited.

A-109

The High-flux Pump-probe 14-ID Beamline Upgrade

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The 14-ID beamline is part of BioCARS, a national user facility for synchrotron-based time-resolved research and an integral part of the multidisciplinary Center for Advanced Radiation Sources at the University of Chicago. With the ability to isolate a high-flux, single x-ray pulse with a duration of 100 picoseconds, the 14-ID beamline provides unique capabilities at the APS. In partnership with the APS, BioCARS is actively broadening its scientific scope to include both physical science and biological time-resolved research. This poster describes the APS-U project enhancements to the beamline that will enable cutting-edge science on irreversible systems and allow for the implementation of complex sample environments.

A-110

Resonant Inelastic X-ray Scattering Beamline

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The resonant inelastic x-ray scattering (RIXS) program at the APS is one of the leading efforts of its kind in the world. Its main focus is on studying correlated electron systems in novel materials of great scientific and technological importance, including complex metal oxide compounds and other electronically active substances such as graphene. The proposed upgrade will make possible entirely new contributions in the domain of "real materials in real conditions in real time" by virtue of substantially improving the energy resolution of the technique, increasing the incident flux and experimental throughput of the RIXS facility, and enhancing the spectrometer with polarization analysis and various extreme and *in-situ* sample environments. Emphasis will be placed initially on 5d-TMOs, such as iridates and osmates, which recently have emerged as materials with great promises.

A-111

Revolver Undulators

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Revolver undulators are being developed that provide two different period undulators in the footprint of a single device. They allow higher x-ray brightness over a broader energy range than a conventional planar undulator with a single magnetic period.

The APS Upgrade will push the forefront of this new technology that provides a long-term path forward to even higher flux and brightness.

A-112

Hard X-ray Magnetic Spectroscopy

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The high penetration power and polarization tunability of synchrotron radiation make x-ray absorption/dichroism techniques in the hard x-rays premier tools for *in situ* characterization of electronic structure and magnetism at extreme pressure conditions. The APS upgrade will enable these experiments to be carried out at pressures beyond 1 Mbar under simultaneous high magnetic field (10 tesla) and low-temperature (2 K) conditions. Upgrades to the x-ray optics, instrumentation and experimental enclosure enabling these new capabilities are described. Furthermore, the installation of an Apple-II insertion device will allow for full polarization control directly at the source resulting in large gains in flux and degree of polarization relative to phase retarding optics. The Apple-II device will also allow studies of element-specific magnetism in *4d* and *5f* systems in addition to the more "conventional" *3d* and *4f* systems, using both x-ray magnetic circular and linear dichroism techniques.

A-113

Advanced Spectroscopy and LERIX Beamlines

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The advanced spectroscopy and lower-energy-resolution inelastic x-ray scattering (LERIX) beamlines (ASL) are a canted undulator upgrade to the current 20-ID beamline, and a relocation of these programs to 25-ID. They will provide separate branch lines optimized for the two primary programs currently at 20-ID. The first branch is a microprobe-based beamline supporting micron-scale fluorescence mapping, micro-x-ray absorption near-edge structure and extended x-ray absorption fine structure, x-ray emission spectroscopy, and x-ray absorption spectroscopy on ultradilute samples. It will provide variable spot size focusing (typically 2–20 micron) capable of collecting the entire undulator beam at the larger spot sizes. It will also have a full complement of miniXS detectors for emission spectroscopy, as well as wavelength dispersive analyzers for ultra-dilute samples. The LERIX branch will support the LERIX spectrometer(s) and the ultrahigh vacuum chambers being operated by our Canadian collaborators through the PNCSRF. The LERIX spectrometer provides q-dependent high-resolution (<1 eV) detection of non-resonant inelastic scattering. To support this, the beamline will provide a variable energy resolution using a secondary monochromator, and KB mirror focusing down to 10 micron to support high-pressure studies using diamond anvil cells. Design of the LERIX-2 spectrometer upgrade will also be presented.

A-114

Horizontal Cavity Testing of a Dressed SPX0 Cavity: CCA3-1

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The short-pulsed x-ray (SPX) project calls for the use of an RF deflecting-mode cavity to chirp electron bunches, giving the electrons a correlation between their longitudinal position in the bunch and their vertical momentum. Synchrotron light produced from this bunch can then be passed through a physical slit to create a shorter light pulse at the proportional sacrifice of total flux. This scheme was first proposed by Zholents.

The current design is a squashed elliptical dipole-mode cavity with a Y-shaped end group and an on-cell damping port. Two of the waveguides from the Y end group will be used for damping of higher-order modes while the third will be used as the forward power coupler. The on-cell damper is used to damp the fundamental mode, called the lower-order mode. The helium vessel is welded to the cavity and waveguides to hold the liquid helium inventory around the cavity while allowing the cavity to be tuned by mechanical action.

This was the first combination test of much of the SPX hardware, including tuner, low-level/digital RF control system, and the 5 kW amplifier. Many of these components had been bench tested separately, but never used together. The goal of this test was to validate their performance as a complete system. In addition to this, the cavity RF performance, thermal properties, and mechanical stability were all topics of study.

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A-115

X-ray Interface Science Beamlines

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X-rays offer a unique opportunity to penetrate many complex environments to probe the structure and chemistry of surfaces and buried interfaces. These interfaces between media with distinct physical and chemical properties offer exciting possibilities for discovery in diverse scientific areas such as catalysis, oxide film growth, semiconductors, geochemistry, surface physics, biomembranes, corrosion, nanoscience, environmental science, tribology, and electrochemistry. By its very nature, interfacial science brings together a diverse community with interests in catalysis, biomembranes, oxide film growth, semiconductors, geochemistry, surface physics, corrosion, nanoscience, tribology, electro-chemistry, and in the development of the next generation of energy-related technologies. One of many grand challenges in this interdisciplinary field is to understand through observation and control the organization of atoms and molecules at well-defined surfaces in complex environments. Increasingly sophisticated *in situ* x-ray methods that exploit the inherent spatial, temporal, and spectral properties of undulator radiation are being developed to meet these challenges. A dedicated x-ray interfacial science facility at a sector of the APS will fully exploit the unique capabilities of the APS to advance our understanding of this area.

A-116

First Experience with Superconducting Undulator at the APS

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The first test superconducting undulator, SCU0, was installed in the APS storage ring in winter 2012-13 shutdown. After a short and successful commissioning the device was employed as a standard user device. The first experience of operating such a novel device at the APS is presented including the undulator cryogenic behaviour as well as its effects on the machine operation, and the first experience of using the device in Sector 6.

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A-117

Fast-switching Variable-polarizing Undulator

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Development of a new fast-switching electromagnetic variably polarizing undulator (EMVPU) is underway at the Advanced Photon Source (APS). The EMVPU will be capable of producing x-rays with a variety of polarizations, including left- and right-circular, and horizontal and vertical linear. Accessible photon energies will range from 400 to 2000 eV. To accommodate studies of magnetic materials using circular dichroism with the lock-in technique, the undulator will be capable of switching between left and right circular polarization at 10 Hz. This handedness switch will be accomplished by switching only the vertical component of the field while the horizontal component stays constant. Details of the EMVPU and of its initial experimental test models are presented.

The development of EMVPU further enhances electromagnetic undulator progress and improvements at the APS. The circular polarizing undulator ($E\gamma \geq 500$ eV, 1 Hz switching) has been in operation at the APS since 2001. The new quasiperiodic variably polarizing undulator ($E\gamma \geq 250$ eV) was designed and built at the APS and commissioned successfully in 2012.

A-118

New HHL and CU Front Ends with the Next-generation XBPMs for the Advanced Photon Source Upgrade

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New high-heat-load (HHL) and canted-undulator (CU) front ends for the APS Upgrade are presented. The new front ends include the next-generation x-ray beam position monitors (XBPM) system, which consists of GRID-XBPM, second XBPM, and two intensity monitors (IM1 and IM2). Due to the large space requirement of the GRID-XBPM, the first photon shutter (PS1) is removed. A low-power photon shutter is introduced to carry out a modified set of functions of PS1. The beamline personnel protection system (PSS) and front-end equipment protection system (FEEPS) are changed. The front end layout, aperture design, thermal analysis, PSS, FEEPS operational logic, and converting the existing front end components to function as IM1, IM2, and XBPM2 will be presented in detail.

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A-119

Soft X-ray Magnetic Spectroscopy

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The APS Upgrade will provide enhanced capabilities for performing magnetic spectroscopy measurements at soft x-ray energies. Because of its element specificity and ability to probe extremely small sample volumes, soft x-ray spectroscopy has become an essential tool in understanding the magnetism of complex materials. Future experiments, however, will require dramatically extending the boundaries of measureable signal levels and applied sample environments. Studies of new advanced magnetic materials, such as ferromagnetic semiconductors, spintronic materials, and complex oxides are currently pushing the sensitivity limits of state-of-the-art dichroism techniques. Improvements for soft x-ray measurements focus on providing increased flux and faster polarization switching in order to improve the probing sensitivity to weak and dilute magnetic moments by two orders of magnitude over that currently possible. This will be accomplished via a combination of improved optics and monochromator efficiency and a new electromagnetic helical undulator.

A-120

Sub-micron Three-dimensional Diffraction (S3DD) Beamline

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The sub-micron three-dimensional diffraction (S3DD) beamline is an upgraded ID beamline to be developed at Sector 34. Canted undulators will allow for simultaneous and independent use of microbeam diffraction and nanoscale diffraction facilities. A new experiment hutch will be constructed downstream of the existing microbeam diffraction hutch for dedicated x-ray polychromatic and monochromatic nanofocusing platforms. Both Kirkpatrick-Baez mirror and zone-plate-based nanoprobes will be instrumented for quantitatively detection and structural characterization of crystalline materials in the sub-100 nanometer scale in 3D.

A-121

The APS *In Situ* Nanoprobe Beamline: A Next-generation Tool for Study of Energy Materials and Devices

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The Advanced Photon Source is developing a suite of new hard x-ray beamlines to study materials and devices under real conditions. One of the flagship beamlines of the APS Upgrade is the *in situ* nanoprobe beamline (ISN beamline), which will provide *in situ* and *operando* characterization of advanced energy materials and devices. The ISN will enable materials studies at variable temperature, under flow of fluids and gases, and under applied electric fields at previously unattainable spatial resolution and throughput. Using nanofocusing mirrors, the ISN will provide several orders of magnitude increase in photon flux at a spatial resolution of 50 nm. It will provide a highest spatial resolution of 20 nm using diffractive optics, and sensitivity to yet smaller sample structures using coherent diffraction. A high-throughput data acquisition system will be deployed to significantly increase beamline productivity, with the goal of providing a user experience similar to that of a modern scanning electron microscope. The ISN will provide full spectroscopy to study the chemical state of most materials in the periodic table, and enable x-ray fluorescence tomography. *In situ* electrical characterization will enable operando study of energy and electronic devices. We will the present the preliminary design and discuss initial scientific studies related to the science thrust of the ISN beamline.

A-122

Short-pulse X-rays

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The Advanced Photon Source Upgrade Project (APS-U) at Argonne will include the generation of short-pulse x-rays based on Zholents' [1] deflecting cavity scheme. We have chosen superconducting (SC) cavities in order to have a continuous train of crabbed bunches and flexibility of operating modes. Since early 2012, in collaboration with Jefferson National Laboratory, we have made significant progress prototyping and testing a number of single-cell deflecting cavities. We have designed, prototyped, and tested silicon carbide as damping material for higher-order-mode (HOM) dampers, which are broadband to handle the HOM power across the frequency spectrum produced by the APS beam. In collaboration with Lawrence Berkeley National Laboratory, we have developing a state-of-the-art timing and synchronization system for distributing stable rf signals over optical fiber capable of achieving tens of femtoseconds phase drift and jitter. Collaboration with the Advanced Computations Department at Stanford Linear Accelerator Center is looking into simulations of complex, multicavity geometries.

[1] A. Zholents et al., NIM A 425, 385 (1999).

A-123

High-energy X-ray Diffraction (HEXD) at 1-ID

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Both an upgraded and a new beamline are proposed at 1-ID through a canted configuration, building new, dedicated stations and having a long straight section with optimized sources, including one superconducting undulator. The properties of high-energy x-rays, which include penetration capability, enable bulk samples to be studied in complex environments; programs already in operation at beamline 1-ID exploit these unique characteristics. These programs are well integrated with the user community (whose diverse base consists of academic, national laboratory, and industrial users) and have high demand as 1-ID is consistently oversubscribed by five or greater. In addition to focusing optics, end-station instruments will be upgraded and/or developed for the following techniques: high-energy diffraction microscopy, combined small-angle x-ray scattering/wide-angle x-ray scattering, imaging, resonant scattering, fluorescence, and buried interfaces. These programs are scientifically aligned with Argonne strategic initiatives including materials for energy, nuclear materials, and advanced computation.

A-124

Wide-field Imaging Beamline

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The wide-field imaging project is a 250 m long beamline that will enable x-ray imaging of centimeter-sized samples, with a spatial resolution in the 1–10 μm range and exposure times down to 80 ps using white beam or 10–60 keV monochromatic x-rays. It expands current capabilities at the APS in three crucial aspects: (1) increases the beam size from the mm to cm scale, (2) increases the sensitivity for phase-contrast imaging, and (3) improves the spatial resolution by reducing the source size effect.

Chemistry

C-1

Structure-Property Relationships in Polyoxovanadate-based NO_x Gas Sensor Materials

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Framework solids composed of three-dimensional (3D) arrays of polyoxovandate clusters potentially combine the shape/size selectivity of conventional zeolites with catalytic and semiconducting properties of transition metals. They are attractive materials for gas sensing. $Li_6[Cd^{II}_3(H_2O)_{12}V^{IV}_{16}V^{V}_2O_{42}(AO_4)]\cdot 24H_2O$ (A= V, S), **1**, is a prototypical example of a new class of framework materials [1–3], composed of 3D arrays of $\{V_{18}O_{42}(AO_4)\}$ (A = V, S) nanoclusters, which exhibits interesting room temperature NO_x $\{NO+NO_2\}$ gas sensing properties. To obtain insight into the structure-property relationships in the context of gas sensing, we have studied the molecular species $(NH_4)_8[V_{18}O_{42}(AO_4)]\cdot 10H_2O$, (A = V, S), **2**, and framework material **1** using conductometric measurements, diffuse reflectance spectroscopy, FTIR spectroscopy, and manganometric titrations. The results showed that the band gap decreases with time, probably due to the protonation of bridging oxygen atoms in the $\{V_{18}O_{42}(AO_4)\}$ cluster. Band gap measured in diffuse reflectance spectroscopy studies was supported by the manganometric titrations and conductometric measurements. During the probe molecules-sensor interaction, oxygen facilitates the oxidation of the cluster leading to the oxidation of NO_2 into nitrate.

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Condensed Matter Physics

C-2

Magnetization Reversal of Patterned Disks with Perpendicular Magnetic Anisotropy

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Magnetic vortex dynamics in magnetic disks have been extensively studied. However, spin dynamics in magnetic disks with perpendicular magnetic anisotropy (PMA) still remain to be fully understood. Magnetic configurations in disks with strong PMA are more complicated than magnetic vortices, resulting in novel spin dynamics with potential applications. In this work, we study the magnetization reversal of Co/Pd multilayered disks with PMA. Magnetic disks (3–8 microns in diameter) with the structure of [Co (0.3 nm)/Pd (0.5 nm)]5/Co(0.3nm) were patterned on Si substrates via direct laser writing lithography, electron beam evaporation, and lift-off methods. A Kerr microscope was used to image magnetization reversal processes at various bias fields. The imaging results revealed a nucleation dominated magnetization reversal process with the growth of dendritic domains. Quantitative analysis of the real-time Kerr imaging results shed light on the magnetization reversal mechanism of the patterned disks with PMA.

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Instrumentation

C-3

Fabrication of Superconducting Resonator Micro-calorimeters for X-ray Applications

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We present an overview and status of fabrication and modeling of superconducting resonator micro-calorimeters for x-ray science applications at Argonne. Superconducting resonators have a wide range of applications from photon detection—single eV (optical) to MeV (γ-ray)—to quantum computing. Traditionally, these resonators function as non-equilibrium detectors, responding to a change in quasi-particle population due to photon absorption. We are developing a micro-calorimeter in which the resonator is thermally couple to an x-ray absorber and the thermal quasi-particle population follows the temperature evolution of the absorber. The calorimeter consists of a superconducting thin film (30–100 nm) pattered into a resonator and a thick film (~1 μm) absorber positioned on a SiN membrane or island. We have fabricated these devices in the CNM cleanroom and simulated their thermal properties using COMSOL. The results of experiment and simulation show good agreement and suggest paths for further improvement of the detector design.

C-4

A Micropatterned Field Emission Cathode Array Based on Ultra-Nanocrystalline Diamond for a Flat-panel X-ray Emitter

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A novel cold-cathode field-emission array (FEA) x-ray source based on ultra-nanocrystalline diamond (UNCD) field emitters is being constructed as an alternative for detection of obscured objects and materials. Depending on the geometry of the given situation, the flat-panel x-ray source could be used in tomography, radiography, or tomosynthesis. It is anticipated that when fully developed, the unit could be used as a portable x-ray scanner or an integral part of an existing detection system. UNCD field emitters show great field emission properties and can be deposited over large areas as the case with carbon nanotube "forest" (CNT) cathodes. Furthermore, UNCDs have better mechanical and thermal properties as compared to CNT tips which further extend the lifetime of UNCD-based FEA. This work includes the first generation of the UNCD-based FEA prototype, which is being manufactured at the Center for Nanoscale Materials within Argonne National Laboratory with standard microfabrication techniques. The prototype is a 3×3 pixel FEA, with a pixel pitch of 500 μm, where each pixel is individually controllable. Experimental testing indicated that the UNCD cathodes could emit electrons above a threshold electric field of 6.24 V/μm, and emission current density of 6.42 mA/cm^2 at an electric field of 20 V/μm could be achieved.

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Materials Science

C-5

Nano XRF and CT Characterization of Fly Ash before and after Reaction

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Synchrotron nano x-ray fluorescence (nXRF) and nanocomputed tomography (nCT) are powerful techniques that allow the microstructure and chemistry to be studied at nano length scales. nXRF is a powerful tool that allows two-dimensional chemical maps of the reactive phases within these particles while nCT gives great insight into the change in the structure of a material at the nanoscale. Our studies were completed at the Hard X-ray Nanoprobe at the Advanced Photon Source. This work shows how these techniques can be used to investigate fly ash particles before and after being subjected to different solutions and to make quantitative comparisons of the environmental changes.

Fly ash is a waste product from the combustion of coal. This material has seen increased demand within the construction industry as a binder in concrete that allows improvements in durability, economy, and sustainability. While other techniques have looked at bulk changes in fly ash in different solutions, this work allows one to look at changes in the major, minor, and trace elements and microstructure within individual particles. The findings from this work offer insight into the chemical makeup, dissolution, and subsequent hydration reaction mechanisms of fly ash in alkaline media never before possible with other techniques. This work has allowed a major leap in the understanding of these complex particles.

Work at 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 DE-AC02-06CH11357.

C-6

Self-heating in $Bi_2Sr_2CaCu_2O_8$ Mesa Devices for Terahertz Generation

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Stacked intrinsic Josephson junctions in the high-temperature superconductor $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) are a promising compact source of coherent terahertz radiation. However, when these devices are electrically biased under conditions suitable for terahertz emission, significant DC power is dissipated in them, causing strong and non-uniform self-heating in the stacked junctions. Theoretical models and experimental evidence suggest that localized self-heating can be beneficial for generation of THz radiation. For optimization of these devices it is therefore important to gain an understanding of self-heating, and the mechanism of its relationship to THz emission.

Here we present thermal maps of Bi-2212 THz mesa devices fabricated at the CNM and imaged via thermoluminescent microscopy at Argonne, as well as via scanning laser thermal microscopy performed at the University of Tuebingen. Using optical microlithography facilities at the CNM, we are also developing mesa devices with 100 nm NiCr thin film heaters fabricated on top of the Bi-2212 stack. These will allow us to introduce artificial hot spots in the mesas in systematically controllable fashion.

C-7

Can Graphene be the Next Best Solid Lubricant?

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Minimizing friction and wear-related mechanical failures remains as one of the greatest challenges in today's moving mechanical systems. The search for new materials, coatings, and lubricants that can potentially avoid such failures continues around the globe. Many studies have pointed out that the friction and wear mechanisms differ for different materials operating under different thermal, environmental, and tribological conditions. We demonstrate that the anti-corrosion property of graphene coupled with its lubricating nature is beneficial in drastically reducing wear (four orders of magnitude) and friction (4–5 times) in the case of the most commonly used tribo-pairs, in particular, steel against steel sliding regardless of the surrounding environments (i.e., humid air or dry nitrogen). In addition, we show that graphene application as well as re-application does not require any additional processing steps other than just sprinkling a small amount of ethanol solution containing graphene flakes on the surface of interest making this process simple, cost effective, and environmental friendly. Most of all, unlike conventional solid lubricants, which are all sensitive to environmental conditions, graphene offers the possibility of being effective regardless of the operating environment.

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C-8

Electrochemical Analysis of Cathodic $AgNa(VO_2F_2)_2$ with Lithium and Sodium Anodes

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This poster describes properties of oxide-fluoride materials that make them attractive candidates for sodium ion batteries. Three issues of energy use concern i) energy storage, ii) expense of lithium sources, and iii) the open circuit voltage (OCV) of a battery. As solar, wind, hydropower, and other renewable energy sources become more common, issue (i) must be addressed to store excess energy for use at a later time. This has been approached with the use of Li+ ion batteries [1–3]. Issue (ii) compounds issue (i) as large Li^+ batteries for energy storage may be prohibitively expensive. Sodium ion batteries have been investigated as a low-cost alternative to this [4, 5], but issue (iii) complicates this as sodium ion batteries have lower OCVs (-0.2 to -0.5 V) as compared to lithium analogs owing to the difficulty of intercalation of the larger Na+ ion within a cathode material [4].

To address these issues, we present structural and electrochemical analyses of a new double-wolframite trimetallic compound: $AgNa(VO_2F_2)_2$ or SSVOF; SSVOF is fully ordered and displays unique electrochemical characteristics. The compound contains tri-oxo vanadium fluoride octahedra, which form one dimensional chains which are characteristic of wolframite ($NaWO_4$). Therefore, to address issues (i–iii) we evaluated SSVOF as a cathode with a sodium anode.

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C-9

CVD Growth of Low-defect Graphene on Copper Substrates and Copper Foil Stacks

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Graphene synthesis has been studied extensively since its discovery by Novoselov [1]. In addition to possessing extremely high intrinsic electronic mobility ~200,000 cm^2/Vs [2], graphene has exceptional mechanical properties [3] such as 97.7% transparency to white light [4] and is a perfect barrier to the flow of all standard gases including He [3]. Graphene growth by CVD process has been well studied on copper thin films and foils. However, there has not been a study that demonstrating growth of low-defect graphene on thin film copper and copper foils simultaneously under equal processing conditions. This study demonstrated growth of large-grain, single-layer graphene with no defect peak on both 700 nm thick evaporated Cu films and bulk copper foils, with implications for the development of approximately millimeter-size single-domain graphene for applications in the Advanced Photon Source (APS).

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C-10

Using Synchrotron-based X-ray Nanoprobe for Three-dimensional Chemical Segmentation of Complex Particles

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A novel data fusion technique is presented that combines synchrotron-based x-ray nanocomputed tomography (nCT) and nano x-ray fluorescence to investigate complex particles. The technique has been named nanotomography-assisted chemical correlation or nTACCo. The method extends the capabilities of nCT and allows areas of unique chemistry to be imaged in three dimensions.

C-11

Transition Edge Sensor Tuning with Proximity Effect

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We have conducted an experimental study tuning the critical temperature, transition width, normal resistance, and critical current of Mo/Au bilayer transition edge sensor (TES) using Nb stripes on the TES surface. The Nb stripes modify the TES parameters through the lateral proximity effect. We summarize the dependence of the shift in transition temperature and the broadening of the transition width on the separation length between the Nb stripes and leads. We calculate the Ginzburg-Landau coherence length of the TES in two methods. One takes advantage of the dependence of the TES normal resistance on the number of the TES and Nb contacts. Another utilizes the temperature dependence of the TES critical current. The two methods are in good agreement with a coherence length of 0.4 μm. Our work provides a phenomenological description of superconducting transition engineering technique and establishes a data set from which to develop theoretical models of its underlying physics.

Nanoscience & Nanotechnology

C-12

Uranium and Plutonium Detection by Plasmonic Graphene-based Nanosensors

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One of the most important pieces of information after a release of nuclear material is identifying the presence of uranium (U) and/or plutonium (Pu). Their presence, especially following a supercritical nuclear event, would severely limit the list of potential actors and provide the White House with critical information to guide a proper and timely response. We are working on the design and fabrication of arrays of electronic molecular devices as sensors for plutonium and uranium at the nanoliter volume, using computational calculations performed at Texas A&M University and experiments performed at Argonne National Laboratory (Center for Nanoscale Materials and Chemical Sciences and Engineering Division). In particular, we are studying graphene, which is a vibronic, plasmonic, and electronic material for molecular circuits and sensors. The idea is to use the plasmonic features of graphene molecules in order to transfer the electrical, magnetic, vibrational, and optical characteristics of nuclear agents into the graphene plasmon, which produces an enhancement (amplification) of observable quantities as successfully done with chemical and biological agents. For nuclear agents, we have additional possibilities due to their radiation features. Theoretical simulations have shown the possible use for sensors to identify single molecules with high selectivity and sensitivity that will contribute to the miniaturization, as well as efficient transport and processing of signals using graphene based devices. It is expected that this approach will allow us not only to sense targeted agents, but also to perform chemical recognition using molecular potentials, which have become the signature at the nanoscale, perfectly suitable for detection and identification of atoms and small molecules. Maps of the molecular potentials around complexes of U and Pu allow us to distinguish their main signatures similar to those observed in biological systems where receptors are able to distinguish to its transmitters or when a donor of electrons is able to match with an acceptor.

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C-13

Optical and Structural Properties of Si Nanoparticles at High Pressures

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Nanocrystalline silicon has generated a great deal of interest as a material that offers improved optical performance with respect to bulk Si. Here, we report on the use of hydrostatic pressure as a tool to investigate the origin of photoluminescence in Si nanocrystals. A combination of classical molecular dynamics and first principles density functional theory is used to calculate the optical, electronic, and structural properties of Si nanocrystals under applied hydrostatic pressure [1]. These results are experimentally corroborated with pressure-dependent photoluminescence spectroscopy and x-ray diffraction [1]. This work extensively leveraged user resources at the Advanced Photon Source (APS) and Center for Nanoscale Materials (CNM). Molecular dynamics calculations were carried out on the Carbon high-performance computing cluster at the CNM. Optical characterization of Si nanocrystals was also carried out using laser spectroscopy facilities at CNM. Pressure-dependent structural characterization was carried out at sector 13 of the APS (GeoSoilEnviroCARS).

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C-14

Nanomanufacturing for Plasmonic and Photonic Crystals

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Nanotechnology holds the promise of revolutionizing a broad range of fields, including medicine, renewable energy, information storage, and imaging. One application that would benefit immediately from nanotechnology is the integration of plasmonic and photonic crystals into light-harvesting devices (e.g., solar cells, photocatalytic cells) to increase their efficiency. For nanotechnology to reach its full potential, methods must be developed to build nanoscale materials quickly and over large areas. To accomplish this task, we rely on soft lithography, which uses elastomeric stamps to pattern <100 nm structures over wafer-scale areas. We create these soft stamps by molding poly(dimethylsiloxane) (PDMS) against patterns that have been made in silicon (Si). Using the interference lithography system at Argonne National Laboratory's Center for Nanoscale Materials, we have been able to create Si masters with periodicities that range from ~300 nm to 1000 nm. The Si masters are not damaged during the molding process, and therefore each master can yield dozens of PDMS stamps. By using these new stamps with a technique we developed in our group, moiré nanolithography, we can fabricate two-dimensional plasmonic and photonic crystals with a large variety of rotational symmetries and spacing. Thus, our lithography methods allow us to make structures that can be specifically tailored to target applications. The ability to make these patterns over large areas will rapidly increase the integration of nanoscale patterns into light-harvesting applications.

C-15

Ultrananocrystalline Diamond (UNCD) TEM Grids for the Electrochemical Deposition of Nanowires

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Electroplate-and-Lift (E&L) lithography [1] has been developed as a fast, simple, scalable technique for the controlled, solution-based, electrochemical synthesis of patterned metallic and semiconducting nanowires. E&L employs a reusable, non-sacrificial template made from alternating layers of insulating and conductive ultrananocrystalline diamond (UNCD)^{TM}. The UNCD is lithographically patterned to expose only edges of the conductive layer to nucleate nanowire growth. Following electrodeposition, the nanowires may be mechanically removed to regenerate the template surface for subsequent depositions.

To produce nanowires with physical and electrical properties tailored for specific device applications, current methods for bulk characterizations must be adapted to more easily analyze individual nanowires. In this work, we discuss the development of a substrate that would enable both *ex situ* and *in situ* nanowire growth directly upon a transmission electron microscopy (TEM) grid, for the rapid, easy characterization of the crystal structure of the deposits. These TEM grids are made of suspended films of ultrananocrystalline diamond (UNCD), with a similar structure to the templates used in E&L. This UNCD film structure consists of a very thin (~ 100 nm) layer of conductive nitrogen-doped UNCD (NUNCD) in between two equally thin insulating layers of UNCD. UNCD film stacks may be suspended over surface areas of up to 1×1 mm, supported only at the edges by a silicon frame. Within the suspended UNCD films, several lithographically defined holes have been etched through the UNCD. This exposes edges of the conductive NUNCD, where thin wires may be directly electroplated and observed by TEM free of obstruction by the substrate. Each of these small holes may be addressed by its own contact pad, to which a wire may be bonded to make a permanent electrical contact. This allows the deposition of different metals in different holes on the same TEM grid. Many variations have been made upon these lithographic patterns, such as the number and size of the holes, the number of circuits connected to each hole, or having multiple holes on the same circuit. Given this adaptability, UNCD TEM grids have great potential for use as substrates in research fields as diverse as materials science, energy and medical technology.

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C-16

Seeing is Believing: Observation of Self-assembly of Charged Gold Nanoparticles by *In Situ* TEM

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Self-assembly of Au nanoparticles (NPs) coated with positively charged etyltrimethylammonium ions (CTA+) and negatively charged citrate ions in aqueous liquid cell was observed by *in situ* liquid cell transmission electron microscopy (TEM). Under electron illumination, the solvated hydrated electrons reduce the overall positive charges of the CTA+-covered Au NPs and decrease the repulsive electrostatic forces among NPs, leading to assembly of individual NPs into one-dimensional structures.

This work was performed at the Center for Nanoscale Materials, a U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences User Facility under Contract No. DE-AC02-06CH11357.

C-17

Preparation of All Inorganic III-V (InP, InAs, and InSb) Quantum Dots Inks for Solution-processed Electronic and Optoelectronic Devices

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Along with organic semiconductors, inorganic nanocrystals (NCs) recently emerged as promising cost competitive semiconductor inks for the electronic and optoelectronic applications. Among them, III-V materials such as GaAs, InP, InAs, and InSb stand out from the II-VI and IV-VI NCs due to their low toxicity and superior physical properties as the bulk semiconductors. Although colloidal synthesis has more than three decades history, development of colloidal approaches to synthesize monodisperse III-V nanocrystals is still a challenging problem. Most synthetic protocols for II-VI NCs combine precursors and surfactants in high-boiling-point solvent with annealing at elevated temperatures. Except for InP and InAs, however, this method does not work for other III-V NCs. Possible reasons include rare suitable precursors for pnictogens and high energetic barriers for crystallinity. Here, we introduce a convenient way to convert the relatively stable precursors into reactive intermediate species by employing the reducing agent $LiBHEt_3$ (superhydride). With this method, we developed the first successful recipe for well-crystallized InSb NCs, an important member of the III-V family. Average sizes from 3.3 to 6.5 nm with narrow standard derivations were obtained after size-selective precipitation. In order to improve the photoluminescence quantum yield, we further extend our work to construct core-shell nanostructures. Additionally, we present the preparation of all inorganic InP, InAs, and InSb NC inks through the surface modification, substituting metal chalcogenide complexes (MCCs) and simple chalcogenide ions for the insolating organic ligands. Carrier transport through the NCs arrays was hugely enhanced afterwards. Very high electronic mobility (15 cm^2/Vs) was obtained for the InAs capped with $Cu_7S_4^-$. Also unprecedented ambipolar photoresponse of MCCs capped InAs NCs was observed.

C-18

Microfilters for Efficient Isolation and Culture of Circulating Tumor Cells

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Circulating tumor cells (CTCs) are cells that released from primary tumors into blood circulation and then lodge at distant organs to initiate new cancer growth. Detection and characterization of CTCs is a promising cancer monitoring test, helping physicians see the effectiveness of therapies and checking for recurrence. One method to achieve personalized cancer therapy is to isolate viable CTCs from a patient and culture them to test for response to drugs.

Detection of CTCs is technically challenging, due to their extremely low numbers (1–3 per milliliter of blood). CTCs are usually larger and less plastic than blood cells and can be isolated by size exclusion. We are developing a microfilter with precisely defined pores for CTC isolation and with surface nanotopography to facilitate growth of captured cells in three dimensions. Nanoscale topography is a key to the cell culture, mimicking *in vivo* conditions. The utility of the microfilters with various topographies is evaluated using cancer cell lines.

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C-19

Selective Electron Valley Occupation in AlAs Quantum Wells with Magnetic, Electrostatic, and Strain Fields

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We investigate the valley index [1] as a controllable degree of freedom in electronic devices. Using either magnetic, electrostatic, or strain fields we can control the population of electrons in a particular valley of a multi-valley system. We demonstrate magnetic field as a probe of valley occupation in triple valley (111) AlAs quantum wells (QWs). First, with novel growth techniques such as slight angle miscut of the substrate and control of the growth parameters we optimize growth of AlAs QWs on (111)B GaAs substrate. A slight miscut of 2°, at which slip-step growth is known to occur, lead to AlAs QWs with record electron mobility μ=13000 cm^2/Vs at a sheet density n_{2D} = 2.17x10^{11} cm^{-2} [2]. We expect to see a three-fold valley degeneracy in the magnetotransport data of these samples. However, magnetotransport data at 15 mK in magnetic fields up to 15 T shows breaking of the three-fold valley degeneracy at the various filling factors. Furthermore, for different directions of net current flow in the sample we observe anisotropy in the peak height of the longitudinal resistance R_{xx} at the various half-filling factors indicating different valley occupation. We present an analysis of the different valley occupations caused by quantum confinement due to magnetic fields.

Electrostatic control of valley population can be achieved by making nanoconstrictions called quantum point contact gates to block the flow of one kind of valley electrons in (001)-AlAs QWs. Our previous proposal at CNM (27351) has successfully shown working electrostatic point contact gates on single valley thin cap GaAs QWs and with similar device fabrication we will make point contacts on double valley AlAs QWs which can select between the two orthogonal valley electrons which have anisotropic mass. Sample fabrication involves the steps of precision photolithography, reactive ion etching, ohmic contact evaporation, rapid thermal annealing, and e-beam lithography;

all the fabrication steps were optimized at the clean room at CNM. A second branch of new research will explore the effectiveness of strain gates for valley selection in (001)-AlAs QWs. In strain gates, boundaries of metallic gates with mismatched thermal coefficients induce strain on the AlAs QWs, thereby selectively blocking one valley and transmitting the other. After fabrication, the (001)-AlAs quantum point contact gate and strain gate devices will be studied at cryogenic temperatures to minimize intervalley scattering effects and observe the strongest possible valley selectivity.

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C-20

Metal-assisted Etching of Silicon Molds for Electroforming

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Template-based metal-assisted chemical etching enables fabrication of Si nanostructures with controlled diameter, shape, length, and packing density.

Ordered arrays of high-aspect-ratio micro/nanostructures in semiconductors stirred a huge scientific interest due to their unique one-dimensional physical morphology and the associated electrical, mechanical, chemical, optoelectronic, and thermal properties. Recently, a simple, fast, and effective nanostructure formation method, metal-assisted chemical etching was reported [1, 2, 3]. The process is based on placing a noble metal (usually gold) in the form of nanoparticles or a pattern onto the surface of Si, then performing a $HF:H_2O_2$ etch. The noble metal catalyzes the etching reaction of Si at the metal/Si interface through electrochemical effects, causing the metal to sink into the Si, forming a deep, vertical-wall pit. At the end of the etch the remnant metal can be removed chemically if undesired, or used as a plating base to fill the etched pit with a metal by electroforming.

We present the results on Si nanostructure fabrication by metal-assisted chemical etching where the metal patterning was done with e-beam lithography, or interference lithography, and lift-off. The metals investigated for patterning were Au and Pt. The detailed geometries of the resulting Si structures depend mostly on the initial morphology of the noble metal coverage. We noticed that, due to gas evolution during the etching, the metal layer delaminates and tends to move along the surface. This problem was resolved by having a thin layer of 4 nm Ti as adhesion layer, resulting in the successful metal-assisted chemical etching of Si.

We are investigating if this process can be extended towards the fabrication of high-aspect-ratio zone plate configurations (e.g., Fresnel zone plates or photon sieves), which could be etched into Si to form molds and thereafter electroformed with gold.

Use of the Center for Nanoscale Materials, Argonne National Laboratory 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-21

Uranium and Plutonium Detection by Plasmonic Graphene-based Nanosensors

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One of the most important pieces of information after a release of nuclear material is identifying the presence of uranium (U) and/or plutonium (Pu). Their presence, especially following a supercritical nuclear event, would severely limit the list of potential actors and provide the White House with critical information to guide a proper and timely response. We are working on the design and fabrication of arrays of electronic molecular devices as sensors for plutonium and uranium at the nanoliter volume, using computational calculations performed at Texas A&M University and experiments performed at Argonne National Laboratory (Center for Nanoscale Materials and Chemical Sciences and Engineering Division). In particular, we are studying graphene, which is a vibronic, plasmonic, and electronic material for molecular circuits and sensors. The idea is to use the plasmonic features of graphene molecules in order to transfer the electrical, magnetic, vibrational, and optical characteristics of nuclear agents into the graphene plasmon, which produces an enhancement (amplification) of observable quantities as successfully done with chemical and biological agents. For nuclear agents, we have additional possibilities due to their radiation features. Theoretical simulations have shown the possible use for sensors to identify single molecules with high selectivity and sensitivity that will contribute to the miniaturization, as well as efficient transport and processing of signals using graphene based devices. It is expected that this approach will allow us not only to sense targeted agents, but also to perform chemical recognition using molecular potentials, which have become the signature at the nanoscale, perfectly suitable for detection and identification of atoms and small molecules. Maps of the molecular potentials around complexes of U and Pu allows us to distinguish their main signatures similar to those observed in biological systems where receptors are able to distinguish to its transmitters or when a donor of electrons is able to match with an acceptor.

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C-22

STM and Optical Investigations of Molecules on Graphene

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Graphene, due to its unique properties, promises new and unexpected capabilities as a platform for nanoscale device applications, which has led to significant interest in graphene-based nano-optical and photovoltaic applications. A thorough understanding of molecular electronic structure and interactions at this scale is pivotal in the development of such devices. Here, we describe efforts to resolve and understand the structural, electronic and optical properties of an archetypal organic molecular building block for these devices. We will present ultrahigh vacuum scanning-tunneling microscopy studies of the structural and electronic properties of pentacene (Pn) molecules deposited on graphene that was grown epitaxially on SiC(0001). Our measurements of the electronic properties of this system indicate a de-coupling of the molecules from the graphene and underlying substrate, similar to results obtained for the complementary molecular system, C60 on grapheme [1], suggesting a path for developing molecular-scale electronic and optically active devices that are not dominated by substrate interactions. Isolated electronic states are observed and associated molecular orbitals are resolved; also, a large HOMO-LUMO spacing indicates that we are probing a 'transport gap' in the monolayer Pn. We will also discuss our efforts to correlate these scanning tunneling microscopy

(STM) studies with the optical properties of these systems using an ultrahigh vacuum STM that incorporates confocal optical microscopy and spectroscopy at the tip-sample junction.

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C-23

Ferromagnetic Microdisks for Biomedical Applications in Low- and High-frequency Magnetic Fields

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Superparamagnetic particles are the most widely employed magnetic carriers, which have found a number of applications ranging from hyperthermia to drug delivery and cell sorting [1]. However, the particle aggregation and the need for the strong magnetic fields for nanoparticle manipulation impose significant limitations on using such particles *in vivo*. Our group has recently developed a new type of ferromagnetic disk-shaped particles with zero net magnetization in the ground state and high saturation magnetization [2, 3]. The former eliminates the problem of particle aggregation in the absence of the external field and the latter allows for using weak magnetic fields below 100 Oe for manipulating the disks. In this presentation we show that ferromagnetic microdisks can be employed for the targeted multimodal treatment of brain cancer cells. In the low-frequency magnetic field, the disks induce apoptosis, the programmed cell death, through magnetomechanical stimulation of the cell membrane as we have previously demonstrated. Here, we demonstrate that in the high-frequency regime, the disks are also very efficient for localized heating resulting in hyperthermic modulation of cell function.

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Polymers

C-24

A Molecular Dynamics Study of the Effect of Water/Methanol Solvent Mixtures on the Conformational Transitions through the LCST of Poly(N-isopropylacrylamide)

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Poly(N-isopropylacrylamide) (PNIPAM) is a thermosensitive polymer that is well known for its lower critical solution temperature (LCST) around 305 K. Below the LCST, PNIPAM is soluble in water, and above this temperature, polymer chains collapse and tend to aggregate. In the presence of methanol, experiments suggest that the LCST of PNIPAM is depressed up to certain mole fraction of methanol (0.35 mole fractions) and it is speculated that addition of methanol affects the PNIPAM-water interactions resulting in the change in LCST. Above the 0.35 mole fraction of methanol, the LCST gets elevated to temperatures above 32°C and cannot be detected up to 100°C. In the present study, we have used molecular dynamics (MD) simulations to investigate the effect of solvent of water mixed with methanol on the conformational transitions and the LCST of PNIPAM. MD simulations of PNIPAM were carried out at fully atomistic level for different water-methanol solvent mixtures (mole fractions of methanol of 0.018, 0.09, 0.27, 0.5, and 0.98) and at different temperatures (260, 278, 310, and 340 K). Simulated trajectories were analyzed for different structural properties, such as the radius of gyration of PNIPAM and the extent of hydration of

PNIPAM. Different dynamical properties such as the diffusion coefficient, hydrogen bonding lifetimes, and residence time of water and methanol near PNIPAM were also determined.

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Materials Science

E-1

In Situ Studies of Nanocrystallization in Fluorochlorozirconate Glasses

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Heat treating fluorochlorozirconate (FCZ) glasses nucleates 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 heating experiments and transmission electron microscopy. These experiments showed that the nucleation of hexagonal $BaCl_2$ nanocrystals first occurs at 230°C, and undergoes a phase transformation to the orthorhombic phase at 280°C. Through the use of different heat treatments it was found that the nucleation and phase transformation processes are kinetically controlled processes.

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E-2

In Situ TEM Observations on CeO_2 Irradiated by Ar and Kr Ions at 800°C

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In order to study inert gas behavior in nuclear fuel, *in situ* transmission electron microscopy (TEM) observations on implanting UO_2 surrogate, CeO_2, with Ar and Kr ions at 800°C were performed. The ion energy of each ion species (150 keV for Kr ions and 65 keV for Ar ions) was chosen in order to generate similar energy deposition profile of the film. The density and size of gas bubbles were recorded at several dose steps by using the technique of under-over focus to the final dose of 5×10^{15} ions/cm^2.

The results show that gas bubble evolution during ion implantation of Kr and Ar is significantly different. The density of Kr bubbles increase linearly with irradiation doses to the final dose of 5×10^{15} ions/cm^2. On the contrast, no significant Ar bubbles could be observed before the dose of 2×10^{15} ions/cm^2. After 2×10^{15} ions/cm^2, the Ar bubble density increases sharply to an value close to the density of Kr bubbles at the final dose of 5×10^{15} ions/cm^2. Despite of the differences in the evolution of bubble density, there was no evident distinction in average bubble sizes for the two gas species, which are both around 1.5 nm.

E-3

Imaging of Interfacial Oxygen Using Chromatic Aberration-corrected TEM

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Gold nanocrystals (Au NCs) on rutile TiO_2 surfaces have attracted considerable interest as a model system for studying the remarkable size-dependent catalytic activities of supported Au NCs, especially for catalyzing the oxidation of carbon monoxide [1]. Several mechanisms have been proposed to explain the surprising chemical activities of Au and almost all of them involve interactions at the Au NCs and support interface [2], which renders the study of interfacial structure tremendously important. Cross-sectional transmission electron microscopy (TEM) provides a powerful way for studying interfaces. While high-angle scattering of electrons (Z-contrast) in scanning transmission electron microscopy (STEM) with aberration correction can characterize interfacial cations at atomic resolution, oxygen atoms are much more difficult to detect due to its low atomic number. High-resolution TEM, in principle, is sensitive to light atoms in phase contrast. But the resolution and information transfer in conventional TEM are limited by both spherical and chromatic aberrations. The chromatic aberration correction enabled by ACAT (Argonne chromatic aberration-corrected TEM) located in Argonne National Lab significantly improves the information transfer and resolution in recorded images. Furthermore, the ability to adjust individual aberration coefficients using the C_c corrector also allows a precise control over the contrast transfer function (CTF) and the use of CTF for optimizing the contrast between heavy and light atoms, and thus improves the sensitivity to light elements for thin samples using phase contrast.

To enable high resolution C_c-corrected TEM investigation, we have developed a novel NC synthesis technique for preparing Au NCs on rutile (TiO_2) surfaces. Au nanoparticles about 2–5 nm in diameters were first deposited onto the single crystal TiO_2 substrate, pre-thinned and annealed in air, by e-beam evaporation deposition at room temperature. Then the sample was annealed in air at 500°C to form epitaxial Au NCs (the same annealing procedure is used for the activation of Au catalyst).

Using ACAT, we recorded HREM images in a focal series using optimized C3 and C5 coefficients. By reconstructing the focal series, we have succeeded in obtaining the exit wave function from several Au NCs supported on TiO_2. Focal series reconstruction improves the signal and noise ratio, removes the lens effect from the recorded images and allows a direct comparison between experiment and simulations. Results show resolved surface bridging oxygen on TiO_2 surface at 1.4 Å distance away from Ti, and oxygen reduction at the interface, which brings the Au atoms closer to Ti. Interfacial oxygen can be seen at stepped, or rough, Au/TiO_2 interfaces. Thus, chromatic aberration correction in ACAT now enables the study of full atomic details at nanocrystal and support interface, and a study of NC and support interaction, which potentially will have a large impact on our understanding of the atomistic mechanism of catalytic activities.

We would like to thank Dr. Jon M. Hiller at EMC, ANL for his help on sample preparation. The work reported here is supported by the NSF Grant No. DMR 0449790. High Resolution Electron microscopy was carried out on ACAT at the Electron Microscopy Center, an Office of Science User Facility 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.), and AC-STEM was carried out in the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois.

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E-4

Structural and Magnetic Study of $CoFe_2O_4$ Using Energy Loss Magnetic Chiral Dichroism

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Energy loss magnetic chiral dichroism (EMCD) is a technique based on energy loss spectroscopy in transmission electron microscopy that can measure locally the magnetic moments of crystalline samples and get quantitative information based on specific sum rules. This technique is closely related to x-ray magnetic circular dichroism. In this work, initial results on two crystalline thin film systems of Fe on MgO substrate and $CoFe_2O_4$ on $SrTiO_3$ substrate will be presented. The Fe thin film was used to establish the experimental protocol required to measure the EMCD signal reliably.

Use of the Electron Microscopy Center of Argonne National Laboratory is gratefully acknowledged.

Nanoscience & Nanotechnology

E-5

Solid Anisotropic Etching on Si(001) by Oxidation of Self-assembled Cu_3Si Nanowires

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Prior studies have shown that a by-product of thin film Cu_3Si oxidation on silicon (Si) was a silicon-oxide (Si-O) compound [1]. For nanoscale Cu_3Si structures, in addition to Si-O, we also discovered that oxidation would produce 'V' grooves on Si(001) [2]. Although a hypothesis was suggested [2] to explain the oxidation mechanics, experimental verifications were needed. Therefore we proposed to use transmission electron microscopy (TEM) techniques to investigate the oxidation of the nanowire-Si system over a period of seven weeks. We initially fabricated the self assembled Cu_3Si nanowires on Si(001) and left to oxidize at ambient conditions at 25°C and 44% humidity. High-resolution TEM (HRTEM) images of different nanowires from the same substrate were obtained on weeks one, two, and seven. The images showed an evolution of oxidation and the sidewalls of the 'V' planes were parallel to Si{111}. The images also showed that the crystallinity of Si around the grooves was preserved. Additionally, an energy-dispersive x-ray spectroscopy (XEDS) technique was used to study the material composition of the nanowires. It appeared that during at the early stages of oxidation, SiO_2 was the dominant oxide, whereas at the later stages SiO was the dominant oxide. This suggests that the rate of oxidation changes with the reaction. Since XEDS can only provide atomic weight ratio data, to confirm these oxides were indeed SiO and SiO_2, another tool is needed to detect those oxide phases. The above oxidation results have similar effects as anisotropic etching on Si(001) that etches along {111} planes, except that the oxidation-etching method does not involve wet chemistry methods, such as with a KOH solution. A common problem associated with wet chemical anisotropic etching is 'overetching' where instead of a 'V' groove, one obtains a 'U' groove or undesired broadening of the features. Overetching is not seen in the HRTEM images. In our findings, oxidation-etching method also preserves the Si crystalline structures. As such the oxidation method is advantageous as compared to the nano-imprinting method, which produces 'V' grooves by mechanical

stamping and damages the Si crystal. Therefore this finding may one day be used as a novel fabrication tool to solid anisotropic etch single-crystalline Si without (1) wet chemistry, (2) overetching, and (3) damaging the Si crystal.

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E-6

Customized Graphitic Nanofluids for Advanced Cooling of Power Electronics

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Power electronics is a critical component of hybrid electric vehicles (HEVs) and electric vehicles (EVs) since it provides control and conversion of electric power. Increasing power loads result in increased heat fluxes, thus uninterrupted operation of power electronics requires liquid cooling systems to enhance heat dissipation, improve energy efficiency, and lengthen device lifetime. To satisfy these increasing thermal management needs, the heat transfer efficiency of conventional fluids must be improved. Nanofluids are nanotechnology-based heat transfer fluids that are engineered by stably dispersing nanometer-sized solid particles in conventional heat transfer fluids at relatively low particle volume concentrations to enhance the thermal conductivity and the heat transfer coefficient.

Nanofluids with carbonaceous nanoparticle additives have shown a wide range of thermal conductivity increases, from very insignificant increase in amorphous carbon black to a 2–3 fold increase in thermal conductivity in some suspensions with carbon nanotubes and graphene oxides. A unique nature of anisotropic carbonaceous nanomaterials (nanotubes and graphene) results in dramatic thermal conductivity increases by engaging several heat transfer mechanisms in suspensions (e.g., effective medium theory, percolation, and plasmon resonances). Besides thermal conductivity other thermo-physical properties of suspensions such as viscosity and specific heat are important for heat transfer efficiency. Viscosity of nanofluids with high aspect ratio particles is incredibly high (up to three orders of magnitude higher than viscosity of the base fluid) resulting in pumping power penalties that are higher than the benefits in thermal conductivity of those suspensions. Thus the practical value of such nanofluids was not sufficient for commercialization of the technology.

We investigated the effects of nanoparticle morphology and surface treatment on the thermo-physical properties of nanofluids with graphitic nanomaterials in EG/H_2O base fluid. Using simple, low-cost, and up-scalable surface modification method for graphitic nanoparticles we were able to formulate the nanofluid coolant with advanced combination of properties that allows 90+% improvement in heat transfer coefficient when used in laminar flow and 30+% enhancements in heat transfer coefficient when used in turbulent flow. The implementation of this technology in HEV's and EV's will result in reducing the size, weight, and number of heat exchangers, further improving vehicle efficiency.

Exemplary Student Research Program

S-1

Time-resolved X-ray Absorption Studies of a Chromium-titanium-oxide-based Cathode Material for Lithium Ion Batteries

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This experiment investigates the local atomic environment and the charge compensation mechanism of a previously uncharacterized chromium-titanium-oxide-based cathode material using element specific *in situ* x-ray absorption studies. Time-resolved x-ray absorption near edge spectra were used to characterize the oxidation state of transition metal ions, and extended x-ray absorption fine structure was used to monitor changes in nearest neighbor distances during electrochemical cycling. Initial results indicated the presence of a hexavalent chromium impurity phase, evidenced by the large characteristic Cr(VI) peaks present in the spectra of as-prepared samples. Additional materials characterization of the Cr-Ti cathodes has been performed, and alternative synthesis methods have been explored as a result of this experiment. Further analysis and interpretation of the data will be presented in the poster.

S-2

XRF Microanalysis of Canine Hair to Evaluate the Relative Sensitivity of Eumelanin Chelation of Copper to Melanin Content as an Expression of Hair Color

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The purpose of this experiment is to determine whether one can infer hair color from the saturation of copper in hair. The two protein pigments found in hair are eumelanin and pheomelanin. Eumelanin creates black and brown pigments in the hair and pheomelanin is responsible for red-brown hair colors. Eumelanin is an organometallic compound. Organometallic compounds contain a bond between carbon and a metal. The process of compounds attracting and binding to a specific metal ion is called chelation and it varies depending on the compound. Copper chelates are derived from eumelanin. In earlier research, scientists have linked the copper found in fossilized feathers to eumelanin. Scientists have also found that the structure of feathers is similar to the structure of hair; therefore, we believe that the relationship between copper and eumelanin in feathers will also be found in hair. Canine hair was collected from pet grooming companies, and half of the samples were soaked in copper while the other samples were kept in distilled water x-ray fluorescence was used to determine the levels of copper in each of the samples. Using this technique a possible correlation between copper levels and hair color could be analyzed.

S-3

The Effect of pH on Lysozyme Crystallization

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The project "The Effect of pH on Lysozyme Crystallization" involves extracting lysozyme from chicken eggs and crystallizing it. This experiment will confirm existing results of others' previous lysozyme experiments. It is hypothesized that varying the pH of the lysozyme enzyme will result in more impurities in lysozyme crystals outside of the pH range of 6–9. The ideal range of the lysozyme enzyme is in this range, so when the pH is not within these bounds the lysozyme will denature and affect the crystal growth. The research will help determine the structure of a lysozyme protein with x-ray crystallography and provide results for the hypothesis while simultaneously imparting educational value in the science of x-ray crystallography. Additionally, the lessons from the results can be applied to other fields of science such as health, as lysozyme is an important enzyme in the immune system, and agriculture, since the lysozyme used comes from chicken eggs and serves an antibacterial purpose. This experiment will confirm conclusions on how lysozyme crystallizes in different pH levels and offer experience with x-ray crystallography while opening doors to exploration in other areas in science.

S-4

The Absorption of Common Metals in Leaf of the Common Dandelion as a Measure of Metals in Soil

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In the literature, there are some organisms that are described as potentially being useful "bioindicators." Bioindicator species are biological organisms that can possibly be used to monitor the environmental health of an ecosystem and can, for example, be used as a monitor of anthropogenic metal contaminants in the environment. It has been proposed the common dandelion (*Taraxacum officinale*) potentially fits the criteria for a bioindicator plant and several published studies have evaluated its potential use as such with mixed results. This group from Glenbard East High School and Wheaton North High Schools proposed an experiment to evaluate this using synchrotron x-ray fluorescence analysis at beamline 13-ID-E of dandelion leaves that they collected throughout the campus of the Glenbard East High School in Lombard, Illinois. The dandelions they collected (almost 30 in total) were geographically located throughout the campus and included areas near buildings, near roads and parking lots, in athletic fields, and near a detention pond area found on the grounds that collects water from the whole campus. For each sample, they selected a single leaf for analysis and then compared the measured metal abundances to evaluate if they see correlations between metal content and proximity to anthropogenic sources of metals, as would be expected for a bioindicator plant. The data has indicated some very pronounced differences in samples from different locales.

S-5

Prevalence of Metal Biomarkers in Fossils of Mazon Creek Fauna and Evolutionary Implications

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The fossils found in Mazon Creek, Illinois, are well-known for their amazing preservation of the soft tissue of animals and plants. These fossil beds were deposited during the Carboniferous period, roughly 300 million years ago. Other published studies have found that microbeam x-ray fluorescence imaging can be powerful analytical technique for providing additional insight into the anatomy of fossilized soft-body tissue by examining the distribution of trace metals (such as copper) that were bound to organic complexes preserved in the rocks. This group from Downers Grove South High School proposed an experiment to evaluate if x-ray fluorescence imaging at beamline 13-ID-E could provide unique insights in to the paleontology of fossils recovered from Mazon Creek. For their study they analyzed a fossil "bristleworm" (phylum *Annelida*, class *Polychaeta*) and one of the unique discoveries they made is that along specific anatomical parts of the animal elevated levels of arsenic (As) were found. One of the unique aspects of Mazon Creek geology is that the preserving sediments contain abundant siderite, an iron carbonate mineral. This unique type of sedimentary deposit, called Laggerstätte, creates fossils with exceptional preservation. Siderite also has a very high adsorption capacity for As species which may explain the observed results.

S-6

Identifying Protein Crystals Using Known Structures

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Bovine insulin was purchased from a commercial supplier. Using commercially available chemicals, well solutions containing polyethylene glycols, a buffer system, and a variety of salts were created and mixed with the protein solution. Crystallization trails were initiated using the hanging drop method in 24 well plates specifically designed for such experiments. After the protein crystals were grown, they were harvested and frozen in liquid nitrogen using a cryogenic solution to prevent ice formation within the crystals. The crystals were then analyzed using the x-rays at LS-CAT and NE-CAT to create data sets. These data sets were then processed using a variety of software suites to produce the three-dimensional structure of the protein.

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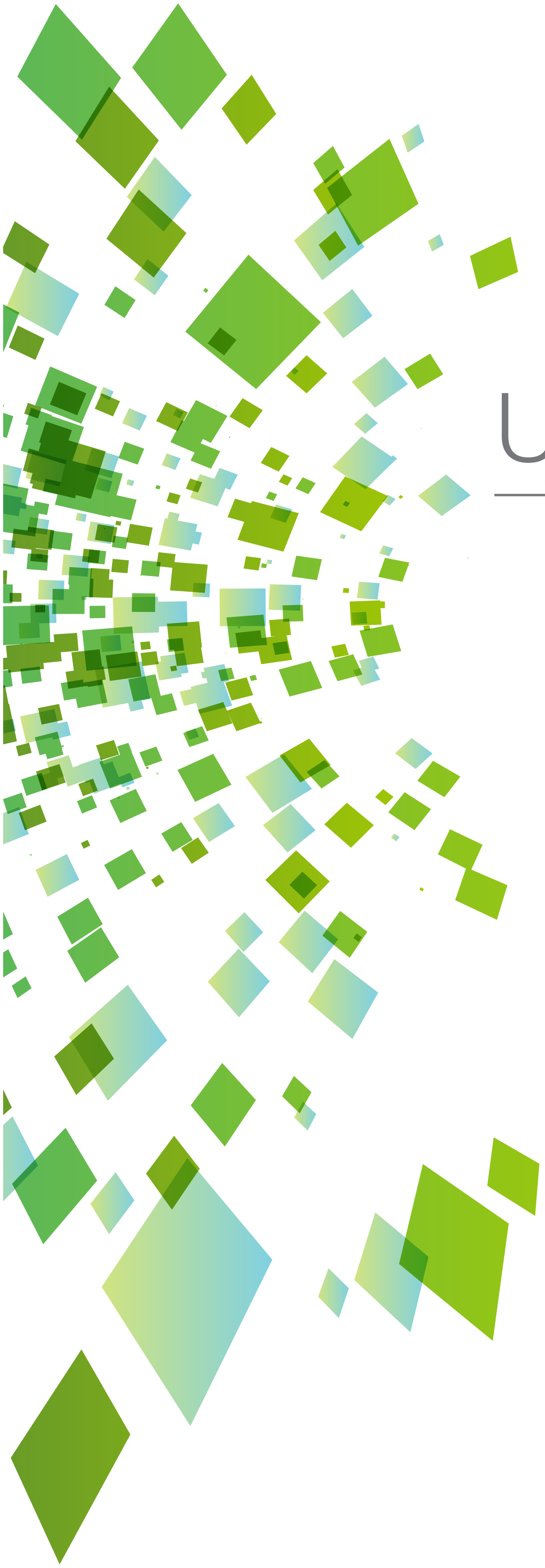

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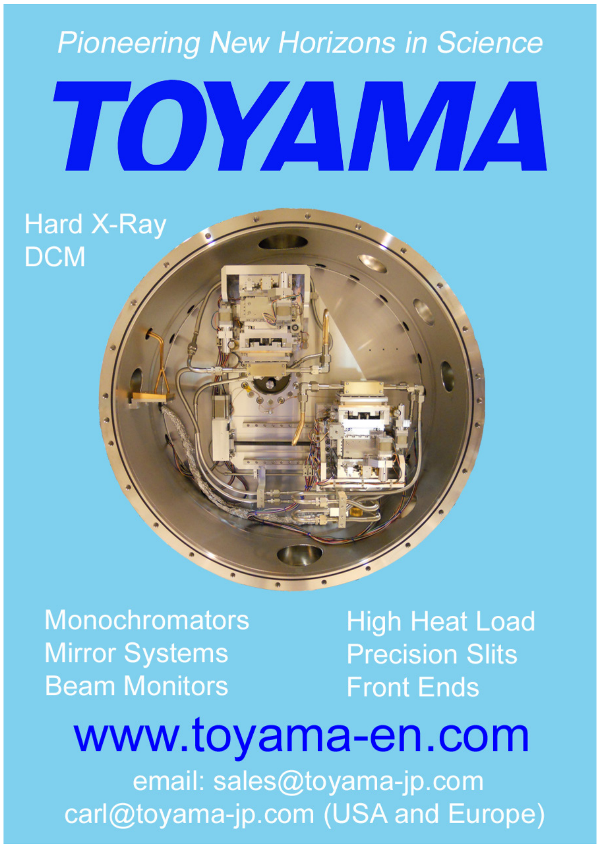

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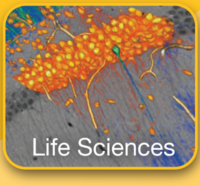
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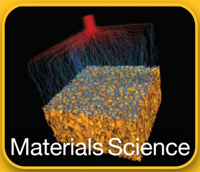
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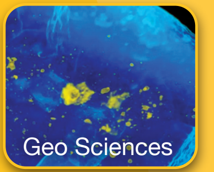
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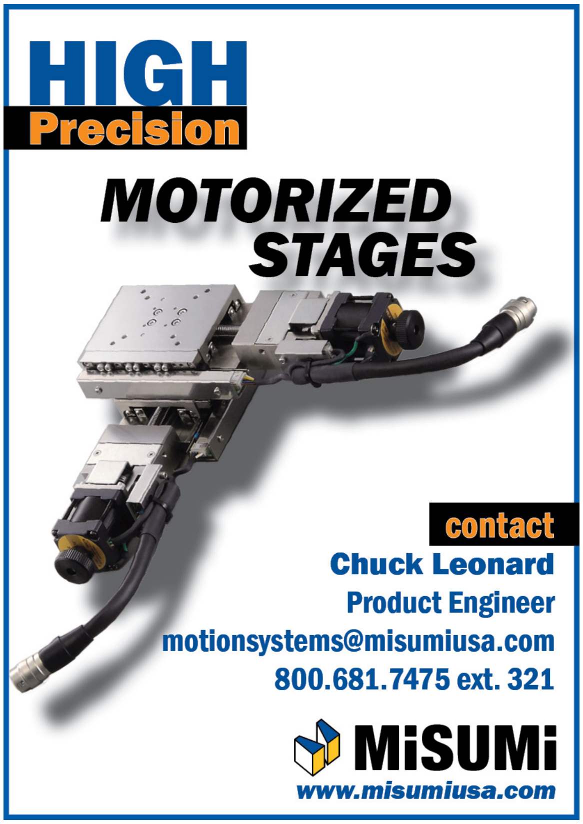

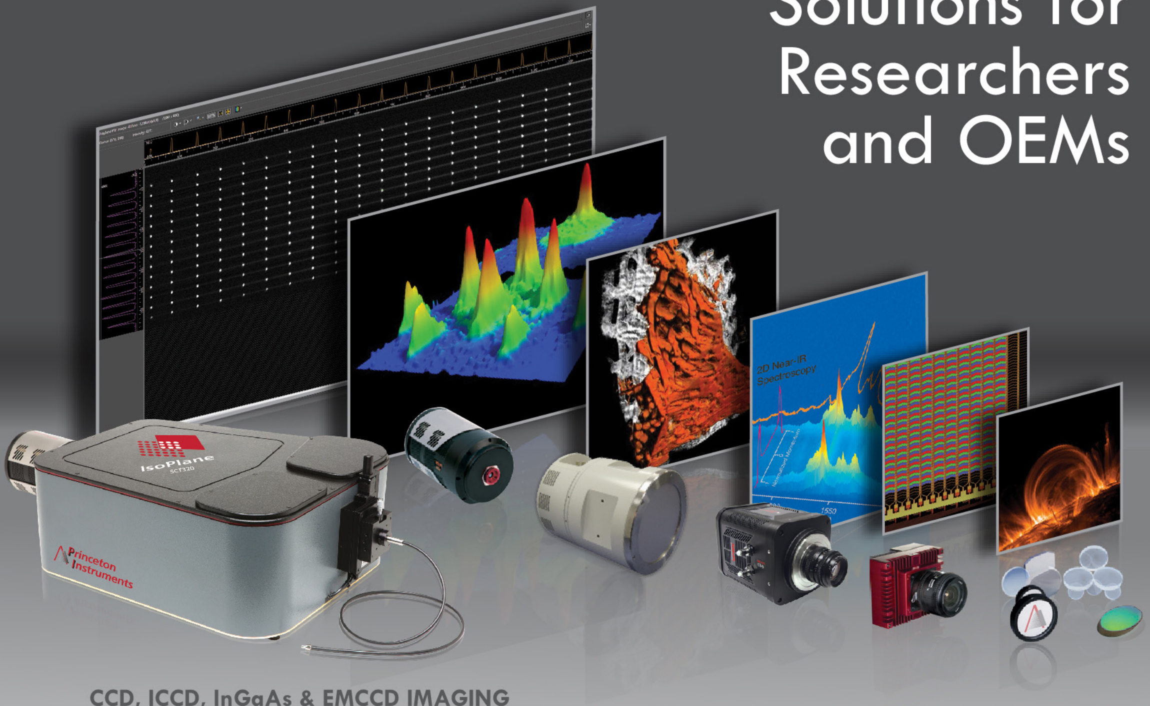
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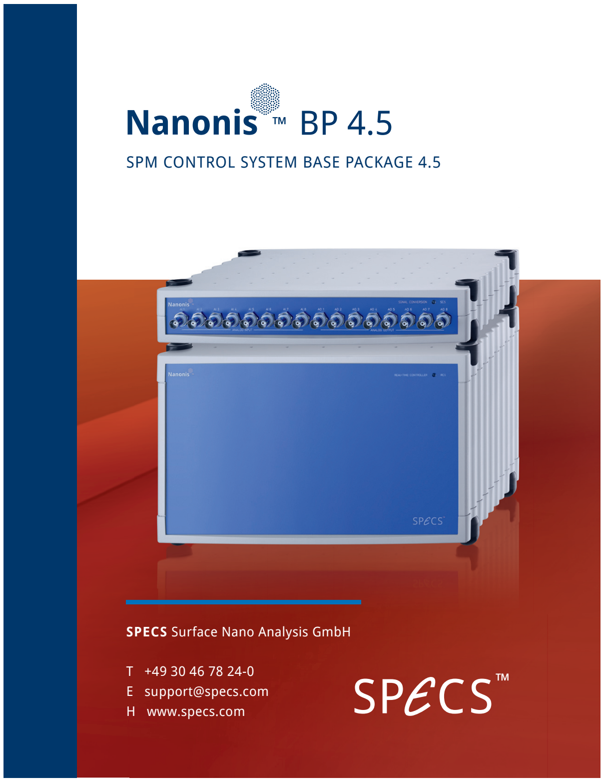

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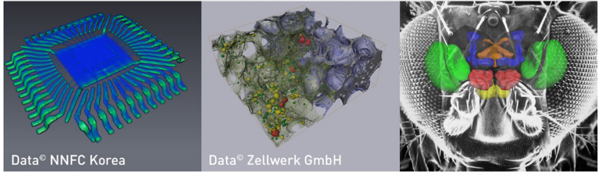

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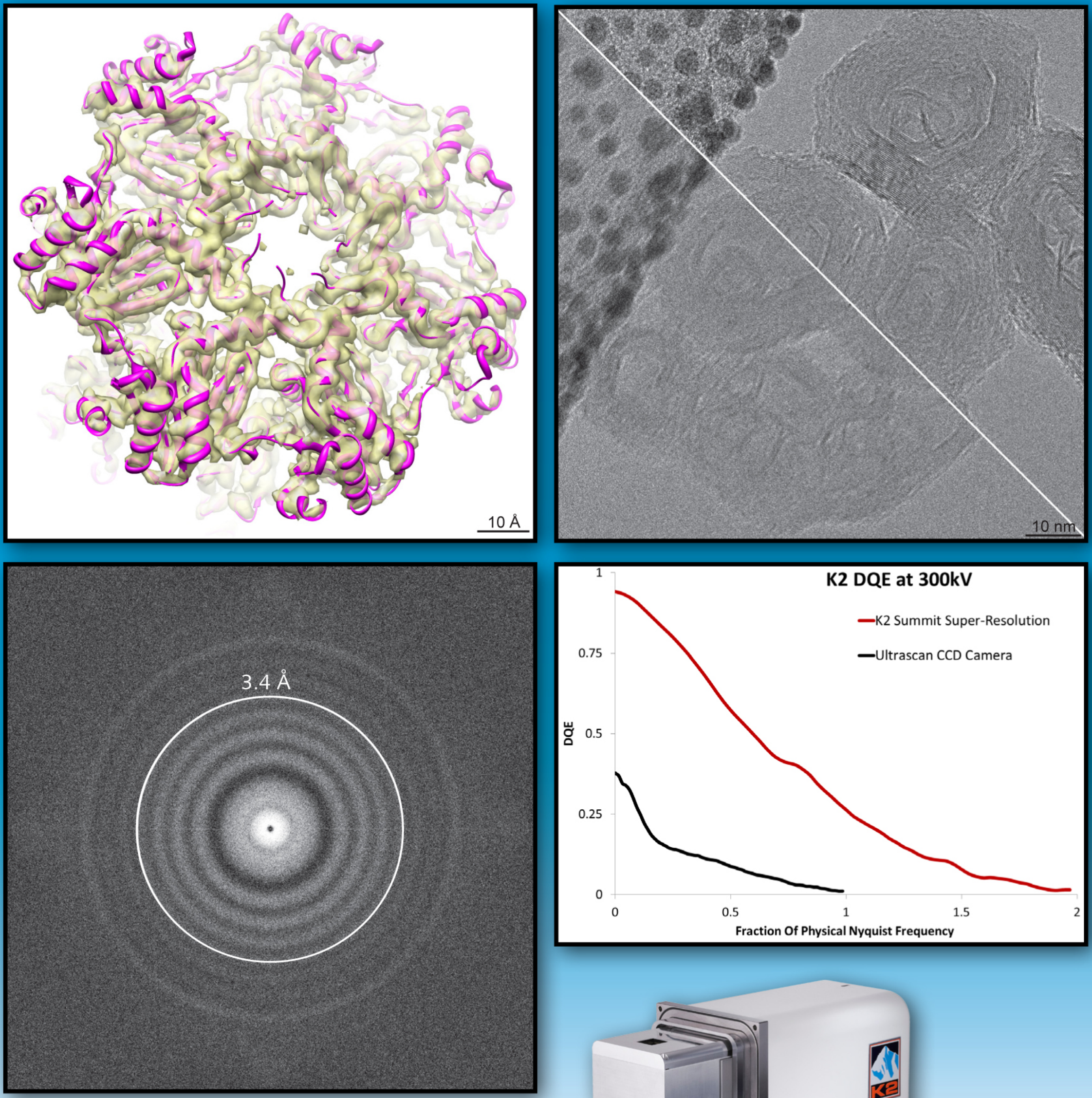

Image, clockwise from top left:
Cryo-EM reconstruction of 20S proteasome at 4.4 Å resolution. Images were collected at 300 kV, 39kx nominal magnification (~1 Å per pixel) with total dose of 25 $e^{-}/\text{Å}^{2}$. All data were collected using the Gatan K2Summit™ Counting mode. Images and reconstructions provided courtesy of Dr. Yifan Cheng and Dr. Xueming Li of the University of California, San Francisco.

Images of graphitized carbon collected using the Gatan K2Summit™ Counting mode using the dose fractionation acquisition method built into Gatan DigitalMicrograph®. Images were collected at 200 kV, 39kx nominal magnification (~1 Å per pixel). 14 frames were acquired over a total exposure time of 7 seconds with a dose rate of 12 electrons/pixel/second. Shown are the drift corrected image (top right) and the non-drift corrected image (lower left).

Detective quantum efficiency (DQE) of the Gatan K2Summit™ camera in Super-Resolution mode was estimated from knife edge images collected at 300 kV. The DQE of the Gatan UltraScan® 4k x 4k CCD camera was measured using the same method.

Images of a Platinum Iridium sample were collected using the Gatan K2Summit™ camera in Super-Resolution mode. The images were collected at 23kx nominal magnification (1.7 Å per physical pixel and 0.85 Å per effective pixel) and 20 $e^{-}/\text{Å}^{2}$. The total exposure time to collect this image was 3 seconds. The white circle indicates 3.4 Å resolution and indicates the information limit (Nyquist frequency) of the camera without Super-Resolution mode. The information in this K2Summit™ Super-Resolution image extends to at least 2.3 Å resolution, well beyond the physical pixel information limit.

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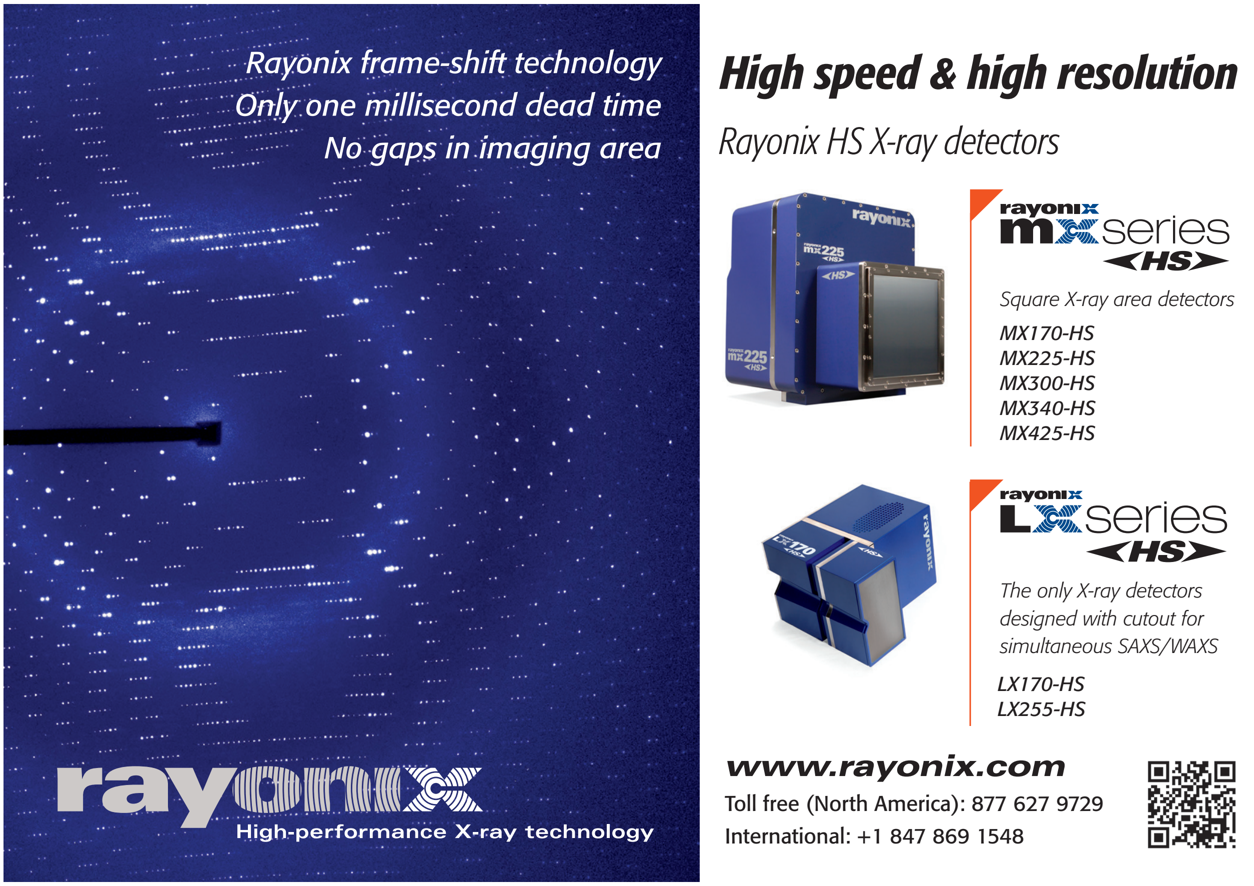

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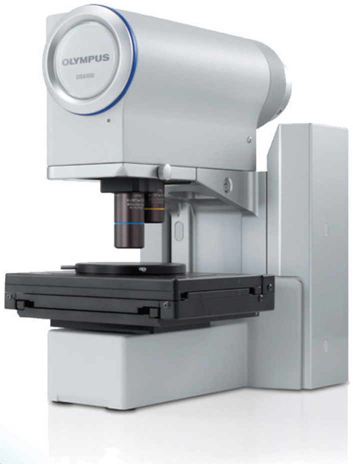
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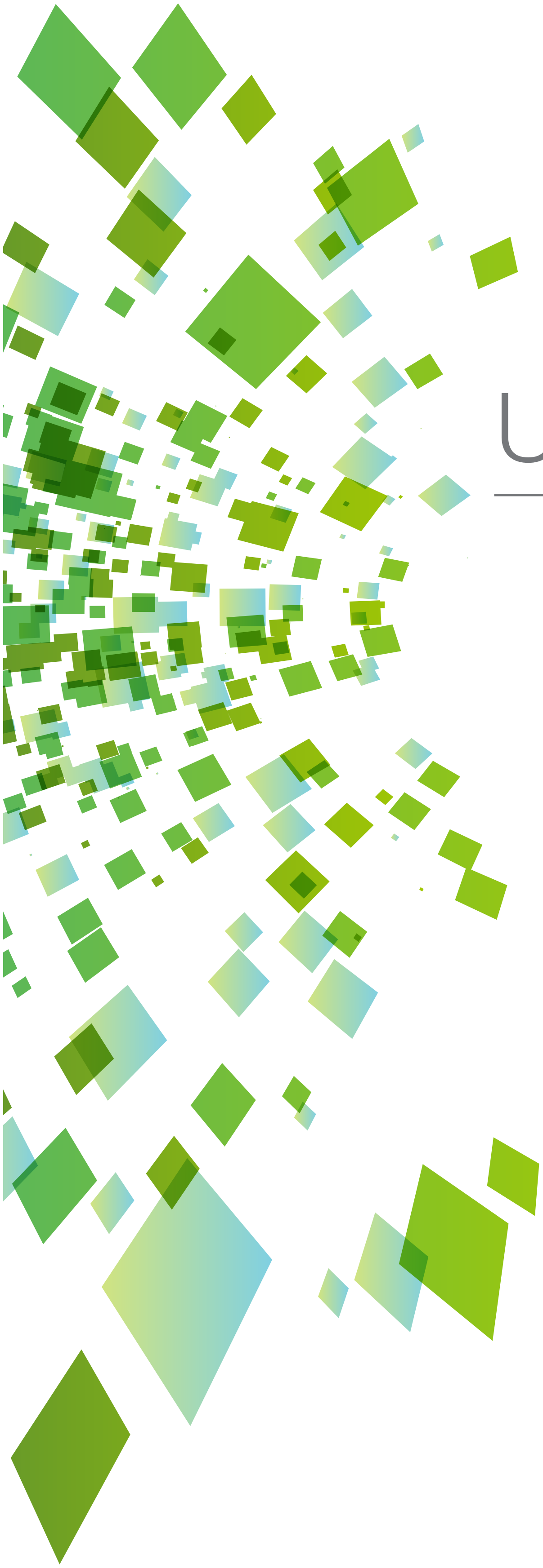

2013
Users Meeting

GENERAL INFORMATION

Practical Matters

Locations

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 and outside E1100-1200. 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 dining room at the Argonne Guest House (bus service provided departing from the lower-level Gallery). 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 9. The 401 Grill will be open for dinner throughout the meeting (closed for lunch, re-opening for both lunch and dinner on Thursday, May 9). 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.

Transportation

Conference staff can make limousine reservations for you during the meeting as long as you make your request before 1:00 pm on Wednesday.

ATM

An automated teller machine is located in Bldg. 233, behind the Argonne cafeteria. This machine accepts the following cards: American Express, Discover/Novus, The Exchange, Master Card, Plus, Visa, and 24 Access.

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).
2. Read and accept the Argonne internet access policy, which will appear as a Web page on your desktop. After you click "accept," a registration Web page will appear.
3. The registration web page asks you for the following information:
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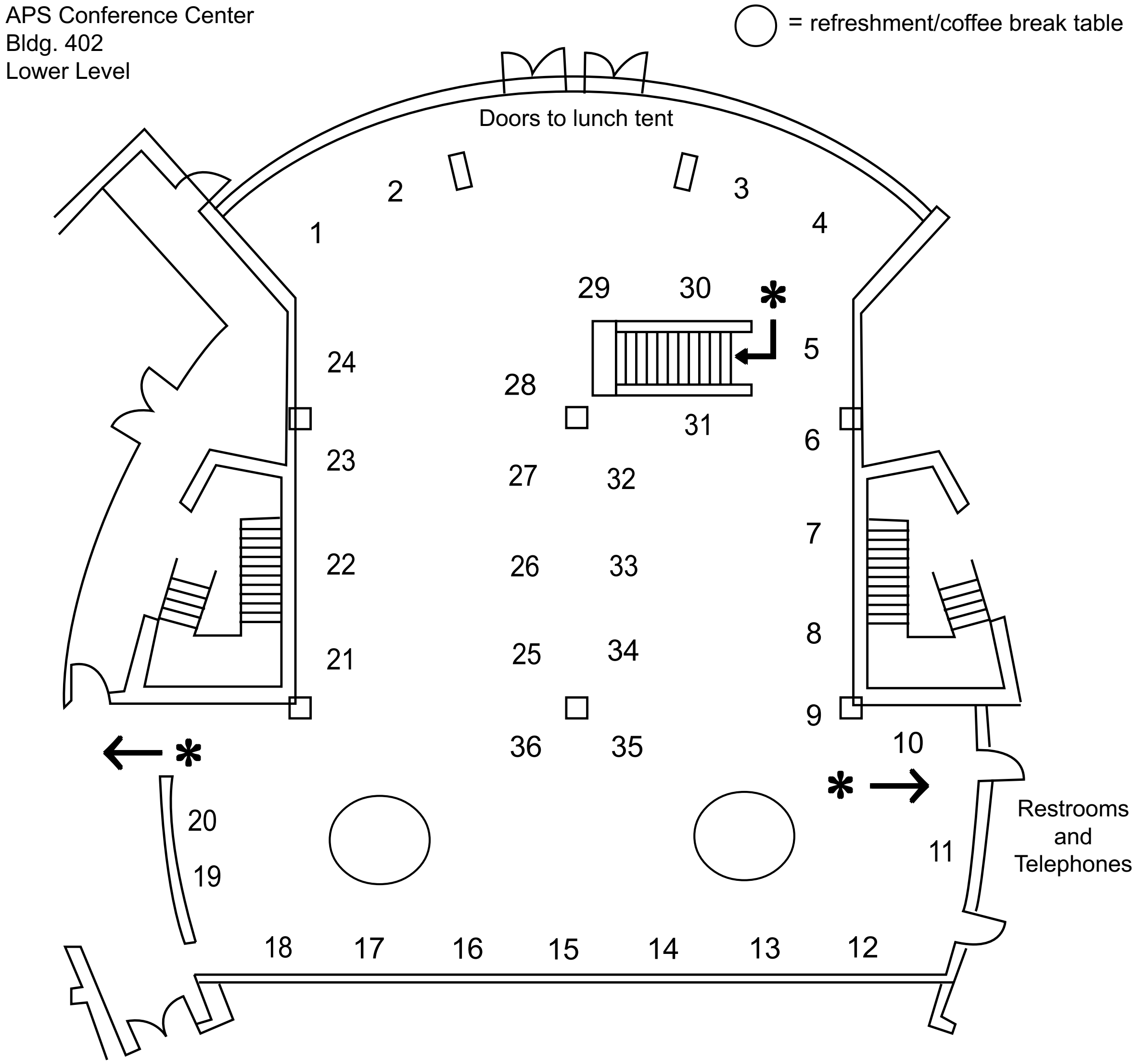
    b. E-mail address
    c. Building and room where you will be located (use 402 conference center)
    d. Phone number where you can be reached on site (use 630-252-9090)
    e. Name of person you are visiting or conference you are attending
    f. Home institution
    g. Do you need to send e-mail directly to an off-site server?
    h. What is the duration of this registration? (You'll be given choices.)

If you have problems, please contact someone in the APS User Office (B1154, located immediately off the Conference Center atrium).

Exhibitor Locations – 2013 APS/CNM/EMC Users Meeting
Argonne National Laboratory



1. attocube systems Inc.
2. MEWASA North America, Inc.
3. Bruker ASC GmbH
4. MICRONIX USA LLC
5. Blake Industries
6. Aerotech, Inc.
7. XIA LLC
8. Canberra
9. Advanced Research Systems
10. Ebara Technologies Inc.
11. Restronics of Illinois
12. TDK-Lambda Americas
13. Oerlikon Leybold Vacuum
14. BellowsTech, LLC
15. Piezosystem Jena
16. Rigaku Innovative Technologies
17. Kurt J. Lesker Company
18. Misumi USA
19. Agilent
20. ALIO Industries
21. Midwest Vacuum, Inc.
22. SPECS Surface Nano Analysis
23. Block Engineering
24. Mantis Deposition Ltd.
25. Global Test Equipment
26. Steinmeyer, Inc.
27. Princeton Instruments
28. DMS, Inc.
29. ADC Corp.
30. Instrument Design Technology Ltd.
31. FMB Oxford
32. Applied Diamond Inc.
33. Navitar, Inc.
34. Toyama Co., Ltd.
35. Newport Corporation
36. Alan Burrill Technical Sales

* UPSTAIRS/ATRIUM EXHIBITORS PLUS REFRESHMENT TABLES

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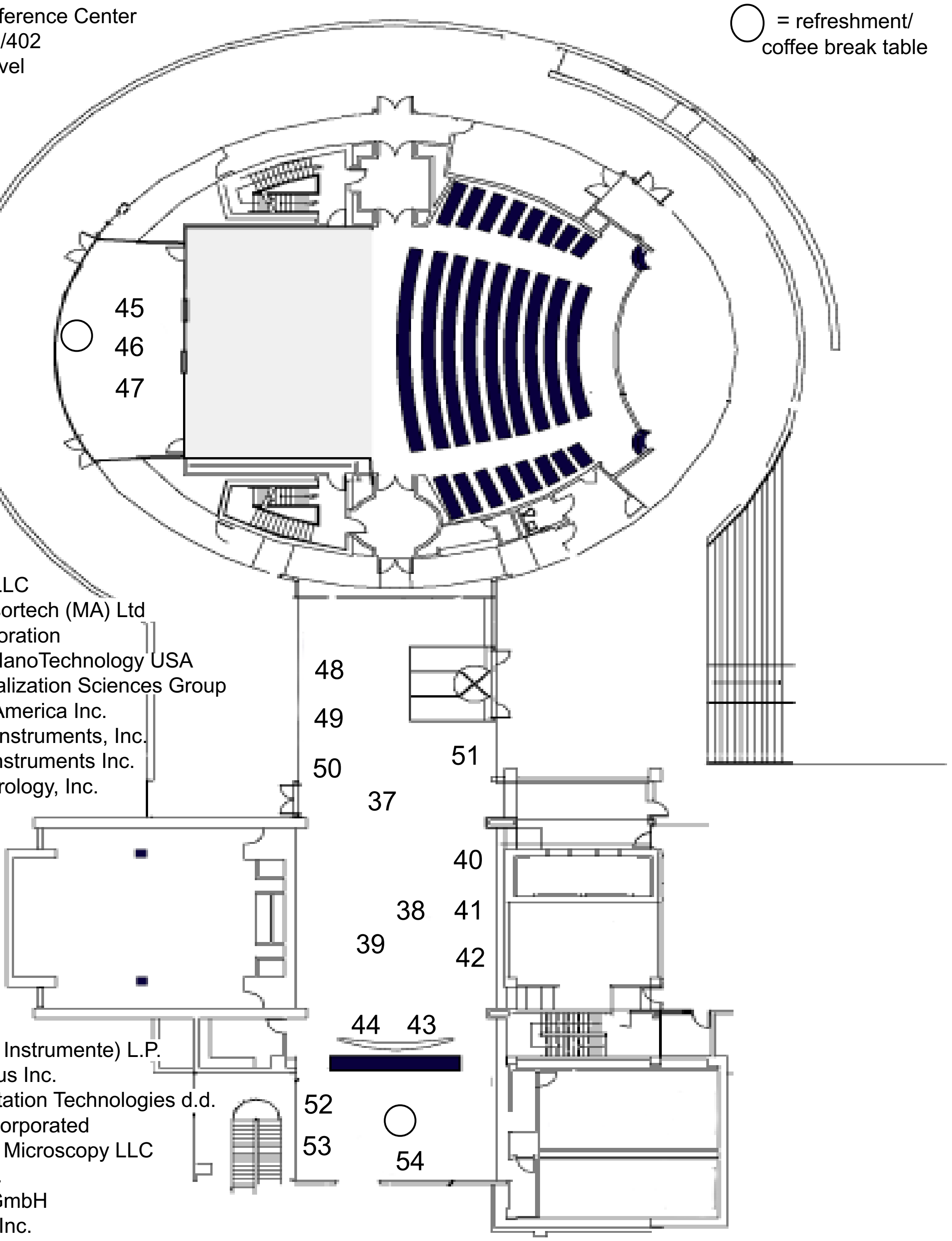
APS Conference Center
Bldg. 401/402
Upper Level

○ = refreshment/
coffee break table



37. Rayonix, LLC
38. SGX Sensortech (MA) Ltd
39. A&N Corporation
40. Omicron NanoTechnology USA
41. VSG-Visualization Sciences Group
42. Olympus America Inc.
43. Scientific Instruments, Inc.
44. Spectral Instruments Inc.
45. Nikon Metrology, Inc.
46. PI (Physik Instrumente) L.P.
47. Control Plus Inc.
48. Instrumentation Technologies d.d.
49. Gatan, Incorporated
50. Carl Zeiss Microscopy LLC
51. nPoint Inc.
52. incoatec GmbH
53 Tek-Matic, Inc.
54. Vacuum One

Additional exhibitors on the Gallery level.

2013 APS/CNM/EMC Users Meeting - Schedule at a Glance

Monday May 6th

Vendor exhibits open daily Mon. -- Wed. in the Gallery (lower level), the Atrium (first floor), and outside E1100-1200 (first floor). Break time snacks offered in all locations!

Opening Session (***Bldg. 402, APS Auditorium***)

8:30 - 8:40	Pamela Focia, APSUO Chair, Welcome
8:40 - 9:00	Eric Isaacs, ANL Director, Welcome from the Laboratory
9:00 - 9:15	The Honorable Bill Foster, U.S. Representative, 11th Congressional District of Illinois, Washington Perspective
9:15 - 9:30	The Honorable Daniel Lipinski, U.S. Representative, 3rd Congressional District of Illinois, Washington Perspective
9:30 - 9:50	James Murphy, Director of Scientific User Facilities, Basic Energy Sciences, DOE, Office of Science Perspective
9:50 - 9:55	Brian Stephenson, APS Director, Introduction of Keynote
9:55 - 10:35	**Keynote Speaker**: Brian Kobilka, 2012 Nobel Prize Winner in Chemistry
10:35 - 11:00	**Coffee Break (Gallery, Atrium, and outside E1100-1200)**
11:00 - 11:25	Brian Stephenson, Director, APS
11:25 - 11:45	Amanda Petford-Long, Director, CNM
11:45 - 12:00	Dean Miller, Director, EMC
12:00 - 12:15	Yves Idzerda, Vice Chair of NUFO
12:15 - 1:45	**Lunch (Guest House dining room, shuttle buses depart from Gallery lower level)**

Lunch will be held Monday-Wednesday at the Argonnne Guest House Dining Room. Shuttle buses will run continuously between the APS Gallery and the Guest House during the lunch hour. Dessert will be offered just outside the Gallery in the tent.

Coffee breaks are offered in 3 locations: the Gallery on the lower level, the Atrium, and outside of E1100-1200 behind Auditorium. **PLEASE BE SURE TO VISIT THE EXHIBITORS IN EACH AREA!**

Parallel Plenary Sessions

APS (*Bldg. 402, APS Auditorium*)		**CNM (*Bldg. 402, Rooms E1100-1200*)**		**EMC (*Bldg. 401, Room A1100*)**	
1:45- 2:15	Peter Abbamonte	1:30 - 2:15	Keynote: Paul Nealey	1:45 - 2:15	J. G. Wen
2:15 - 3:00	2013 Compton Award	2:15 - 2:45	Junhong Chen	2:15 - 2:45	Jim Zuo
3:00 - 3:30	Mark Stalzer	2:45 - 3:15	Chad Folkman	2:45 - 3:15	David McComb
3:30- 3:55	**Coffee Break**	**3:15 - 3:40**	**Coffee Break**	**3:15 - 3:45**	**Coffee Break**
3:55 - 4:25	Jay Schuren	3:40 - 4:10	Greg Wurtz	3:45 - 4:15	Molly McCartney
4:25 - 4:55	Paul G. Evans	4:10 - 4:40	Sanja Tepavcevic	4:15 - 4:45	Masashi Watanabe
4:45 - 5:15	Christopher M. Dettmar	4:40 - 4:55	Daniel Hannah	4:45 - 5:15	Wenpei Gao

Poster Session set up will take place on Tuesday, May 7.
For poster set up, shuttle buses and vans will run between the APS, the Guest House, and the TCS *between 12 noon and 2:00 pm* .

5:30 - 9:00	**Social Event: Banquet at Morton Arboretum (buses depart promptly at 5:30 pm from the front of APS)**

Tuesday May 7th

APS-U Workshop: Beamlines and Scientific Opportunities (*Bldg. 402, APS Auditorium*)		**Driving Discovery: Visualization, Data Management, and Workflow Techniques (*Bldg. 401, Room A5000*)**		**Nanoscale Imaging of Next-generation Materials (*Bldg. 402, Rooms E1100/E1200*)**		**Pushing the Boundaries of Energy Technology: Materials Design for Battery Applications (*Bldg. 401, Room A1100*)**	
9:00 - 9:35	Overview & Status	8:30 - 8:50	Welcome & Intro. Remarks	8:45 - 9:00	Welcome & Intro. Remarks		
9:35 - 10:00	RIXS Beamline	8:50 - 9:20	Gayle Woloschak	9:00 - 9:40	Cheng-Hsuan Chen	8:30 - 8:35	Welcome & Intro. Remarks
10:00 - 10:25	S3DD Beamline	9:20 - 9:50	Jean-Christophe Olivo-Marin	9:40 - 10:20	Robert Klie	8:35 - 9:10	Shirley Meng
10:25 - 10:40	**Coffee Break**	9:50 - 10:20	Yali Amit	**10:20 - 10:50**	**Coffee Break**	9:10 - 9:45	Bruce Dunn
10:40 - 11:05	Producing SPX-rays	**10:20 - 10:50**	**Coffee Break**	10:50 - 11:30	Wei Chen	9:45 - 10:05	Jason Croy
11:05 - 11:35	SPX Beamline	10:50 - 11:20	Rachana Ananthakrishnan	11:30 - 12:15	Mariana Bertoni	10:05-10:25	Matthew McDowell
11:35 - 12:00	Detector Development	11:20 - 11:50	Daniela Ushizima	**12:15 - 1:45**	**Lunch** *(Guest House dining room)*	**10:25 - 10:50**	**Coffee Break**
12:15 - 1:45	**Lunch** *(Guest House dining room)*	11:50 - 12:15	Todd Munson	1:50 - 2:30	Charlie Sykes	10:50 - 11:25	Debra Rolison
2:00 - 2:30	Superconducting Undulator	**12:15 - 1:45**	**Lunch** *(Guest House dining room)*	2:30 - 3:10	Wenge Yang	11:25 - 12:00	Yury Gogotsi
2:30 - 2:55	*In Situ* Nanoprobe	1:45 - 2:15	Michael Groeber	**3:10 - 3:40**	**Coffee Break**	12:00 - 12:20	Maria Chan
2:55 - 3:20	Beam Stability	2:15 - 2:45	Subramanian Sankaranarayanan	3:40 - 4:20	Sophie-Charlotte Gleber	**12:20 - 1:45**	**Lunch** *(Guest House dining room)*
3:20 - 3:35	**Coffee Break**	2:45-3:10	Josh Kacher	4:20 - 5:00	Nathan Guisinger	1:50 - 2:25	Jun Liu
3:35 - 4:00	Interface Science	**3:10 - 3:40**	**Coffee Break**			2:25 - 3:00	Tim Fister
4:00 - 4:25	HEXD	3:40 - 4:10	Salman Habib			3:00 - 3:20	Andrea Paolella
4:25 - 4:50	Wide-field Imaging	4:10 - 4:40	Anton Barty			**3:20 - 3:40**	**Coffee Break**
4:50 - 5:05	Wrap-up	4:40 - 5:00	Discussion			3:40 - 4:15	Joy Andrews Hayter
						4:15 - 4:50	Jerry Seidler
						4:50 - 5:10	Sanja Tepavcevic
						5:10 - 5:20	Closing Remarks

12:15 - 1:30	**CNM Users Executive Committee Meeting (*Bldg. 440, Room A201*)**
12:15 - 1:30	**APS Partner User Council Meeting (*Bldg. 401, A5000 Gallery*)**
5:00 - 7:30	**Poster Session and Reception (Bldg. 240 TCS--bus transportation provided between APS, Guest House, and TCS)**

Wednesday May 8th

Parallel Facility-specific Workshops: Full- and Half-day

APS WK1 - full	Bldg. 402, APS Auditorium	CNM WK8 - full	Bldg. 401, Room A5000
APS WK2 - full	Bldg. 440, Room A105/106	EMC WK9 - full	Bldg. 402, Room E1100
APS WK3 - full	Bldg. 401, Room A1100		
APS WK4 - ½ a.m.	Bldg. 402, Room E1200	\	
APS WK5 - ½ a.m.	Guest House, Conf. Room A		
APS WK6 - ½ p.m.	Bldg. 402, Room E1200		
APS WK7 - ½ p.m.	Guest House, Conf. Room A		

12:15 - 1:45	**Lunch (Guest House dining room)**
12:15 - 1:30	**APSUO Steering Committee Meeting (Bldg. 401, Fifth Floor Gallery)**

Thursday May 9th

CNM Short Courses (all in CNM Bldg. 440)	
Short Course A	Room A105-106 (full day)
Short Course B	Room B108 (morning)
Short Course C	Sector 26 Control Rm. (morning)
Short Course D	Room A201 (morning)

APS Satellite Workshops	
APS WK10	Bldg. 401, Room A5000
APS WK11	Bldg. 401, Room A1100
APS WK12	Guest House Conf. Rm. A
APS WK13	Bldg. 402, APS Auditorium

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

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