



2015

APS/CNM Users Meeting



WORKSHOP AGENDAS AND ABSTRACTS



Tuesday, May 12

Facility-specific Workshops

CNM Workshop 1

Nanophotonic Structures, Surfaces, and Composites for Radiative Control

Location: Bldg. 401, Room A5000

Organizers: Steve Smith (South Dakota School of Mines & Technology), Il Woong Jung (Nanofabrication & Devices Group, CNM), Zhe Fei (Nanophotonics Group, CNM)

The scope of this workshop encompasses all aspects of the photonic control of quantum systems, including the fabrication, characterization, simulation, and theory of composite photonic-electronic systems, that is, those specific materials and nano-structured composite systems which intentionally modify and/or exhibit control of light matter interactions as a consequence of their nanostructure. Examples are quantum emitters (e.g., molecules, ions or quantum dots) whose radiative properties are modified by their interactions with nano-optical structures, including photonic crystals, cavities, plasmonic surfaces and/or high-aspect ratio optical nano-structures. Development of improved optical materials, nanostructures, and composites and their applications will be emphasized as well as photonic crystals, micro-cavities, photonic control, plasmonics, fabrication, and the properties of photonic nano-structures.

8:30 – 8:45	Welcome & Introductory Remarks
8:45 – 9:25	Marko Loncar (Harvard University) <i>Quantum and Nonlinear Nanophotonics with Diamond</i>
9:25 – 10:05	George Schatz (Northwestern University) <i>Plasmonic Arrays</i>
10:05 – 10:35	Break
10:35 – 11:15	Yugang Sun (Argonne National Laboratory) <i>Interfacial Influence on Surface Plasmon Resonances in “Quantum-sized” Metal Nanoparticles</i>
11:15 – 12:00	Zhiqun Lin (Georgia Tech) <i>Crafting Nanophotonic Structures</i>
12:00 – 1:30	Lunch
1:30 – 2:10	Peng Zhang (University of Cincinnati) <i>SERS Inside Metal Nanoshell and Its Applications</i>
2:10 – 2:50	Shaung Fang Lim (North Carolina State University) <i>Multifunctional Diagnostic, Nanothermometer and Photothermal Nano-devices</i>
2:50 – 3:20	Break
3:20 – 4:00	Stephen Gray (Argonne National Laboratory) <i>Theoretical Studies of Hybrid Plasmon/Quantum-dot Systems</i>

- 4:00 – 4:40 Nathaniel Stern (Northwestern University)
Photons in Flatland: Manipulating Light and Matter in Two-dimensional Nanomaterials
- 4:40 Wrap-up and concluding remarks
-

WK1

Quantum and Nonlinear Nanophotonics with Diamond

Marko Loncar

School of Engineering and Applied Science, Harvard University, Cambridge, MA 02138

Diamond possesses remarkable physical and chemical properties, and in many ways is the ultimate engineering material — “the engineer’s best friend!” For example, it has high mechanical hardness and large Young’s modulus, and is one of the best thermal conductors. Optically, diamond is transparent from the ultra-violet to infra-red, has a high refractive index ($n = 2.4$), strong optical nonlinearity and a wide variety of light-emitting defects. Finally, it is biocompatible and chemically inert, suitable for operation in harsh environment. These properties make diamond a highly desirable material for many applications, including high-frequency micro- and nano-electromechanical systems, nonlinear optics, magnetic and electric field sensing, biomedicine, and oil discovery. One particularly exciting application of diamond is in the field of quantum information science and technology, which promises realization of powerful quantum computers capable of tackling problems that cannot be solved using classical approaches, as well as realization of secure communication channels. At the heart of these applications are diamond’s luminescent defects — color centers — and the nitrogen-vacancy (NV) and silicon-vacancy (SiV) color center in particular. These atomic systems in the solid-state possesses all the essential elements for quantum technology, including storage, logic, and communication of quantum information.

I will review recent advances in nanotechnology that have enabled fabrication of nanoscale optical devices and chip-scale systems in diamond that can generate, manipulate, and store optical signals at the single-photon level. Examples include a room temperature source of single photons based on diamond nanowires [1] and plasmonic apertures [2], as well as single-photon generation and routing inside ring [3] and photonic crystal resonators [4]. Novel, fabrication technique [5] — *angled-etching* — suitable for realization of nanophotonic [6] and nanomechanic [7,8] devices in bulk diamond crystals will also be discussed. Finally, I will present our recent result on frequency comb generation at telecom wavelengths using high Q-factor ($>10^6$) diamond ring resonator [9], and discuss our ongoing efforts towards realization of diamond comb in visible range. (<http://nano-optics.seas.harvard.edu>.)

This work has been supported by DARPA, AFOSR and NSF.

- [1] T.M. Babinec et al., “A bright single photon source based on a diamond nanowire,” *Nature Nanotechnology* **5**, 195 (2010).
- [2] J.T. Choy et al., “Enhanced Single Photon Emission by Diamond-Plasmon Nanostructures,” *Nature Photonics* **5**, 738 (2011).
- [3] B.J.M. Hausmann et al., “Integrated Diamond Networks for Quantum Nanophotonics,” *Nano Letters* **12**, 1578 (2012).
- [4] B.J.M. Hausmann et al., “Coupling of NV centers to photonic crystal nanobeams in diamond,” *Nano Letters* **13**, 5791–5796 (2013).
- [5] M.J. Burek et al., “Free-standing mechanical and photonic nanostructures in single-crystal diamond,” *Nano Lett.* **12**, 6084 (2012).
- [6] M. Burek, Y. Chu, M. Liddy, P. Patel, J. Rochman, W. Hong, Q. Quan, M.D. Lukin, and M. Loncar, “High-Q optical nanocavities in bulk single-crystal diamond,” *Nat. Comm.* **5**, 5718 (2014).
- [7] M. Burek et al., “Nanomechanical resonant structures in single-crystal diamond,” *Appl. Phys. Lett.* **103**, 131904 (2013).
- [8] Y.I. Sohn et al., “Dynamic Actuation of Single-Crystal Diamond Nanobeams,” *arXiv:1408.5822*.
- [9] B. Hausmann et al., “Diamond Nonlinear Photonics,” *Nature Photonics* **8**, 369 (2014).



WK1

Plasmonic Arrays

George C. Schatz

Northwestern University, Evanston, IL 60208

Silver and gold nanoparticles have unique optical properties that are associated with the excitation of collective excitations of the conduction electrons known as plasmon resonances. The resonance frequencies are sensitive to particle shape and size, which means that the color of the nanoparticles can be tuned over a wide range of wavelengths, and they are also sensitive to the arrangement of the nanoparticles into aggregates and arrays. This talk will emphasize recent theory and experiments that have probed the effect of arrays of these particles in 1D, 2D and 3D on optical response. The arrays in 1D and 2D can be made using standard lithography tools, but much of the talk will emphasize bottom-up assembly of arrays that is possible using DNA-functionalized nanoparticles and self-assembly of nanoparticle superlattices driven by DNA hybridization. We show that the array structures lead to new kinds of hybrid optical modes in which localized surface plasmon resonances in the nanoparticles are coupled with photonic modes of the lattices, including Bragg modes, Fabry-Perot modes and other modes. These hybrid modes are often much narrower than the isolated particle plasmons, and films composed of these superlattices have unusual metamaterials properties. We also show that for 2D lattices it is possible to generate a new class of sub-wavelength laser in which excitons in laser dyes are coupled with the hybrid lattice modes to produce enhanced stimulated emission.

WK1

Interfacial Influence on Surface Plasmon Resonances in “Quantum-sized” Metal Nanoparticles

Sheng Peng, Zheng Li, Jonathan J. Foley, IV, Stephen K. Gray, Gary P. Wiederrecht, and Yugang Sun

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

Nanoparticles made of noble metals such as silver and gold exhibit strong optical absorption due to their surface plasmon resonance (SPR) that corresponds to the collective oscillation of surface conduction electrons in response to the incident electromagnetic waves. As the nanoparticles are smaller than 20 nm (i.e., the size in the range similar to that of quantum dots), the interfaces formed on the surfaces of these noble metal nanoparticles significantly influence the nanoparticles' SPR. For example, the monodispersed silver nanoparticles synthesized *via* a well-defined chemical reduction process exhibit an exceptional size-dependence of SPR peak positions: as particle size decreases from 20 nm the peaks blue-shift but then turns over near ~12 nm and strongly red-shifts. Theoretic modeling and calculations reveal that the surface chemistry corresponding to the interactions between the capping molecules and the surface silver atoms in the nanoparticles become pronounced in determining their optical properties because the surface silver atoms represent a significant fraction of the total number of atoms in small nanoparticles. Such surface chemistry reduces the density of conduction band electrons (i.e., free electrons) in the surface layer of metal atoms, thus consequently influences the frequency-dependent dielectric constant of the metal atoms in the surface layer and the overall SPR absorption spectrum. In this presentation, a number of interfaces including the aforementioned metal/surfactant interface, metal/inorganic dielectric interface, and metal/metal interface will be discussed to highlight the importance of interface conditions on SPRs in “quantum-sized” noble metal nanoparticles. A comprehensive understanding of the relationship between interfacial coupling/chemistry and optical properties will be beneficial to exploit new applications of small colloidal metal nanoparticles, such as colorimetric sensing, electrochromic devices, surface enhanced spectroscopies, and photocatalysis.

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.

WK1

Crafting Nanophotonic Structures

Zhiqun Lin

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332

Colloidal nanocrystals exhibit a wide range of size and shape dependent properties and have found application in a myriad of fields such as photonics, optics, electronics, mechanics, drug delivery and catalysis to name but a few. Synthetic protocols that enable simple and convenient production of colloidal nanocrystals with controlled size, shape and composition are therefore of key general importance. Current strategies, however, often require stringent experimental conditions, are difficult to generalize, or require tedious multi-step reactions and purification. Recently, linear amphiphilic block copolymer micelles have been used as template for the synthesis of functional nanocrystals, but the thermodynamic instability of these micelles limits the scope of this approach. In this talk, I will elaborate general strategies for synthesizing a large variety of functional nanoparticles and nanorods (in particular, photonic nanoparticles and nanorods) with precisely controlled dimensions, compositions and architectures by using nonlinear block copolymers as templates. This new class of copolymers forms unimolecular micelles that are structurally stable under various experimental conditions and therefore overcomes the intrinsic instability of linear block copolymer micelles. Our approach enables the facile synthesis of organic solvent- and water-soluble nearly monodisperse photonic nanoparticles and nanorods with desired composition and architecture, including core/shell and hollow nanostructures.

WK1

SERS Inside Metal Nanoshell and Its Applications

Peng Zhang

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221

The observation of giant enhancement of Surface-enhanced Raman scattering (SERS) in the late 1990s had reignited the tremendous interests in the field. A great variety of nanostructures have been explored as SERS substrates, with various successes in terms of consistency and reproducibility. We approached the subject from a different aspect by placing the Raman probe molecules inside the metal nanoshell, in contrast to other previous experimental works, where SERS effect was studied only for molecules located in the proximal distance outside a nanostructure.

We show that enormous SERS enhancement inside metal (Au, Ag or mixed Ag/Au) nanoshell can be consistently and reproducibly achieved experimentally in the solution. The results provide new insights to the SERS effect, and pave ways for a new design of nanostructures to be used in Raman-based assays and imaging. Nanostructures of such design may also have profound implication in other plasmonic applications.

WK1

Multifunctional Diagnostic, Nanothermometer, and Photothermal Nano-devices

Kory Green, Janina Wirth, Megan O'Connor, and Shuang Fang Lim

Department of Physics, North Carolina State University, Raleigh, NC 27595

In this study, the known therapeutic capabilities of gold nanorods (AuNRs) have been combined with the diagnostic and nanothermometer abilities of upconversion nanoparticles (UCNPs) to develop a system for simultaneous biological imaging, photothermal therapy, and nanothermal sensing. Both the excitation of UCNPs and the finely tuned longitudinal surface plasmon resonance (LSPR) mode of AuNRs lay in a window of relatively high light penetration of tissue in the infrared. The nanothermometer property of the UCNPs allows direct quantification of the localized temperature of the photothermally heated AuNRs chemically adsorbed to their surface and is free from the bleaching problems inherent in dye thermal sensing systems, especially at high laser fluences required to kill tissue. Spectroscopy on single particles, verified by transmission electron microscopy (TEM), has been performed at varying temperatures to confirm 1) the thermal sensing properties of UCNPs and 2) to finely tune their upconversion



enhancement arising from the LSPR coupling of the AuNRs. Preliminary quantification of the localized AuNR temperatures upon photothermal heating will be confirmed through single particle spectroscopy of the attached UCNPs. HeLa cell viability studies have also been performed.

WK1

Theoretical Studies of Hybrid Plasmon/Quantum-dot Systems

Stephen K. Gray

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

I discuss classical electrodynamics and cavity quantum electrodynamics approaches to understanding and predicting the behavior of systems composed of metal nanoparticles and quantum dots such as CdSe nanocrystals. The plasmon resonance of the metal nanoparticle can significantly alter the radiative properties of the quantum dots and its correct incorporation into the modeling is emphasized. New avenues in nonlinear optical phenomena and quantum information are explored with these systems.

WK1

Photons in Flatland: Manipulating Light and Matter in Two-dimensional Nanomaterials

Nathaniel P. Stern

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

Hybrid systems integrating light with matter offer a highly controllable landscape for understanding the interface between disparate physical entities. The emergence of materials with atomic-scale thickness suggests a new landscape in which to play with the coupling between light and low-dimensional materials. Exemplifying the interest of this new regime, the crystal symmetry of monolayer two-dimensional (2D) semiconductors can exhibit degenerate, yet distinct, valleys in momentum space that can be separately addressed by polarized light. In this talk, I will describe how these optical transitions in 2D semiconductors can be harnessed for manipulating electronic excitations and charge motion in two-dimensional materials. Drawing on the developments in cavity quantum electrodynamics of the last several decades, I will discuss the behavior of 2D semiconductors when integrated into optical cavities and photonic devices. I will use this approach to illustrate the potential for exploring new hybrid regimes of light-matter coupling based on engineering quantum interactions with nanoscale materials.

Tuesday, May 12

Facility-specific Workshops

APS Workshop 2 High-energy-resolution Inelastic X-ray Scattering

Location: Bldg. 401, Lecture Hall

Organizers: Ayman Said, Ahmet Alatas, and Bogdan M. Leu (APS)

The workshop is intended as a forum for researchers using high-energy-resolution inelastic x-ray scattering (IXS) to present recent results. Diverse areas of research, including superconductivity, geophysics, charge density waves, and quantum phase transitions, will be covered, as well as theoretical approaches to IXS. The timing of this workshop is ideal for us to update users on recent developments that took place on the HERIX instruments and to discuss new ideas.

- | | |
|---------------|--|
| 8:30 – 8:35 | Linda Young (Argonne National Laboratory)
<i>Welcome & Introductory Remarks</i> |
| 8:35 – 8:45 | Ayman Said (Argonne National Laboratory)
<i>An Update about Sector 30</i> |
| 8:45 – 9:25 | Frank Weber (Karlsruhe Institute of Technology)
<i>Soft Phonon Mode and Wave Vector Dependent Electron-phonon Coupling at Charge-density Wave</i> |
| 9:25 – 10:05 | Matthieu Le Tacon (Max Planck Institute for Solid State Research)
<i>CDW and Electron-phonon Interaction in High-temperature Superconducting Cuprates</i> |
| 10:05 – 10:35 | Break |
| 10:35 – 11:15 | Jiawang Hong (Oak Ridge National Laboratory)
<i>Modeling the Phonon Dynamical Structure Factor $S(Q,E)$ from First-principles Calculations: The Case Study of Thermoelectrics and Complex Oxides</i> |
| 11:15 – 12:00 | Charles W. Myles
<i>Clathrate Semiconductors: Novel, Open Framework, Crystalline Materials Based on Si, Ge, and Sn</i> |
| 12:00 – 1:30 | Lunch |
| 1:30 – 2:10 | John Budai (Oak Ridge National Laboratory)
<i>Comprehensive Scattering Studies of Microstructure, Anharmonic Phonons and Thermodynamics near the Metal-insulator Transition in VO_2</i> |
| 2:10 – 2:50 | Jason Hancock (University of Connecticut)
<i>Critical Soft Modes and Negative Thermal Expansion</i> |
| 2:50 – 3:20 | Break |



3:20 – 4:00	Jung-Fu Lin (The University of Texas at Austin) <i>High-pressure Acoustic Phonons and Elasticity of Iron Alloys and Oxides</i>
4:00 – 4:40	Nicholas Butch (NIST Center for Neutron Research) <i>Looking for Hidden Phonons in URu₂Si₂</i>
4:40 – 5:00	Wrap-up and concluding remarks
5:00	Adjourn

WK2

Soft Phonon Mode and Wave Vector Dependent Electron-phonon Coupling at Charge-density-wave Transitions

Frank Weber¹, Michael Maschek¹, Stephan Rosenkranz², Rolf Heid¹, Roland Hott¹, Dmitry Reznik³, Goran Karapetrov⁴, P. Giraldo-Gallo^{5,7}, I.R. Fisher^{6,7}, A. Alatas⁸, and Ayman H. Said⁸

¹Institute for Solid State Physics, Karlsruhe Institute of Technology, D-76021 Karlsruhe, Germany

²Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

³Department of Physics, University of Colorado at Boulder, Boulder, CO 80309

⁴Department of Physics, Drexel University, Philadelphia, PA 19104

⁵Geballe Laboratory for Advanced Physics and Department of Physics, Stanford University, CA 94305

⁶Geballe Laboratory for Advanced Physics and Department of Applied Physics, Stanford University, CA 94305

⁷The Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

⁸Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

I will review our work on lattice dynamics in the charge-density-wave (CDW) compounds *2H-NbSe₂* [1], *1T-TiSe₂* [2] and *TbTe₃* [3]. Each of them is different with regard to the interplay of electronic structure and electron-phonon coupling properties. Nevertheless, all emphasize the general applicability of the stability criterion derived for a CDW by Chan & Heine [4].

$$\frac{4\eta_q^2}{\hbar\omega_{bare}} \geq \frac{1}{\chi_q} + (2\tilde{U}_q - \tilde{V}_q)$$

where η_q is the electron-phonon coupling associated with a mode at a bare energy of $\hbar\omega_{bare}$, χ_q is the dielectric response of the conduction electrons, and \tilde{U}_q and \tilde{V}_q are their Coulomb and exchange interactions. Although both sides of this inequality are essential in stabilizing the CDW order, the common assumption is that the modulation wave vector, \vec{q}_{CDW} , is determined by the right-hand side (i.e., by a singularity in the electronic dielectric function χ_q originating from a Fermi surface nesting).

Using high-energy resolution inelastic x-ray scattering and ab initio calculations of the lattice dynamical properties we analyzed the situation in the three above mentioned materials and find the following:

- ▶ There is no Fermi surface nesting in *2H-NbSe₂* and \vec{q}_{CDW} is completely defined by η_q .
- ▶ *TbTe₃* features a weak nesting close to \vec{q}_{CDW} but only including η_q yields the correct ordering wave vector.
- ▶ η_q in *1T-TiSe₂* has a comparatively small wave vector dependence and the \vec{q} dependence of one particular electronic scattering path defines \vec{q}_{CDW} .

- [1] F. Weber, S. Rosenkranz, J.P. Castellán, R. Osborn, R. Hott, R. Heid, K.P. Bohnen, T. Egami, A.H. Said, and D. Reznik, *Physical Review Letters* **107** (10), 107403 (2011); F. Weber, R. Hott, R. Heid, K.P. Bohnen, S. Rosenkranz, J.P. Castellán, R. Osborn, A.H. Said, B.M. Leu, and D. Reznik, *Physical Review B* **87** (24), 245111 (2013).
- [2] F. Weber, S. Rosenkranz, J.P. Castellán, R. Osborn, G. Karapetrov, R. Hott, R. Heid, K.P. Bohnen, and A. Alatas, *Physical Review Letters* **107** (26), 266401 (2011).
- [3] M. Maschek, S. Rosenkranz, R. Heid, A. Said, P. Giraldo-Gallo, I.R. Fisher, and F. Weber, arXiv: cond-mat:1410.7592 (2014).
- [4] S.K. Chan and V. Heine, *Journal of Physics F: Metal Physics* **3**, 795 (1973).

WK2

CDW and Electron-phonon Interaction in High-temperature Superconducting Cuprates

Matthieu Le Tacon

Max Planck Institute for Solid State Research, Stuttgart, 70569, Germany

I will present an overview of the results obtained from various x-ray scattering experiments on high temperature superconducting cuprates in the last couple of years. I will first focus on Cu L-edge resonant scattering experiments that led us to uncover charge density wave (CDW) correlations competing with superconductivity in the YBCO family [1–3], for which a complete temperature and doping dependent phase diagram has been worked out [4]. Further information was gained from high-resolution inelastic x-ray scattering that allows us to discuss the nature of the CDW. The observation of a quasi-elastic ‘central peak’ unraveled the static nature of the CDW correlations, attributed to the pinning of CDW nanodomains on defects. Low energy phonons exhibit anomalously large superconductivity induced renormalizations close to the CDW ordering wave vector, providing new insights regarding the long-standing debate of the role of the electron-phonon interaction in the cuprates, a major factor influencing the competition between collective instabilities in correlated-electron materials [5].

- [1] G. Ghiringhelli et al., *Science* **337**, 821 (2012).
- [2] A.J. Achkar et al., *Phys. Rev. Lett.* **109**, 167001 (2012).
- [3] S. Blanco-Canosa et al., *Phys. Rev. Lett.* **110**, 187001 (2013).
- [4] S. Blanco-Canosa et al., *Phys. Rev. B* **90**, 054513 (2014).
- [5] M. Le Tacon et al., *Nature Physics* **10**, 52 (2014).

WK2

Modeling the Phonon Dynamical Structure Factor $S(\mathbf{Q},E)$ from First-principles Calculations: The Case Study of Thermoelectrics and Complex Oxides

Jiawang Hong, Jennifer Niedziela, Chen Li, Vickie Lynch, and Olivier Delaire

Oak Ridge National Laboratory, Oak Ridge, TN 37830

SimPhonies, a python-based application developed within CAMM at SNS, enables users to calculate the x-ray/neutron-weighted dynamical structure factor for phonon scattering, $S(\mathbf{Q},E)$, from first-principles calculations. It enables direct, quantitative comparison with large datasets from inelastic x-ray/neutron scattering measurements on single-crystals. The SimPhonies code leverages first-principles electronic structure packages to calculate the x-ray/neutron scattering intensities convolved with instrumental resolution, including anharmonic effects, and outputs the scattering in the region of interest in reciprocal space. The benefits of reliable $S(\mathbf{Q},E)$ simulations, and comparisons with measurements at HERIX/SNS, are illustrated with several scientific studies in a wide range of materials, including thermoelectrics, ferroelectrics and complex oxides.

Research was supported by the Center for Accelerating Materials Modeling from SNS data (CAMM), funded by the U.S. DOE, BES, MSED.



WK2

Clathrate Semiconductors: Novel, Open Framework, Crystalline Materials Based on Si, Ge, and Sn

Charles W. Myles and Dong Xue

Department of Physics, Texas Tech University, Lubbock, TX 79409

The Group IV elements Si, Ge, and Sn usually crystallize in the diamond lattice structure, which is the ground state phase for each. Less well-known is the fact that these elements can also form novel crystalline solids, called clathrates because of their structural similarities to clathrate hydrates. Group IV clathrates are metastable, expanded volume phases. As in the diamond structure, in the clathrates, the atoms are tetrahedrally coordinated in sp^3 covalent bonding configurations with their near-neighbors. In contrast to the diamond lattice, however, the clathrates contain pentagonal rings of atoms and their lattices are open frameworks containing large (20-, 24-, 28-atom) “cages”. The two common clathrate varieties are Type I, a simple cubic lattice with 46 atoms per unit cell and Type II, a face centered cubic lattice with 34 atoms per unit cell. The cages can contain weakly bound impurities (“guests”), usually Group I or Group II atoms. A reason that the clathrates are interesting is that the choice of guest may be used to tune the material properties. The guests act as electron donors, but because of their weak bonding, they have only small effects on the host electronic band structures. However, they can vibrate with low frequency vibrational modes, which can strongly affect the vibrational properties. Some laboratory-synthesized, guest-containing clathrates show promise for thermoelectric applications precisely because the guests only weakly perturb the electronic properties, while strongly affecting the vibrational properties.

In this talk, the clathrates and their lattices will be introduced. The results of calculations of the properties of some Si, Ge and Sn-based Type I and Type II clathrates will then be presented. Where data is available, some results will be compared with experiments. Our calculations are motivated by experiments performed by G. Nolas and his group [1] at the U. of South Florida. Among the experimental techniques they have used to study the structural properties of these materials is powder x-ray diffraction (XRD). Our calculations have used a density-functional based, planewave, pseudopotential method. The results include equations of state, structural parameters, electronic bands, vibrational spectra, mean-square atomic displacements, and thermodynamic properties. Some recent results [2–5], obtained in collaboration with some present and former students will be discussed.

[1] M. Beekman, E.N. Nenghabi, K. Biswas, C. Myles, M. Baitinger, Y. Grin, and G.S. Nolas, *Inorganic Chemistry* **49**, 5338 (2010).

[2] Dong Xue and C. Myles, in preparation. See on-line March, 2015 APS Bulletin, papers F12-00007 and F12-00008.

[3] E.N. Nenghabi and C. Myles, *Phys. Rev. B* **77**, 205203 (2008); *Phys. Rev. B* **78**, 195202 (2008).

[4] K. Biswas, C. Myles, M. Sanati, and G. Nolas, *J. Appl. Phys.* **104**, 033535 (2008).

[5] P. Norouzzadeh, C. Myles, and D. Vashaee, *J. Appl. Phys.* **114**, 163509 (2013); *J. Alloys and Compounds* **587**, 474 (2014).

WK2

Comprehensive Scattering Studies of Microstructure, Anharmonic Phonons, and Thermodynamics near the Metal-insulator Transition in VO_2

J. D. Budai¹, J. Hong¹, O. Delaire¹, M. Manley¹, E. Specht¹, C. Li¹, J. Tischler², A. Said², B. Leu², D. Abernathy¹, A. Tselev¹, L. Boatner¹, and R. McQueeney¹¹Oak Ridge National Laboratory, Oak Ridge, TN 37831²Argonne National Laboratory, Argonne, IL 60439

Vanadium dioxide is a strongly correlated material that exhibits a well-studied, but poorly understood, metal-insulator transition (MIT) coupled with a tetragonal (rutile) to monoclinic (M1) structural phase transition just above room temperature. Competing models for this coupled electronic and structural transition are based on either a Peierls MIT driven by instabilities in electron–lattice dynamics or a Mott MIT where strong electron–electron correlations drive charge localization. In spite of early predictions of a soft-mode lattice instability at the rutile R-point, phonon dispersions have not been measured in VO_2 because the incoherent neutron scattering cross-section precludes traditional single-crystal neutron scattering measurements. To shed light on changes in microstructure, lattice

dynamics, and thermodynamics in VO_2 , we have combined a comprehensive set of x-ray and neutron scattering results with *ab initio* molecular dynamics calculations (AIMD). Four complementary scattering studies included: (1) x-ray microdiffraction at APS 33-BM, (2) single-crystal inelastic x-ray scattering studies of phonon dispersions at APS-HERIX, (3) inelastic neutron powder measurements of phonon density of states at SNS-ARCS, and (4) x-ray thermal diffuse scattering at APS 33-BM. We found good agreement between the experimental results and the AIMD predictions, and the calculations help reveal the physical mechanisms driving the MIT. Our results show, first, that previous proposals of a “soft mode” phase transition at a particular wavevector are incorrect. Second, we find that changes in the phonon spectra across the transition are responsible for most of the total entropy change, that is, the entropy change is dominated by vibrational rather than electronic contributions. Finally, we observe strongly anharmonic phonons across a wide region of reciprocal space in the tetragonal phase, and conclude that these short-lived, low-energy phonons are responsible for thermodynamically stabilizing the metallic phase at high temperatures.

Support by DOE Office of Basic Energy Sciences, Materials Sciences and Engineering Division; APS and SNS facilities supported by DOE-BES.

WK2

Critical Soft Modes and Negative Thermal Expansion

Jason Hancock

University of Connecticut, Storrs, CT 06269

We report a high resolution inelastic x-ray scattering study of phonons in a perovskite material which not only displays strong negative thermal expansion, but also exhibits a particularly stable high symmetry cubic phase down to 0.5 K. Our observations include a strong softening of a branch of excitations as the system is cooled, and strong signatures of critical fluctuations are apparent at the lowest temperatures measured. General aspects of the avoided ferroelastic phase boundary to a lower symmetry phase and the broad connection to the physics of perovskite materials will be discussed.

WK2

High-pressure Acoustic Phonons and Elasticity of Iron Alloys and Oxides

Jung-Fu Lin

Department of Geological Science, The University of Texas at Austin, Austin, TX 78712

Iron is the most abundant transition metal in the universe and also exists abundantly in the Earth's interior. Studying the physical and chemical properties of iron-bearing compounds, including Fe-Ni-Si alloys and oxides (e.g., magnetite, hematite, wustite), in extreme pressure-temperature environments are thus of great interest to deep-Earth mineral physicists as well as condensed matter physicists [1–3]. Due to the nature of the unfilled $3d$ electronic orbitals, these compounds can potentially undergo a number of transitions in extreme conditions including structural, magnetic, spin-pairing, metallic, and/or charge-ordering. These transitions can significantly affect our understanding of the properties of these Fe-bearing compounds at high pressures. Since these compounds are opaque to visible lights, studying their elastic properties had been a challenge. In this presentation, I will highlight the use of the high-energy-resolution inelastic x-ray scattering (HERIX) technique coupled with a high-pressure diamond anvil cell at the Sector 3 and Sector 30 of the Advanced Photon Source to investigate the behavior of acoustic phonons and elasticity (full elastic tensors) of iron alloys and oxides at high pressures and/or temperatures. These experimental elasticity results, together with complimentary x-ray and laser spectroscopic measurements, are used to understand a number of outstanding questions in these systems including how the charge-ordering occurs in the mixed-valence magnetite at high pressure [1] and what are the alloying effects of light elements on the velocity profiles of iron in the deep-Earth core [2,3].

[1] J.F. Lin, J. Wu, J. Zhu, Z. Mao, A. H. Said, B. M. Leu, J. Cheng, Y. Uwatoko, C. Jin, and J. Zhou, Abnormal elastic and vibrational behaviors of magnetite at high pressures, *Scientific Reports* 2, 6282, 2014.



- [2] J. Liu, J.F. Lin, A. Alatas, and W. Bi, Sound velocities of bcc-Fe and Fe_{0.85}Si_{0.15} alloy at high pressure and temperature, *Phys. Earth Planet. Inter.* **233**, 24–32, 2014.
- [3] Z. Mao, J.F. Lin, J. Liu, A. Alatas, L. Gao, J. Zhao, and H.K. Mao, Sound velocities of Fe and Fe-Si alloys in the Earth's core, *Proc. Natl. Acad. Sci.* **109**, 10239–10244, 2012.

WK2

Looking for Hidden Phonons in URu₂Si₂

Nicholas Butch

NIST Center for Neutron Research, Gaithersburg, MD 20899

Among the outstanding problems in condensed matter physics, the identity of the order parameter in the hidden order phase of URu₂Si₂ is among the most conspicuous. I will discuss our recent x-ray and neutron study of the lattice, and inevitably, magnetic excitations in this material. I will highlight how HERIX measurements were essential to conclusively disentangle phonon dispersions from the magnetic excitations along certain directions. As a result, we have calculated directly the phonon contribution to the specific heat and analyzed the temperature dependence of the magnetic excitations. I will also present our measurement of phonons under pressure.

Tuesday, May 12

Facility-specific Workshops

APS Workshop 3

Developing Synchrotron Sample Environments to Study Next-generation Field-driven Device Physics

Location: Bldg. 401, Room A1100

Organizers: Philip Ryan (APS), Markys Cain (National Physical Laboratory, UK), and Paul Thompson (XMaS, European Synchrotron, France)

Condensed matter physics dominates our technological and economic trajectory, and new exotic phenomena are always considered in the light of applications. Strongly correlated electron physics is a particularly exciting subfield that promises many device variations. It relates to a large class of materials that show extraordinary coupling between several degrees of freedom, including electronic, structure, and magnetic orders. In fact, we are witnessing the emergence of novel device scenarios such as piezotransistors [1], magnetoelectronics [2,3], and mottronics [4], among others.

Microscopically, charge ties many of these behaviors together through piezoelectricity, magneto-electricity, magneto-caloric effects, pyro-electric effects, or multiferroicity. Macroscopically, strain through varying strictive forces acting over longer length scales linearly couples these order parameters, generating exciting possibilities for the innovative device engineer. Use of state-of-the-art synchrotron capabilities has already generated a deep understanding of these coupling properties, and as we develop ways to control these behaviors (either directly through applied fields or physically, i.e., through piezo-strain) we inadvertently generate a new paradigm of physical parameters to be explored. In addition, as we prepare the next generation of smaller and more coherent x-ray synchrotron sources, we are compelled to consider how to take advantage of these properties in order to probe and ultimately control such intricate and powerful phenomena.

It is the goal of this workshop to bring together experts with a strong emphasis on exciting topics regarding emerging device physics and additionally examples of more fundamental topics of strongly correlated phenomena. The resulting discussions will help to guide the APS to envision cutting-edge sample environments and supplemental *in situ* (x-ray) measurements that will augment experimental data and enrich our understanding of the underlying physics.

References

- [1] National Physical Laboratory, "New global research effort to measure nanoscale strain," November 6, 2013, <http://www.npl.co.uk/news/new-global-research-effort-to-measure-nanoscale...>
- [2] The Piezo Institute, "National Physical Laboratory: Metrology for Advanced Sensors through Engineered Magnetolectric Coupling," <http://www.piezoinstitute.com/about/current-research/metrology-for-advan...>
- [3] J.T. Heron et al., "Deterministic switching of ferromagnetism at room temperature using an electric field," *Nature* **516**, 370–373 (2014), doi:10.1038/nature14004.
- [4] H. Yamada et al., "Ferroelectric Control of a Mott Insulator," *Scientific Reports* **3**, 2834 (2013), doi:10.1038/srep02834.

Tuesday, May 12 (all day)

8:30 – 9:00 Philip Ryan (Argonne National Laboratory)
Introductory Remarks



- 9:00 – 9:40 Markys Cain (National Physical Laboratory, UK)
“Nanostrain Project” — Novel Electronic Devices Based on Control of Strain at the Nanoscale
- 9:40 – 10:00 Glenn Martyna (IBM T.J. Watson Research Center)
The Piezoelectronic Transistor: A Stress-driven Next-generation Transduction Device
- 10:00 – 10:35 Break
- 10:35 – 11:15 Paul Evans (University of Wisconsin)
Nanosecond Electric-field-driven Structural Phase Transitions in Complex Oxides
- 11:15 – 11:55 Jacob Jones (North Carolina State University)
New Direct Measurements of Polarizability Mechanisms in Ferroelectrics via Diffraction and Scattering
- 11:55 – 1:30 Lunch
- 1:30 – 2:10 Siddharth Saxena (University of Cambridge, UK)
Searching for Multivariable Quantum Criticality
- 2:10 – 2:50 Peter Fischer (Center for X-ray Optics, Lawrence Berkeley National Laboratory)
Magnetic Soft X-ray Spectro-microscopy: Seeing Nanoscale Magnetism in Action
- 2:50 – 3:20 Break
- 3:20 – 4:00 Xavi Marti (Institute of Physics, Czech Republic)
Antiferromagnetism: Applications of Invisible Magnets
- 4:00 Sae Hwan Chun (Materials Science Division, Argonne National Laboratory)
Static and Dynamic Magnetoelectric Effects in Multiferroic Hexaferrites
- Wednesday, May 13 half-day**
- 9:00 – 9:40 Martin Holt (Center for Nanoscale Materials, Argonne National Laboratory)
Strain Imaging of Nanoscale Semiconductor Heterostructures with X-ray Bragg Projection Ptychography
- 9:40 – 10:20 Jian Liu (University of California, Berkeley)
Toward in situ Control and Probe over Novel Magnetoelectric Effects in Magnetic Thin Films and Heterostructures
- 10:20 – 11:00 Raegan Johnson (Sandia National Laboratory)
In situ Electric Field Measurements of Ferroelectric Domain Wall Motion in PZT Thin Films
- 11:00 – 11:40 Sean McMitchell (University of Liverpool, UK)
Developing Traceable Links between Mesoscopic Strain and Crystallography through in situ Interferometry
- 11:40 – 12:20 Yong Choi (X-ray Science Division, Argonne National Laboratory)
Interfacial Orbital Modification Probed by Polarization-dependent Anomalous X-ray Reflectivity
- 12:20 Philip Ryan (Argonne National Laboratory)
Wrap-up

WK3

Introductory Remarks

Philip Ryan

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

I will present a brief vision of the future experimental environment given the anticipated coherence and spatial dimensions that will come with the APS-U project. The general condensed-matter end-user community may question how this affects their user relationship with the facility. My aim in these introductory remarks is to explore how the facility may assuage concerns of negative impacts and more importantly how we, the beamline scientist and user community, can take advantage of the improvements to the beam characteristics. In fact the net potential benefit to the broader community is quite exciting; however, we need to coordinate our efforts to maximize the optimal utilization of the future facility.

WK3

“Nanostrain Project” — Novel Electronic Devices Based on Control of Strain at the Nanoscale

Markys Cain

National Physical Laboratory, Teddington, Middlesex, TW11 0LW, UK

Faster, smaller and more energy efficient computing, based on miniature electronic devices, will benefit almost every industrial sector. Recently, materials such as piezoelectrics have been used to develop miniature electronics by allowing the control of properties at the nanoscale via the application of mechanical strain. Piezoelectric materials are uniquely capable of generating precisely defined strains down to very small length scales and are the technology driver for new types of electronic devices.

Currently, there is no measurement framework or facility for traceable measurement of the electromechanical coupling (shown as strain through application of voltage) in piezoelectric materials down to a size of 1 nm.

This project will develop traceable measurements of strain at lengths down to 1 nm and at high electric fields. These measurements need to be non-destructive and should be able to operate on the commercial scale. The results will help develop computing products based on the principles of functional materials such as piezoelectrics.

In this presentation I will explain the following key objectives of the scientific research project, with an emphasis on the first technical goal:

- ▶ Develop links between traceable mesoscale strain metrology and crystallographic strain via *in situ* interferometry and synchrotron x-ray diffraction. This provides for an assessment of the intrinsic piezo response to its, industrially highly relevant, extrinsic (domain mediated) response.
- ▶ Develop ultra-high spatial resolution (100 nm or less) optical methods of strain measurements using IR-SNOM by utilising the PTB synchrotron radiation facility (MLS) in Berlin as an IR light source.
- ▶ Develop traceable validation of macroscale strain metrology in destructive methods including Transmission Electron Microscopy (TEM) and novel holographic TEM, to map intra-grain residual and active (electric field induced) strains. The uncertainty caused by the additional strain from the preparation of TEM slices will also be investigated.
- ▶ Develop the multiphysics materials modelling to underpin all the experimental activities described above, considering both residual, process-related strains in thin film and nano/micro-scale released structures, and electrically driven strains in active devices.



WK3

The Piezoelectronic Transistor: A Stress-driven Next-generation Transduction Device

G.J. Martyna¹, P.M. Solomon¹, M. Copel¹, J. Chang¹, T.M. Shaw¹, R. Keetch², S. Troler McKinstry², and D.M. Newns¹

¹IBM T.J. Watson Research Center, Yorktown Heights, NY 10598

²Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802

We have invented a transduction based post-CMOS device based on a piezoelectrically driven metal insulator transition [1]. An input voltage pulse activates a piezoelectric element (PE) which transduces input voltage into an electro-acoustic pulse that in turn drives an insulator to metal transition (IMT) in a piezoresistive element (PR); the transition effectively transduces the electro-acoustic pulse to voltage. Using the known properties of *bulk* materials, we predict using modeling that the PET achieves multi-GHz clock speeds with voltages as low as 0.1 V and a large On/Off switching ratio ($\approx 10^4$) for digital logic [1]. The PET switch is compatible with CMOS-style logic. At larger scale the PET is predicted to function effectively as a large-area low voltage device for use in sensor applications.

PET device performance is enabled by the properties of two materials, a relaxor piezoelectric for the PE and a rare earth chalcogenide piezoresistor for the PR — provided the materials exhibit bulk properties at the nanoscale. Thus it is critical to investigate materials scaling using a combined theoretical/experimental approach. The development of thin film piezoresistive and piezoelectric materials and patterned structures, and associated characterization tools is presented, along with the theoretical models that yield insight into their behavior [2–4]. Integration of these novel materials into 3 evolutionary generations of PET devices, and device characterization, is given [5] to show that a proof of concept has been achieved.

DARPA Mesodynamic Architectures Program under contract number N66001-11-C-4109.

- [1] “High Response Piezoelectric and Piezoresistive Materials for Fast, Low Voltage Switching: Simulation and Theory of Transduction Physics at the Nanometer-Scale,” D.M. Newns, B.G. Elmegreen, X.-H. Liu, and G.J. Martyna, *Adv. Mat.* **24**, 3672 (2012).
- [2] “Giant Piezoresistive On/Off Ratios in Rare-Earth Chalcogenide Thin Films Enabling Nanomechanical Switching,” M. Copel, G.J. Martyna, and D.M. Newns et al., *Nano Lett.* **13**, 4650 (2013).
- [3] “Anisotropic strain in SmSe and SmTe: implications for electronic transport,” M.A. Kuroda, Z. Jiang, M. Povolotskiy, G. Klimeck, D.M. Newns, and G.J. Martyna, *Phys. Rev. B.* **90**, 245124 (2014).
- [4] “Lateral scaling of PMN-PT thin films for piezoelectric logic,” R. Keetch, S. Shetty, M.A. Kuroda, X.-H. Liu, G.J. Martyna, D.M. Newns, and S. Troler-McKinstry, *J. Appl. Phys.* **115**, 234106 (2014).
- [5] “Pathway to the PiezoElectronic Transduction Logic Device,” accepted *NanoLetters* (2014).

WK3

Nanosecond Electric-field-driven Structural Phase Transitions in Complex Oxides

Paul G. Evans

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

Complex oxide electronic materials, including ferroelectric and multiferroics, can exhibit large responses to externally applied fields when the system has a composition or external stresses that place the system near a boundary between structural phases. The development of time-resolved x-ray diffraction and scattering techniques allows us to probe the dynamics and energetics of piezoelectric distortion and phase transformation in complex oxide electronic materials at such boundaries, with both nanosecond time resolution and a high level of structural precision. Compressive epitaxial stresses can place thin films of the multiferroic oxide BiFeO₃ at a boundary between phases with different structural extent. The electric-field driven transition exhibits contributions from both stably switching and reversible components, and can occur at times as short as tens of nanoseconds. Comparison with density functional theory results shows that the transition can be understood by comparing the free energies of the piezoelectrically distorted structures. Control of this transition, and other field-driven phase transition phenomena, has the potential to provide an additional route to the control of electronic and magnetic properties of complex oxides.

WK3

New Direct Measurements of Polarizability Mechanisms in Ferroelectrics via Diffraction and Scattering

J.L. Jones¹, T.-M. Usher¹, C.C. Chung,¹ and C.M. Fancher¹, I. Levin², S. Brewer,³ and N. Bassiri-Gharb³

¹Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695

²Materials Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

³G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332

The functionality of many dielectric and ferroelectric materials is dependent on the external application of electric fields. Characterizing the response of the material at length scales ranging from sub-nanometer to micrometer is important for understanding and engineering these functionalities. For field-induced strain, for example, both the contribution of the intrinsic piezoelectric effect (originating at sub-nanometer dimensions) and ferroelectric/ferroelastic domain wall motion (at the nanometer length scale) contribute to strain. For both polarizability and permittivity, it is important to characterize and understand the field-induced response of the local structure (i.e., ionic polarizability) and changes in the domain structure (i.e., dipolar). In this talk, we present the new development of two different methods to characterize both local structure and domain structure changes during field application and the contribution of these mechanisms to polarization.

In the first method, we have used x-ray diffraction *in situ* during application of electric fields in BaTiO₃ to determine the contribution of ferroelectric/ferroelastic (i.e., non-180°) domain walls to the polarization. We have used a complementary analysis approach to further determine the contribution from ferroelectric (i.e., 180°) domain walls to the polarization.

In the second method, we have used *in situ* total x-ray scattering during application of electric fields and determined pair distribution functions (PDFs). The field-dependent PDFs enable the assessment of local structure changes in BaTiO₃ and Na_{0.5}Bi_{0.5}TiO₃. A unique dipolar mechanism is observed at the unit-cell level in Na_{0.5}Bi_{0.5}TiO₃ which involves rearrangements of Bi³⁺ displacements. In contrast, BaTiO₃ exhibits a smaller local scale response to the electric field which is nonetheless consistent with piezoelectric strain.

The results are interpreted holistically to enable ascription of dominant mechanisms of polarizability in dielectric and ferroelectric materials. For example, the first and second largest contributions to polarizability in BaTiO₃ are 180° domain wall motion and non-180° domain wall motion. The new characterization methods can be readily applied to other materials.

WK3

Searching for Multivariable Quantum Criticality

Siddharth S. Saxena

Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, Great Britain

This talk will discuss pressure induced phenomena in the vicinity of magnetic quantum phase transitions and Quantum Criticality in Metallic and Insulating Systems.

Materials tuned to the neighbourhood of a zero temperature phase transition often show the emergence of novel quantum phenomena. Much of the effort to study these new emergent effects, like the breakdown of the conventional Fermi-liquid theory in metals has been focused in narrow band electronic systems. Ferroelectric crystals provide a very different type of quantum criticality that arises purely from the crystalline lattice. In many cases the ferroelectric phase can be tuned to absolute zero using hydrostatic pressure. Close to such a zero temperature phase transition, the dielectric constant and other quantities change into radically unconventional forms due to the fluctuations experienced in this region. The simplest ferroelectrics may form a text-book paradigm of quantum criticality in the



solid-state where there are no complicating effects of electron damping of the quantum charge fluctuations. We present low temperature high precision data demonstrating these effects in pure single crystals of SrTiO₃ and KTaO₃. We outline a model for describing the physics of ferroelectrics close to quantum criticality and highlight the expected 1/T² dependence of the dielectric constant measured over a wide temperature range at low temperatures. In the neighbourhood of the quantum critical point we report the emergence of a small frequency independent peak in the dielectric constant at approximately 2K in SrTiO₃ and 3K in KTaO₃. Looking to the future, we imagine that quantum paraelectric fluctuations may lead to new low temperature states and mediate novel interactions in multi-ferroic systems (e.g., EuTiO₃) and ferroelectric crystals supporting itinerant electrons.

WK3

Magnetic Soft X-ray Spectro-microscopy: Seeing Nanoscale Magnetism in Action

Peter Fischer

Center for X-ray Optics, Lawrence Berkeley National Laboratory, Berkeley, CA 94720
Physics Department, University of California, Santa Cruz, CA 94056

The era of nanomagnetism, which aims to understanding and controlling magnetic properties and behavior on the nanoscale, is currently expanding into the mesoscale [1], which will harness complexity and novel functionalities, which are essential parameters to meet future challenges in terms of speed, size and energy efficiency of spin driven devices. Multimodal characterization techniques, such as tomographic magnetic imaging and investigations of spin dynamics down to fundamental magnetic length and time scales with elemental sensitivity in emerging multi-component materials will enable future scientific breakthroughs. I will review recent developments with full-field magnetic soft x-ray transmission microscopy [2] to study spin configurations in magnetic nanotubes [3], the stochastic behavior in vortices [4] and the local distribution of magnetic properties near domain walls [5].

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy under Contract No. DE-AC02-05-CH1123 and by the Leading Foreign Research Institute Recruitment Program (Grant No. 2012K1A4A3053565) through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (MEST).

- [1] R. Service, *Science* **335** 1167 (2012).
- [2] P. Fischer, *Materials Science & Engineering* **R72** 81–95 (2011).
- [3] M.-Y. Im et al., *Nature Communications* **5** 5620 (2014).
- [4] R. Streubel, *Adv. Mater.* **26** 316 (2014).
- [5] M.J. Robertson et al., *J Appl. Phys.* **117** 17D145 (2015).

WK3

Antiferromagnetism: Applications of Invisible Magnets

X. Marti^{1,2}, I. Fina^{3,4}, and T. Jungwirth^{1,5}

¹Institute of Physics ASCR, v.v.i., Prague 6 162 53, Czech Republic

²IGSresearch, La Pobla de Mafumet (Taragona) 43140, Spain

³Max Planck Institute of Microstructure Physics, Halle D-06120, Germany

⁴Department of Physics, University of Warwick, Coventry CV4 7AL, UK

⁵School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, UK

In 1970, at the time when compact cassettes made it to the market after a century of experimenting with ferromagnetic storage, the Nobel Prize was awarded for the “*fundamental work and discoveries concerning antiferromagnetism.*” Louis Neel pointed out in his Nobel lecture that while abundant and interesting from a theoretical viewpoint, antiferromagnets did not seem to have any applications. Indeed, the alternating directions of magnetic moments on individual atoms and the resulting zero net magnetization make antiferromagnets hard to control by tools common in ferromagnets. While preoccupied with the inherent difficulties to read and write magnetic information in antiferromagnets, scientists and engineers have largely overlooked the positive sides of antiferromagnets as being magnetically invisible [1] and uniquely robust against magnetic perturbations [2]. In this talk, we will review recent developments in the emerging field of antiferromagnetic spintronics, retracing the footsteps

of the ferromagnetic based technologies. We will examine the path starting from seminal basic science experiments that took place at the Advanced Photon Source down to a survey of the potential markets for the coming up *invisible magnetism*.

[1] https://www.youtube.com/watch?v=X1Ft_OnRaq4.

[2] <https://www.youtube.com/watch?v=HWZLJ02sb0U>.

WK3

Static and Dynamic Magnetoelectric Effects in Multiferroic Hexaferrites

Sae Hwan Chun

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

Multiferroics, wherein magnetism and ferroelectricity coexist, are of great interest for the prospect of new multifunctional devices by using magnetoelectric (ME) effects through the cross-coupling between the magnetic and electric properties. In most multiferroics currently known, however, controlling electric polarization with magnetic field or magnetization with electric field has been realized only at low temperatures. In addition, their ME susceptibilities are too small for practical applications. Hence, it is essential to improve both the operating temperature and the ME sensitivity of magnetic ferroelectrics for use in ME devices. Investigating the multiferroic hexaferrites, we discovered a novel chemical route effectively tailoring the electric polarization induced by a low magnetic field in $(\text{Ba,Sr})_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ (Zn_2Y -type) hexaferrite by Al-substitution to possess a giant magnetoelectric susceptibility (MES) [1]. Furthermore, in $(\text{Ba,Sr})_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ (Co_2Z -type) hexaferrite single crystals with large MES, we realized the control of magnetization by an electric field at room temperature [2]. In addition to those static ME properties, a dynamic ME effect, electric-dipole-active magnon resonance in THz frequency range, is found in the Co_2Z -type hexaferrite, exhibiting the spectral weight even at room temperature [3]. The unprecedented supreme static and dynamic ME phenomena in the hexaferrites may provide a pathway to overcome the challenge in application of multiferroics for real devices.

[1] S.H. Chun et al., *Phys. Rev. Lett.* **104**, 037204 (2010).

[2] S.H. Chun et al., *Phys. Rev. Lett.* **108**, 177201 (2012).

[3] S.H. Chun et al., in preparation.

WK3

Strain Imaging of Nanoscale Semiconductor Heterostructures with X-ray Bragg Projection Ptychography

M.V. Holt¹, S.O. Hruszkewycz², C.E. Murray³, J.R. Holt⁴, D.M. Paskiewicz², and P.H. Fuoss²

¹Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

²Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

³IBM T.J. Watson Research Center, Yorktown Heights, NY 10598

⁴IBM Semiconductor Research and Development Center, Hopewell Junction, NY 12533

We report the imaging of nanoscale strain distributions in complementary components of lithographically engineered epitaxial thin film semiconductor channel heterostructures using synchrotron x-ray Bragg Projection Ptychography (BPP). A new phase analysis technique applied to the reconstructed BPP phase images from two laterally adjacent, stressed materials produced lattice strain and lattice rotation maps with a spatial resolution of ~15 nm, a strain sensitivity of better than 0.01%, and an angular resolution of ~0.1 mrad [1].

Bragg projection ptychography is a coherent diffraction x-ray imaging technique capable of mapping structural perturbation, such as strain, in single crystal thin films with nanoscale spatial resolution [2,3]. In this study, analysis of the orthogonal derivatives of the reconstructed phase maps provides insight into two distinct lattice responses that quantitatively agree with linear elastic predictions. This demonstrates that Bragg ptychography can be used to quantitatively visualize extremely subtle lattice perturbations at the nanoscale under realistic conditions without sectioning or otherwise modifying the boundary conditions of the sample.



- [1] M.V. Holt et al., *Phys. Rev. Lett.* **112**, 165502 (2014).
[2] S.O. Hruszkewycz et al., *Nano Lett.* **12**, 5148 (2012).
[3] S.O. Hruszkewycz et al., *Phys. Rev. Lett.* **110**, 177601 (2013).

WK3

Toward *in situ* Control and Probe over Novel Magnetoelectric Effects in Magnetic Thin Films and Heterostructures

Jian Liu

Department of Physics, University of California, Berkeley, CA 94720
Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Magnetoelectric effects, which couple the spin and charge degree of freedom, are the key to the great success of various magnetic material-based technologies, such as recording and memories. The development of the next generation of magnetic devices with improved performance or new functionalities relies on creating, understanding, and controlling novel magnetoelectric effect/coupling. As a class of materials where the magnetic and electronic properties are tightly related, complex oxides present great potential in this area. The challenge, however, has been imposed by the fact that most magnetic oxides are antiferromagnetic and difficult to harness or probe at nanoscale. In this talk, I will show some of our recent work on different magnetoelectric effects in oxide heterostructures with antiferromagnetism as a key component. In particular, results that utilize synchrotron-based probes will be discussed.

WK3

In situ Electric Field Measurements of Ferroelastic Domain Wall Motion in PZT Thin Films

Raegan L. Johnson-Wilke¹, Margeaux Wallace², Rudeger H.T. Wilke¹, Giovanni Esteves³, Jacob Jones³, and Susan Trolier-McKinstry²

¹Sandia National Laboratory, Albuquerque, NM 87123

²Pennsylvania State University, Department of Materials Science and Engineering, University Park, PA 16802

³North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC 27695

Lead zirconate titanate (PZT) thin films are used in microelectromechanical systems (MEMS) due to their large piezoelectric response. In order to quantitatively study this response, *in situ* electric field measurements were performed at the Advanced Photon Source at Argonne National Laboratory. The electromechanical response in PZT is a result of both the intrinsic (lattice) piezoelectric effect as well as the motion of ferroelectric and ferroelastic domain walls (extrinsic effect). In-depth studies of the intrinsic and extrinsic effects in bulk materials has been performed on a number of ceramic materials, however, thin films present a challenge due to the significantly smaller volume of material. This talk will outline the challenges and describe the experimental setup used to perform the *in situ* measurements on PZT thin films. In addition, the work presented will describe direct measurements of ferroelastic domain wall motion in 2- μm thick {001} oriented PZT (30/70) films under different release states. Films that were fully clamped to the underlying substrate are compared with films that are up to 75% released from the wafer. The released films showed significantly larger domain wall motion response based on the changes in peak intensity between the 200 and 002 diffraction peaks. Quantitative details of the influence of the release state and electric field will be discussed.

WK3

Developing Traceable Links between Mesoscopic Strain and Crystallography through *in situ* Interferometry

S.R.C. McMitchell^{1,2}, P. Thompson^{1,2}, C. Lucas^{1,2}, C. Vecchini³, J. Wooldridge³, M. Stewart³, A. Muniz-Piniella³, M. Cain³, and T. Hase^{1,4}

¹XMaS Beamline, European Synchrotron Radiation Facility, Grenoble, France

²Department of Physics, University of Liverpool, Liverpool, L69 7ZE, UK

³National Physical Laboratory, Teddington, Middlesex, TW11 0LW, UK

⁴Department of Physics, University of Warwick, Coventry, CV4 7AL, UK

Recently, there has been considerable research effort on understanding the complex interplay between material structure and the internal strain in piezo and ferroelectrics, and multiferroics. This is a key factor in the functional efficiency of devices.

Of particular relevance is the correlation between strain and electric polarisation, which is being exploited to develop a novel Piezoelectric-Effect-Transistor (PET), which offers a possible route to replace current CMOS technology. To aid the development of this transformative technology, several European national laboratories, academic and commercial partners formed a consortium funded through the European Metrology Research Programme (EMRP) Project IND54 Nanostrain. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

The operation of the PET will be controlled through application of an electric field. It is therefore imperative to investigate the physical deformation and strain state that occurs under applied electric fields *in situ* and *in operando*. We have incorporated a dual-beam optical interferometer onto the XMaS beamline at the ESRF. *In situ* polarisation, lattice parameter, and deformation measurements allow new insights into the correlation between induced strain and material properties in piezoelectrics. We will detail experimental strategies employed to reduce noise and show results from both static (d.c.) and dynamic cycles (up-to 55Hz) of electric field. Standard piezoelectric single crystals and thin films were used to develop quantitative and traceable metrologies for the precise determination of bulk and atomic strain within these structures. The addition of magnetic field and temperature dependence is also discussed.

WK3

Interfacial Orbital Modification Probed by Polarization Dependent Anomalous X-ray Reflectivity

Yong Choi

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

In a lattice matched multilayer structure, materials with similar structures but dissimilar properties can be forced to coexist at the interfaces. Numerous recent studies have shown novel interfacial properties that are not intrinsic to either of the constituent materials. We investigate the role of interfacial modification in the metal-to-insulator transition observed from superlattices of two RNiO₃ (R=rare earth) with different transition behaviors, using a combined approach between spectroscopy and scattering to take advantage of the element-specificity of x-ray absorption near edge spectroscopy and the enhanced interfacial sensitivity of x-ray reflectivity.



Tuesday, May 12

Facility-specific Workshops

CNM Workshop 4 **Exploring the Flatland of 2D Materials for Tribological Manipulation**

Location: Bldg. 402, Room E1100/E1200

Organizers: Anirudha Sumant (CNM), Diana Berman (CNM), and Ali Erdemir (Argonne National Laboratory)

The purpose of this workshop is to bring together experts from academia, national labs, and industry to discuss the latest developments in the synthesis, functionalization, and characterization of nanostructured 2D materials, with an emphasis on uncovering their unique tribological properties at the micro/nano-scale and to develop the next generation of energy-efficient moving systems based on the unique wear/friction performance of these 2D materials.

The materials of interest include graphene, boron nitride, molybdenum disulfide, maxenes, and others. With recent fast-paced advances in the development of 2D materials and understanding of their mechanical and tribological properties, we now have a completely new perspective on how they behave as a lubricant compared to traditional thin film or bulk solid lubricants.

The exceptional physical, chemical, mechanical, electrical, and tribological properties of 2D materials, combined with the ability to apply or introduce them on the contacting interfaces of tribological systems, make them ideal new solid lubricant materials for a wide variety of applications, ranging from nano/micro scales (NEMS/MEMS) to macro/meso scales (e.g., moving electrical contacts, sliding/rolling contacts, rotating contacts, bearings, etc.).

The Center for Nanoscale Materials (CNM) at Argonne has expertise and state-of-the-art facilities for the synthesis, functionalization, and characterization of 2D materials. In the last few years the CNM has developed a strong research program in fundamental studies of the physical properties of these materials, with particular emphasis on understanding their tribological properties at the nano, micro, and macro scale.

This workshop will include topics covering fundamental studies on the development of 2D materials and their systematic characterization to understand their structural, surface chemical, mechanical, and tribological properties. It will also cover theoretical and modeling approaches that can provide in-depth understanding of tribo-physical and chemical interactions with the substrate and counterface materials under severe contact pressure and shear stress, issues related to dispersibility, substrate interactions, and possibilities for industrial applications.

Workshop Agendas and Abstracts

8:30 – 8:45	Anirudha Sumant (Argonne National Laboratory) <i>Welcome & Introductory Remarks</i>
8:45 – 9:25	Robert Carpick (University of Pennsylvania) <i>Mechanisms of Atomic-scale Friction for 2D Materials</i>
9:25 – 10:05	James Batteas (Texas A&M University) <i>2D or not 2D? The Impact of Nanoscale Roughness and Substrate Interactions on the Tribological Properties of Graphene</i>
10:05 – 10:35	Break
10:35 – 11:15	Elena Polyakova (Graphene Supermarket Inc.) <i>The Use of Graphene and Other 2D Materials in 3D Printing</i>
11:15 – 12:00	Alex Smolyanitsky (National Institute of Standards and Technology) <i>The Effects of Intrinsic Rippling on the Frictional Properties of Atomically Thin Membranes: A Pathway to Real-time Controllable Surface Properties</i>
12:00 – 1:30	Lunch
1:30 – 2:10	Yury Gogotsi (Drexel University) <i>MXenes and MXene-polymer Composites: Manufacturing, Nanoindentation and Nanotribology</i>
2:10 – 2:50	Christopher Muratore (University of Dayton) <i>Ultra-thin Transition Metal Dichalcogenides Grown by Physical Vapor Deposition</i>
2:50 – 3:20	Break
3:20 – 4:00	Nikhil Koratkar (Rensselaer Polytechnic Institute) <i>Wear in Graphene-polymer Composites</i>
4:00 – 4:40	Diana Berman (Argonne National Laboratory) <i>Tapping into Graphene's Potential as a Solid Lubricant</i>
4:40	Ali Erdemir (Argonne National Laboratory) <i>Wrap-up and concluding remarks</i>

WK4

Mechanisms of Atomic-scale Friction for 2D Materials

Robert W. Carpick

University of Pennsylvania, Philadelphia, PA 19104

Two-dimensional materials provide a rich playground for exploring new and unexpected physical phenomena, including tribological. This talk will focus on interfacial friction and adhesion behavior of nanoscale contacts with such materials. We find that single layer graphene reduces friction by an order of magnitude for surfaces including copper [1]. However, the friction reduction is layer dependent: for contacts to graphene, MoS₂, NbSe₂, and BN, the friction force exhibits a significant dependence on the number of 2-D layers [2] which we attribute to an out-of-plane “puckering” deformation that occurs when the 2-D material is weakly bound to its substrate. However, adhesive behavior does not follow this dependence. Instead, we find that sliding can induce an increased adhesive



force due to local delamination of the topmost layer of graphene [3]. Finally, we observe a large, order-of-magnitude increase in friction that occurs when graphene is fluorinated [4]. This result is interpreted in the context of the Prandtl-Tomlinson model of stick-slip friction, where static friction arises from the high electronic roughness of fluorinated graphene.

- [1] Frictional behavior of atomically thin sheets: Hexagonal-shaped graphene islands grown on copper by chemical vapor deposition. P. Egberts, G.H. Han, X.Z. Liu, A.T. Johnson, and R.W. Carpick. *ACS Nano* **8**, 5010–21 (2014). (<http://dx.doi.org/10.1021/nn501085g>.)
- [2] Frictional characteristics of atomically thin sheets. C. Lee, Q. Li, W. Kalb, X.-Z. Liu, H. Berger, R.W. Carpick, and J. Hone. *Science* **328**, 76–80 (2010). (<http://dx.doi.org/10.1126/science.1184167>.)
- [3] Nanoscale adhesive properties of graphene: The effect of sliding history. X.-Z. Liu, Q. Li, P. Egberts, and R.W. Carpick. *Adv. Mat. Interf.* **1**, 1300053 (2014). (<http://dx.doi.org/10.1002/admi.201300053>.)
- [4] Fluorination of graphene enhances friction due to increased corrugation. Li, Q., Liu, X.Z., Kim, S.P., Shenoy, V.B., Sheehan, P.E., Robinson, J.T., and Carpick, R.W. *Nano Letters* **14**, 5212–5217 (2014). (<http://dx.doi.org/10.1021/nl502147t>.)

WK4

2D or not 2D? The Impact of Nanoscale Roughness and Substrate Interactions on the Tribological Properties of Graphene

Jessica Spear and James Batteas

Departments of Chemistry and Materials Science and Engineering, Texas A&M University, College Station, TX 77843

Control of friction and wear is a ubiquitous challenge in numerous machined interfaces ranging from biomedical implants, to engines, to nano- and micro-scaled electromechanical systems (MEMS) devices. A key challenge in developing boundary lubrication schemes for such systems is how to reduce wear at the rough surfaces of such devices, where nanoscaled asperities dominate the interfacial contacts. The robust mechanical properties of two-dimensional (2D) nanomaterials, such as graphene, has made it a material of interest for modifying surface frictional properties. While graphene can readily adapt to surface structure on the atomic scale, when deposited on substrates with nanoscopic roughness (~ 10 — 20 nm rms as is common in many machined interfaces) a conformal coating cannot be fully formed due to competition between adhesion to substrate nanoscopic asperities and the bending strain of the graphene. This often leaves a mixture of supported and unsupported regions which respond differently to applied load. Here we describe a combination of AFM nanomechanical and confocal Raman microspectroscopy studies of graphene on silica surfaces with controlled nanoscopic roughness to examine the how this impacts the frictional properties of graphene. Composite interfaces where graphene is supported on self-assembled alkylsilane monolayers will also be described along with the synergistic influence of such mixed interfaces on the frictional properties of the surface.

WK4

The Use of Graphene and Other 2D Materials in 3D Printing

Elena Polyakova

Graphene 3D Lab, Calverton, NY 11933

The 3D printing market is expected to grow quickly over the course of the next few years, without factoring in the likelihood of advances in both printer and filament technologies. One advance is the use of graphene, a 2D material known for its extraordinary attributes, in filament production. Adding graphene to filaments increases the strength and adds conductivity to end-products made via 3D printing — a major advancement when considering using 3D printing for energy storage, electronic, and other commercial applications. I will overview the recent progress made in this area at Graphene 3D Lab, as well as the applications of other 2D materials for 3D printing.

WK4

The Effects of Intrinsic Rippling on the Frictional Properties of Atomically Thin Membranes: A Pathway to Real-time Controllable Surface Properties

Alex Smolyanitsky

National Institute of Standards and Technology, Boulder, CO 80305

Frictional properties of atomically thin layers and lamellar materials have recently become a topic of significant research interest. As a result, graphene and its chemical derivatives have been suggested as revolutionary solid-state lubricants with unique tribological properties. Possible uses range from novel methods of determining exfoliation energies to nanoelectromechanical (NEMS) applications. Most studies to date have focused on the structural properties, including the effects of chemical modification and substrate interactions.

The first simulated friction force microscopy study of the dependence of the frictional properties of free-standing graphene as a function of temperature is presented. In contrast with the long-standing theory for dry surfaces of solids, sliding friction is predicted to *both increase and decrease* with increasing temperature. The qualitative behavior is demonstrated to depend on the local lateral strains, normal contact force, sample size, and the lateral scanning rate. Our observations are likely due to the intrinsic presence of dynamic flexural ripples in atomically thin layers at finite temperatures. The effect of random thermally excited waves on dry friction suggests the concept of real-time controllable dynamic roughness in free-standing atomically thin layers via imposed lateral strains or externally excited low-energy flexural waves.

The effect of externally engineered rippling content on the frictional properties of free-standing atomically thin layers is described. It is shown that, depending on the excitation amplitude and frequency, sliding friction at identical normal loads can be modified significantly. In addition to possible uses in NEMS applications, the observed real-time control of the effective surface “roughness” may be employed for controllable gas and fluid passage at the nanoscale, as well as for separation of species in gas or fluid mixtures.

WK4

MXenes and MXene-polymer Composites: Manufacturing, Nanoindentation and Nanotribology

Babak Anasori¹, Xin Liu², Michel Barsoum¹, Robert W. Carpick², and Yury Gogotsi¹

¹Department of Materials Science and Engineering, and A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, PA 19104

²Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104

Two-dimensional (2D) solids – the thinnest materials available to us – offer unique properties and a potential path to device miniaturization. The most famous example is graphene, which is an atomically thin layer of carbon atoms bonded together in-plane with sp² bonds. Recently, an entirely new family of 2D solids – transition metal carbides (Ti₂C, Ti₃C₂, Nb₄C₃, etc.) and carbonitrides – was discovered by our group [1,2]. Selective etching of the A-group element from a MAX phase results in formation of 2D M_{n+1}X_n solids, labeled “MXene.” We have produced about 15 different carbides and carbonitrides [2–6]. Their elastic constants along the basal plane are expected to be similar to or even higher than that of the binary carbides. Oxygen or OH terminated MXenes, are hydrophilic, but electrically conductive.

Here we report on manufacturing of Ti₃C₂-PVA composite films [7] and initial studies of their mechanical properties using nanoindentation. At 22±1 GPa, the elastic modulus of the 60 wt.% Ti₃C₂-PVA composite film was measured to be significantly higher than its end members (pure MXene or pure PVA). In addition, tribological properties of different MXenes and effect of the surface termination on friction were studied using atomic force microscopy.



- [1] M. Naguib et al., *Advanced Materials* **23** (37), 4207–4331 (2011).
- [2] M. Naguib et al., *ACS Nano* **6** (2), 1322–1331 (2012).
- [3] O. Mashtalir et al., *Nature Communication* **4**, 1716 (2013).
- [4] M. R. Lukatskaya et al., *Science* **341**, 1502–1505 (2103).
- [5] M. Naguib et al., *Advanced Materials* **26**, 992–1005 (2014).
- [6] M. Ghidui et al., *Nature* **516**, 78–81 (2014).
- [7] Z. Ling et al., *PNAS* **111** (47) 16676–16681 (2014).

WK4

Ultra-thin Transition Metal Dichalcogenides Grown by Physical Vapor Deposition

C. Muratore¹ and A.A. Voevodin²

¹Department of Chemical and Materials Engineering, University of Dayton, Dayton, OH 45469

²Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH 45433

Physical vapor deposition (PVD) is a thin film growth technique allowing exquisite control of structure and composition and freedom from many thermodynamic constraints. This is evidenced by the common use of sputter deposition in a significant fraction of the total fabrication steps required to produce ubiquitous commercial electronic devices. By employing well-known theories of film growth and making the necessary conditions a reality through the use of surface engineering technology, thin film microstructures become very tailorable via PVD. This is of particular importance in the field of two dimensional (2D) materials, where processing of continuous and uniform films with thicknesses on the order of 1 nm is currently a major challenge. Transition metal dichalcogenides (TMDs), such as MoS₂ are currently under extensive study as high-performance 2D semiconductors. Using PVD techniques, which are easy to integrate into existing semiconductor device fabrication processes, 2D TMDs can be grown on diverse substrates including SiO₂, graphene, metals, and polymers. This is surprising as it is more common for such thin films to form isolated islands on substrates. Using a variety of *in situ* and conventional *ex situ* materials characterization tools such as Raman spectroscopy and x-ray photoelectron spectroscopy, the mechanisms governing continuous growth of TMDs have been examined for all of the substrates listed above. These substrates possess a broad range of surface energies. It appears that under some conditions a continuous metal monolayer is formed initially on higher surface energy substrates, and normal TMD growth continues on that interfacial metal layer. This is typically observed at high temperature where preferential desorption of the chalcogen atoms during growth is enhanced. How the crystalline domain size within 1–5 nm thick TMD films can be manipulated during PVD growth over at least one order of magnitude, and how the domain boundary density affects electronic, thermal, surface reactivity, and mechanical properties in diverse 2D devices.

WK4

Wear in Graphene-polymer Composites

Nikhil Koratkar

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

Polytetrafluoroethylene (PTFE) is one of the most widely used solid lubricants but suffers from a high wear rate which limits its applications. Here we report four orders of magnitude reduction in the steady state wear rate of PTFE due to graphene additives. The wear rate of unfilled PTFE was measured to be $\sim 0.4 \times 10^{-3}$ mm³/Nm which is reduced to $\sim 10^{-7}$ mm³/Nm by the incorporation of 10 weight % of graphene platelets. We also performed a head-to-head comparison of wear rate with graphene and micro-graphite fillers at the same weight fractions. In general, we find that graphene fillers gave 10 to 30 times lower wear rates than micro-graphite at the same loading fraction. Scanning electron microscopy analysis indicated noticeably smaller wear debris size in the case of graphene/PTFE composites indicating that graphene additives are highly effective in regulating debris formation in PTFE leading to reduced wear. We systematically varied the weight fraction and thickness of the graphene platelets and find that when

the wear results are normalized by the filler specific surface area per unit mass, the results for the various graphene samples fall on a master curve. We use percolation theory to explain these results.

WK4

Tapping into Graphene's Potential as a Solid Lubricant

Diana Berman¹, Sanket A. Deshmukh¹, Subramanian K.R.S. Sankaranarayanan¹, Ali Erdemir², and Anirudha V. Sumant¹

¹Nanoscience and Technology Division, Argonne National Laboratory, Argonne, IL 60439

²Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439

In recent years minimizing friction and wear-related failures in mechanical/tribological and electronic subsystems remains as one of the greatest challenges in today's moving mechanical assemblies. It is estimated that nearly 1/3 of the fuel used in automobiles is spent to overcome friction. Accordingly, the search continues for novel materials, coatings, and lubricants (both liquid and solid) that can potentially reduce friction and wear.

In this study we show, that few layers of graphene are able to drastically reduce friction (by factors of 4–5) and wear (by as much as 4 orders of magnitude) of sliding metallic surfaces in both humid and dry environment. This tribological behavior of graphene is strikingly different from its bulk counterpart graphite. Additionally, we observed that the lifetime of such few-layer graphene coating improves significantly, when tested in hydrogen environment [1]. Separate studies on evaluating the electrical contact properties of these graphene sheets demonstrated that graphene, as a two-dimensional material, shears easily during mechanical sliding tests even under high contact pressures, while retaining excellent electrical conductivity of metal-metal contacts for thousands of sliding passes [2]. We elucidate the mechanism of wear/friction of graphene using reactive molecular dynamic simulation. Our findings demonstrate that tuning the atomistic scale chemical interactions holds the promise of realizing extraordinary tribological properties of monolayer graphene coatings.

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.

- [1] D. Berman, S. Deshmukh, S. Sankaranarayanan, A. Erdemir, and A.V. Sumant, "Extraordinary macroscale wear resistance of one atom thick graphene layer," *Advanced Functional Materials* **24**, 6640–6646 (2014).
- [2] D. Berman, A. Erdemir, and A.V. Sumant, "Graphene as a protective coating and superior lubricant for electrical contacts," *Applied Physics Lett.* **105**, 231907 (2014).



Wednesday, May 13

Facility-specific Workshops

APS Workshop 6 APS Upgrade: Planning the First Experiments

Location: Bldg. 402, Lecture Hall

Organizers: Eric Landahl (DePaul University) and Stefan Vogt (Argonne National Laboratory)

The purpose of this workshop is to discuss the opportunity to create Partner User Proposals (PUPs) for developing experimental systems, methods, and technologies needed to lay the foundation for the first experiments at the APS Upgrade. It is expected that a significant fraction of beam time over the next several years will need to be dedicated to the efforts of the Upgrade Partner Users.

Following a brief status update on the Upgrade, including a discussion of anticipated performance parameters, this workshop will break into self-organized groups of interested participants. An APS beamline staff member will serve as moderator for each working group and will be able to provide additional beamline-related information. PUPs resulting from this workshop might include the following:

Development of new model systems or samples that will take advantage of the improved coherence of the upgraded storage ring. PUPs are encouraged that will exploit existing capabilities to conduct preliminary studies on new samples that are candidates for the first experiments at the Upgrade

Development of experimental or analysis techniques that will reach their full potential using the improved coherence of the upgraded storage ring. PUPs might include exploiting coherence in existing techniques (e.g., applying coherence methods to macromolecular crystallography or EXAFS) or in testing entirely new approaches to coherent x-ray science.

Development of technologies necessary for successful use of the upgraded storage ring. PUPs might be used to provide beam time for testing optics, detectors, or data acquisition aspects of anticipated first experiments.

PUPs contribute to the development of the facility in exchange for a set amount of beam time. Further information is available on the PUP web page.

8:30 – 8:40	Eric Landahl <i>Welcome & Introduction</i>
8:40 – 8:55	Stuart Henderson <i>Overview of the APS Upgrade</i>
8:55 – 9:20	Stefan Vogt <i>The APS Upgrade: Unique Opportunities</i>
9:20 – 9:30	Dennis Mills <i>The Partner User Proposal Process</i>
9:30 – 10:15	Open forum and single-slide staff presentations to seed breakout discussions groups
10:15 – 10:45	Coffee Break

Workshop Agendas and Abstracts

10:45 – 12:00 Breakout discussions groups (locations announced during workshop)

12:00 Adjourn



Wednesday, May 13 Facility-specific Workshops

APS/CNM Workshop 7 Experimental and Computational Challenges of *in situ* Multimodal Imaging of Energy Materials

Location: Bldg. 401, Room A1100

Organizers: Yuzi Liu (CNM), Yang Ren (APS), Maria Chan (CNM), and Xianghui Xiao (APS)

Real-time imaging, scattering, and spectroscopy are primary experimental techniques to probe the dynamic process of materials formation, evolution, and structure–property relationships in energy materials.

In recent years, transmission electron microscopy (TEM) and synchrotron-based x-ray methods have been further developed to incorporate new environments and detectors to meet fast-growing research needs in energy materials science. Scientists have applied these techniques to investigate myriad processes, such as nanoparticle nucleation and growth and phase transitions of energy storage materials during the charge and discharge cycling. For example, *in situ* TEM provides a platform to study materials nucleation, growth, and electrochemically driven growth of dendrites on lithium anodes at the atomic scale.

In addition, the improvements in synchrotron x-ray optics and high-brightness coherent light sources allow investigation of phase changes and other chemical transformations with high spatial and temporal resolution.

Both electron and x-ray imaging methods provide opportunities to study energy materials in three-dimensional views, in addition to providing spectroscopic information.

Integration of these different techniques to study the energy materials in multimodal approaches at different length scales and temporal scales will help scientists further understand the working mechanisms of energy materials.

High-performance computation is crucial for the deployment of such multimodal imaging capabilities, both in the form of high-volume and high-speed data acquisition and processing and in the form of data interpretation via atomistic and first-principles simulations. The coupling of the experimental and computational development requires integrated teams and multidisciplinary efforts. Argonne National Laboratory has established the Integrated Imaging Initiative to emphasize the importance of multimodal imaging.

This workshop will cover the most recent developments and applications of *in situ* characterization techniques and high-performance computations for the study of energy materials. Particular attention will be paid to *in situ* multimodal imaging in the investigation of phase transformations, dynamics, crystal growth, crystal defect formation and elimination, chemical reactions, and interface dynamics in environmental conditions. The goal of this workshop is to provide a forum for experimental and computational scientists and facility users from various fields who are utilizing *in situ* methods to understand the structure, physics, and chemistry of energy materials.

8:30 – 8:40 Opening Remarks

8:40 – 9:30 Nigel Browning (Pacific Northwest National Laboratory)
Quantitative in situ Transmission Electron Microscopy

9:30 – 10:00	Haimei Zheng (Lawrence Berkeley National Laboratory) <i>Real-time Imaging of Materials Transformations in Liquids</i>
10:00 – 10:35	Break
10:35 – 11:05	Chongmin Wang (Pacific Northwest National Laboratory) <i>In situ and ex situ TEM Study of Anode and Cathode for Lithium-ion Battery and Beyond</i>
11:05 – 11:35	Scott Warren (University of North Carolina at Chapel Hill) <i>Identifying Champion Nanostructures with Electron, Light, and Force Microscopies</i>
11:35 – 12:00	Jeffrey Greeley (Purdue University) <i>Computational Investigations of Interfacial Structure and Reactivity</i>
12:00 – 1:30	Lunch
1:30 – 2:20	Paul Fenter (Argonne National Laboratory) <i>In situ Studies of Structures and Processes at Model Electrode/Electrolyte Interfaces</i>
2:20 – 2:50	Jiajun Wang (Brookhaven National Laboratory) <i>In situ 2D/3D Imaging of Battery Materials with Full-field Transmission X-ray Microscopy</i>
2:50 – 3:20	Break
3:20 – 3:50	Raymond Osborn (Argonne National Laboratory) <i>Single Crystal Diffuse Scattering: Big Data beyond the Workflow</i>
3:50 – 4:20	Todd Turner (Air Force Research Laboratory) <i>Microstructural Modeling of a Combined High-energy Diffraction Microscopy Experiment</i>
4:20 – 4:50	Mark Hereld (Argonne National Laboratory) <i>An Integrated Platform for Studying Complex Biological Systems</i>
4:50	Closing Remarks

WK7

Quantitative *in situ* Transmission Electron Microscopy

N.D. Browning^{1,2}, B.L. Mehdi^{1,2}, E. Jensen^{1,2}, P. Abellan¹, L.R. Parent^{1,2}, A. Stevens³, D.A. Welch⁴, R. Faller⁴, J.E. Evans⁵, C. Park⁶, C.M. Wang^{2,5}, J.-G. Zhang^{2,7}, and K.T. Mueller^{2,5,8}

¹Fundamental and Computational Science Directorate, PNNL, Richland, WA 99352

²Joint Center for Energy Storage Research, PNNL, Richland, WA 99352

³National Security Directorate, PNNL, Richland, WA 99352

⁴Dept Chemical Engineering and Materials Science, UC-Davis, Davis, CA 95616

⁵Environmental Molecular Sciences Laboratory, PNNL, Richland, WA 99352

⁶Department of Industrial and Manufacturing Engineering, FSU, Tallahassee, FL 32306

⁷Energy and Environmental Directorate, PNNL, Richland, WA 99352

⁸Department of Chemistry, Penn State University, University Park, PA 16802

Many processes in materials science, chemistry and biology take place in a liquid environment — such as the synthesis of nanoparticles, biological cellular functions and the operation of Li-ion/next generation batteries. In these cases, the overall process/function of the system is a result of a series of complicated transients, where a change in the order, magnitude or location of any of the individual steps can lead to a radically different result. Understanding



and subsequently controlling the final system outcome can therefore be greatly aided by the ability to directly observe these fundamental transient processes as and where they happen. Aberration corrected (scanning) transmission electron microscopy [(S)TEM] has the spatial resolution (typically < 0.1 nm) to directly visualize the atomic scale structural and chemical variations taking place in materials. Historically, such high resolution microscopy has been used to analyze materials before and after a process takes place to infer the dynamics of what happened in between. While there are still great advances that can be made with such analyses (at the very least in providing benchmark structures for nanoscale systems), a major breakthrough in recent years has been the design and implementation of *in situ* gas and liquid stages that allow (S)TEM images to be obtained while the transient processes are actually taking place. Performing experiments using these *in situ* stages presents numerous challenges to the traditional means of analyzing samples in an electron microscope — we are now dealing with the variability of dynamic process rather than a more straightforward static structure. In this presentation, I will discuss the recent developments in the design and implementation of *in situ* stages being pursued at the Pacific Northwest National Laboratory (PNNL) that permit quantitative information to be extracted from the observations. Examples of the use of these capabilities for the direct imaging of the fundamental processes important for energy storage and conversion materials will be presented. As the *in situ* stages have been designed to be incorporated into both high spatial resolution aberration corrected (S)TEM and high temporal resolution Dynamic TEM (DTEM), the potential for future experiments to study fast dynamics, including those involving live biological structures, will also be discussed.

This work was supported in part by the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the Department of Energy, Office of Science, Basic Energy Sciences. The development of the stages was supported by the Chemical Imaging Initiative, a Laboratory Directed Research and Development Program at Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated by Battelle for the U.S. Department of Energy (DOE) under Contract DE-AC05-76RL01830. A portion of the research was performed using the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at PNNL.

WK7

Real-time Imaging of Materials Transformations in Liquids

Haimei Zheng

Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

An understanding of how materials grow and transform in their working environment is essential to the development of functional materials and efficient devices for energy applications. We study the growth and transformation of materials in liquids by the development and application of liquid cell transmission electron microscopy (TEM). In this talk, I will present our study of shape evolution mechanisms of colloidal nanoparticles using liquid cell TEM. There have been a lot of studies on controlling shape of nanoparticles since the catalytic or other surface-enhanced properties of the nanocatalysts are highly dependent on their shape. However, how facets develop during nanoparticle growth is largely unknown due to the lack of direct observation. Using *in situ* liquid cell TEM, we have been able to identify unique growth mechanisms and have discovered rules that are applied to bulk systems break down at the nanoscale. At the end, I will also briefly show our development of electrochemical liquid cells for the study of dissolution-deposition at the electrode-electrolyte interfaces in battery applications.

WK7

In situ and *ex situ* TEM Study of Anode and Cathode for Lithium-ion Battery and Beyond

Chong-Min Wang

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354

Over the last decades, we have witnessed tremendous progress on the development of aberration corrected transmission electron microscopy and scanning transmission electron microscopy. As a result of this development, imaging of materials at atomic scale and spectroscopy at sub-nanometer scale become a routine practice. The

questions now come to how we extend the microscopy and spectroscopy methodologies to analyze materials at or near realistic/operating condition, typically such as real-time observation of catalytic process, oxidation and reduction, bio-tissue in a liquid cell, defects generation and interaction under deformation conditions, mass transport and microstructural evolution, charge and ion transport process in electrochemical cells. In this presentation, I will focus on *in situ* TEM techniques that developed for probing into the structural and chemical information of energy storage materials. *In situ* high-resolution imaging enables direct observation of structural evolution, phase transformation and their correlation with mass, charge and electron transport, which provide insights as how active materials failure with cyclic charging and discharging of a battery. In perspective, challenges and possible direction for further development of the *in situ* TEM imaging and spectroscopic methods for energy storage materials and other field will also be discussed.

WK7

Identifying Champion Nanostructures with Electron, Light, and Force Microscopies

Scott C. Warren

Departments of Chemistry and of Applied Physical Sciences, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599

Assemblies of 0D, 1D, and 2D materials have emerged as one of the most important architectures for solar cells, fuel cells, batteries, and water-splitting devices. The complexity of these materials, as exemplified by the huge number of unique interfaces, has frustrated attempts to identify the relationships between structure and electronic properties, a knowledge of which are crucial for improving device performance. I describe the development of several techniques and instruments based on electron, light, and force microscopies that allow *ex situ* and *in situ* imaging of single nanostructures with a spatial resolution that is often below 2 nm. This presentation will focus on our recent efforts to correlate structure and properties in aggregates of nanoparticles that are of interest in solar water splitting. By performing correlations on statistically significant sample sizes, we are able to deduce how specific types of nanoparticle interfaces result in high performance in water splitting, ultimately allowing us to design macroscopic devices with record (“champion”) performance. We will briefly describe how new microscopy techniques and instruments are allowing this approach to be generalized to new material systems.

WK7

Computational Investigations of Interfacial Structure and Reactivity

Jeff Greeley

Purdue University, School of Chemical Engineering, West Lafayette, IN 47907

Advances in the theoretical understanding of interfacial electrocatalysis have, over the past decade, permitted the extension of periodic Density Functional Theory studies, which have traditionally been applied to probe chemistry at gas/solid interfaces, to electrochemical systems where potential-dependent reactions occur at liquid/solid interfaces. Indeed, such techniques have been employed to study a surprisingly wide class of chemical processes, ranging from electrochemical oxygen reduction to carbon dioxide reduction to water splitting. In this talk, I will briefly review the application of these simple techniques to the classic case of the hydrogen evolution reaction on transition metal alloys. Next, I will demonstrate how very similar approaches can be applied to understand certain aspects of reactivity at bifunctional oxide/metal interfaces, and I will close by drawing analogies between these electrocatalytic processes and traditional heterogeneous catalytic chemistries at metal/support interfaces.



WK7

***In situ* Studies of Structures and Processes at Model Electrode/Electrolyte Interfaces**

Paul Fenter

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

Understanding and controlling reactions within electrochemical energy storage systems is a significant scientific and technical challenge. This is due to the complexity of these systems (e.g., for both the solids and electrolytes), as well as the extreme environments and significant structural and chemical changes that can take place as a function of applied potential. The behavior at the solid-electrolyte interface itself is especially poorly understood. I will review our recent work in which we seek to isolate and understand the role of interfacial reactivity in these systems through *in situ*, real-time, observations of electrochemically driven reactions. This is achieved by observing well-defined model electrode-electrolyte interfaces using x-ray reflectivity. I will discuss two distinct types of electrochemical energy storage systems: 1) lithium ion battery chemistries in which energy is stored by lithium ion insertion into electrodes (e.g., Si, Si_xCr, Ge, NiO). The goal of this work is to control the complex lithiation reaction path of these conversion reactions through the use of thin-film and multilayer electrode structures; and 2) super-capacitor systems, in which energy is stored by surface adsorption. For these systems, we are studying the static structures and dynamical response of room temperature ionic liquids at potential-controlled carbon interfaces which we find have inherently slow dynamics associated with the reorganization of the interfacial RTIL structure.

This work was supported as part of the Center for Electrochemical Energy Science (CEES) and the Fluid Interface Reactivity Structure and Transport Center (FIRST), which are Energy Frontier Research Centers funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. The work was done in collaboration with T. Fister, S.S. Lee, A. Uysal, H. Zhou (ANL), J. Esbensen, B. Long, A. Gewirth (UIUC), X. Chen, G. Evmenenko, M. Bedzyk (Northwestern), G. Feng, S. Li, P. Cummings (Vanderbilt), S. Dai (ORNL), and Y. Gogotsi (Drexel).

WK7

***In situ* 2D/3D Imaging of Battery Materials with Full-field Transmission X-ray Microscopy**

Jiajun Wang and Jun Wang

Photon Sciences Directorate, Brookhaven National Laboratory, Upton, NY 11973

Electrochemically driven phase transformation directly influences electrode performance in lithium ion batteries. Advancing our understanding of the mechanism necessitates the development of advanced tools with *in situ* capability to track the dynamic phase and structural changes of battery materials at 2D and 3D. The synchrotron hard x-ray imaging technique is particularly interesting for applications in battery studies because of its natural characteristics: it is non-destructive, chemically and elementally sensitive, environmentally friendly, and highly penetrative to enable *in situ* study of a real battery [1–3]. Considerable progress in this field has been reported recently from our group, beamline X8C at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), where a new full-field hard x-ray imaging technique, transmission x-ray microscopy (TXM), has been developed and applied to battery microstructure study [4,5]. In this talk, we will present our recent work using *in situ/in operando* TXM approach to track phase transformation at 2D and 3D for anode (Tin) and cathode (LiFePO₄) battery materials [1–3]. Challenges and opportunities of TXM technology for energy materials research will be also discussed. This *in situ* imaging approach has a wide variety of applications in other fields, such as fuel cells, catalysis, environmental science and biological science.

- [1] Wang, J., Chen-Wiegart, Y.K., and Wang, J. *In operando* tracking phase transformation evolution of lithium iron phosphate with hard x-ray microscopy. *Nat. Commun.* **5**, 4570 (2014).
- [2] Wang, J., Chen-Wiegart, Y.K., and Wang, J. *In situ* three-dimensional synchrotron x-ray nanotomography of the (de)lithiation processes in tin anodes. *Angew. Chem. Int. Ed.* **126**, 4549–4553 (2014).
- [3] Wang, J., Chen-Wiegart, Y.K., and Wang, J. *In situ* chemical mapping of a lithium-ion battery using full-field hard x-ray spectroscopic imaging. *Chem. Commun.* **49**, 6480–6482 (2013).

- [4] Wang, J., et al., Automated markerless full field hard x-ray microscopic tomography at sub-50 nm 3-dimension spatial resolution. *Appl. Phys. Lett.* **100**, 143107 (2012).
- [5] Wang, J., et al., Size-dependent surface phase change of lithium iron phosphate during carbon coating. *Nat. Commun.* **5**, 3145 (2014).

WK7

Single Crystal Diffuse Scattering: Big Data beyond the Workflow

Raymond Osborn

Argonne National Laboratory, Argonne, IL 60439

Single crystal diffuse x-ray scattering is a three-dimensional probe of complex defect structures embedded in an otherwise perfect lattice, providing insight into the role of disorder in generating materials properties such as fast-ion conduction or relaxor ferroelectricity. With the new generation of fast area detectors, full three-dimensional volumes of reciprocal space can be generated using continuous sample rotations, with several thousand images collected in less than 10 minutes. We have been developing methods of handling data collected at rates of several GB per minute by streaming images to a data server, combining the frames in NeXus files that contain comprehensive experimental metadata, and transforming the arrays into reciprocal space for real-time inspection and manipulation. A collaboration with Argonne computational scientists is developing interactive tools for the data analysis of very large (10–50GB) remote data sets using resources such as Globus catalogs and the Swift parallel scripting language to enable flexible script-based approaches to ‘playing’ with the data once the basic data reduction workflow is complete. These tools are being written in a sufficiently general way that they may be useful in other scientific domains.

WK7

Microstructural Modeling of a Combined High-energy Diffraction Microscopy Experiment

Todd Turner

Air Force Research Laboratory, Yellow Springs, OH 45387

The strategic development of new engineering materials with improved performance rests upon establishing computational models that link materials processing, microstructure, and properties/performance. However, validating micro mechanical models that capture the relevant deformation at the microstructural level has remained elusive without access to experimental data at the relevant grain-level scale. 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 at the mesoscale, where the response of grains and similar microstructural features are explicitly tracked. This presentation will focus on work done at the 1-ID beamline at the Advanced Photon Source, where grain level morphology and elastic strain evolution were tracked through HEDM techniques. A crystal plasticity finite element model based on this experiment will be presented, and the results of the model will be compared to the experimentally obtained HEDM data.



WK7

An Integrated Platform for Studying Complex Biological Systems

Mark Hereld¹, Kenneth M. Kemner², Robin Lambert Graham³, Gyorgy Babnigg², Frank R. Collart², Olliver Cossairt⁴, Nicola J. Ferrier¹, Benjamin S. Glick⁵, Philippe H. Noirof², Sarah L. O'Brien², Norbert F. Scherer⁶, and Rosemarie Wilton²

¹Mathematics and Computer Science Division, Argonne National Laboratory, Argonne, IL 60439

²Biosciences Division, Argonne National Laboratory, Argonne, IL 60439

³Computing, Environment, and Life Sciences Directorate, Argonne National Laboratory, Argonne, IL 60439

⁴Department of Electrical Engineering and Computer Science, Northwestern University, Evanston, IL 60208

⁵Biological Sciences Division, University of Chicago, Chicago, IL 60637

⁶Department of Chemistry, University of Chicago, Chicago, IL 60637

Imaging is one of the most important and powerful methods yet devised to learn about the world around us. In the Small Worlds project, an interdisciplinary team of scientists at Argonne, University of Chicago, and Northwestern University are developing a new multi-modal imaging capability for studying complex multi-agent processes in cells and systems of cells across spatial and temporal scales. This experimental platform is composed of integrated hardware, software, and molecular-scale reporters that will enable the study of systems biology problems involving many parts and spanning spatial scales from the nanometer to the millimeter and temporal scales from subseconds to days.

We have begun to develop and integrate three imaging methods that, when used together, will lead to tremendous new understanding of the organization and dynamic function of a wide range of complex biological systems. The first approach, scanning x-ray fluorescence (XRF) imaging, allows sub-micron scale measurements of intact complex systems in their native environment, even if that environment is opaque to visible light. The second method, correlative electron-optical imaging, allows ultra-resolution imaging of whole organisms by transmission electron microscopy (TEM) and 3D spatial correlation with optical imaging of the identical (fixed) samples. The third proposed development, the novel 3D snapshot interferometric holographic microscope (3D-SIHM), is optical 3D microscopy of dynamic living systems with nanoscale resolution by interferometry, plus multi-scale volumetric imaging by holography in a “snapshot” mode for quantitative determination of transport on nanometer to 100 μm scales. The three approaches are synergistic when used in tandem with reporters that function across one or more of the imaging methods.

The contingent of capabilities developed in this project will enable construction of dynamic experiments that can track and correlate interrelated molecular actors in complex processes, while providing detailed corroboration and supplementary data across physical scales with qualitatively different imaging modalities.

Wednesday, May 13

Facility-specific Workshops

APS Workshop 8

In situ X-ray Characterization of Microstructure during Manufacture

Location: Bldg. 401, Room A5000

Organizers: Don Brown and John Carpenter (Los Alamos National Laboratory)

Recent years have seen tremendous advances in the ability to monitor materials microstructure, in both spatial and temporal resolution, at third-generation synchrotron x-ray sources. Concurrently, in an effort to rebuild manufacturing capability in the United States toward lower cost, more efficient production, “advanced manufacturing” techniques are being developed. Because of this timing, a marriage between manufacturing and characterization techniques is possible. Indeed, because of the particularly simple geometry of many of the characterization techniques, such as high-energy diffraction, small angle scattering, and radiography, it is natural to explore *in situ* x-ray characterization measurements during manufacturing.

The purpose of this workshop is to bring together both researchers who have already initiated *in situ* manufacturing programs and those who could benefit from such work. The intent is to draw scientists interested in either materials (including polymers, electronics, metals, and ceramics) or manufacturing processes (from traditional casting to simple heat treatments to the most modern advanced manufacture techniques) or both. The session will consist of several talks to sample the state of the field, followed by discussion of instrumentation needs (e.g., power or water needs) necessary to enable continued advancement of capabilities.

8:30 – 8:40	Welcome & Introductory Remarks
8:40 – 9:20	Amy Clarke (Los Alamos National Laboratory) <i>Multi-scale Prediction and Control of Metal Alloy Solidification Dynamics to Achieve Advanced Manufacturing</i>
9:20 – 10:00	Jon Emery (Argonne National Laboratory) <i>A Portable, Modular Reactor for in situ Synchrotron X-ray Investigation of Atomic Layer Deposition Processes</i>
10:00 – 10:30	Break
10:30 – 11:10	Ruipeng Li (Cornell University) <i>Evolution of Organic Thin Film Transistors Controlled by Blade-coating Method</i>
11:10 – 11:50	Aaron Stebner (Colorado School of Mines) <i>A Novel in situ Planar Biaxial Experiment</i>
11:50	Wrap Up



WK8

Multi-scale Prediction and Control of Metal Alloy Solidification Dynamics to Achieve Advanced Manufacturing

A.J. Clarke¹, D. Turret¹, S.D. Imhoff¹, J.W. Gibbs¹, P.J. Gibbs¹, Y. Song², A. Karma², N.N. Carlson¹, K. Fezzaa³, W.-K. Lee⁴, pRad Team¹, D.R. Coughlin¹, J.K. Baldwin¹, and J.T. McKeown⁵

¹Los Alamos National Laboratory, Los Alamos, NM 87545

²Northeastern University, Boston, MA 02115

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

⁴Brookhaven National Laboratory, Upton, NY 11973

⁵Lawrence Livermore National Laboratory, Livermore, CA 94550

Metal alloy solidification provides the first opportunity to affect structural, chemical, and defect evolution that dictates mechanical performance. Because solidification is multi-scale, we use state-of-the-art synchrotron x-ray and proton imaging to study solidification dynamics and inform advanced computational models. At the microscopic scale, we control thermal gradient and solid-liquid interface velocity during directional solidification to manipulate microstructural and chemical evolution. We quantitatively compare our x-ray imaging of a dilute aluminum-copper alloy with three-dimensional phase-field simulations. We are able to successfully predict microstructural characteristics with phase-field, but only if solutal convection — a key factor identified from our experiments — is incorporated. At the mesoscopic scale, the evolution of dendritic arrays in aluminum-based alloys is compared to dendritic needle network modeling. We also predict casting mold filling and local thermal gradients and solid-liquid interface velocities with continuum-scale process modeling to yield microstructural predictions within a casting. Our multi-scale integration of *in situ* characterization, modeling, and controlled processing will enable the prediction and control of microstructural evolution during solidification and advanced manufacturing of metal alloys.

This work was supported by an Early Career award from the U.S. DOE, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering.

WK8

A Portable, Modular Reactor for *in situ* Synchrotron X-ray Investigation of Atomic Layer Deposition Processes

Jeffrey A. Klug¹, Matthew S. Weimer^{1,2}, Jonathan D. Emery¹, Angel Yanguas-Gil³, Christian M. Schlepütz⁴, Sönke Seifert⁴, Seth B. Darling⁵, Mike J. Pellin¹, Jeffrey W. Elam³, Alex B.F. Martinson¹, Adam S. Hock^{2,6}, and Thomas Proslie^{1,7}

¹Material Science Division, Argonne National Laboratory, Argonne, IL 60439

²Department of Chemistry, Illinois Institute of Technology, Chicago, IL 60616

³Energy Systems, Argonne National Laboratory, Argonne, IL 60439

⁴X-ray Science Division, Argonne National Laboratory, Argonne, IL 60439

⁵Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

⁶Chemical Science Division, Argonne National Laboratory, Argonne, IL 60439

⁷High Energy Physics Division, Argonne National Laboratory, Argonne, IL 60439

Atomic layer deposition (ALD) is a thin film growth technique that utilizes alternate self-limiting surface reactions of vapor-phase precursors. The self-limiting growth process afforded by ALD provides unique advantages that are unavailable through other vapor-phase deposition methods. Specifically, ALD excels at: 1) growth of highly uniform and conformal films on large area substrates or high aspect ratio nanostructures and 2) precise and accurate control over thin film coating thickness (sub-nanometer) and composition (atomic-scale). These characteristics are particularly applicable in, for example, manufacturing processes for microelectronics, catalysis, and solar energy conversion and storage. Ultimately, to best understand ALD processes, *in situ* monitoring of structural and chemical properties during deposition is required. This is particularly important during the early stages of deposition — a growth regime that critically influences the films' morphology, crystallinity, and composition. Furthermore, as ALD is increasingly applied in ultrathin film applications (< 10 nm), the early-cycle ALD nucleation behavior, which often deviates from linear, steady-state growth modes, begins to dominate film properties and has critical influence for device applications.

Synchrotron characterization techniques provide some of the most powerful tools for the study of film structure and chemistry. The brilliance and tunability of the source at the APS allow us to access scattering and spectroscopic techniques unavailable with in-house laboratory setups and provide us with the opportunity to probe various ALD processes *in situ* starting at the very first deposition cycle. Here, we present the design and implementation of a portable ALD reactor that possesses a modular reactor scheme that enables simple experimental switchover between various characterization techniques and beamlines. As first examples, we present *in situ* results for 1) x-ray surface scattering and reflectivity measurements of epitaxial ALD of ZnO on sapphire, 2) grazing-incidence small angle scattering of ALD-related sequential infiltration of trimethylaluminum and water into PS-*b*-PMMA block copolymer lamellar thin films, and 3) grazing-incidence x-ray absorption spectroscopy of nucleation-regime growth of Er₂O₃. Importantly, the *in situ* ALD reactor is designed to serve a broad user base with diverse experimental requirements and objectives, and is available for use to researchers upon request.

WK8

Evolution of Organic Thin Film Transistors Controlled by Blade-coating Method

Ruipeng Li and Detlef-M. Smilgies

Cornell High Energy Synchrotron Source, Cornell University, Ithaca, NY 14850

Solution-processed organic thin film transistors (OTFTs) have attracted considerable attention due to their high performance, low cost and easy manufacture. Achieving high performance requires that the microstructure and morphology of solution-cast thin films — that develops via nucleation and growth processes — exhibit a high degree of crystallinity with two-dimensional in-plane π -stacking, a low density of grain/domain boundaries exhibiting low crystallographic misorientation. Efforts to tune the microstructures and morphologies of solution-cast thin films have been hampered by the lack of understanding and control over the nucleation and growth of the thin films as the molecules crystallize from the solution phase under highly non-equilibrium conditions.

Here, we demonstrate *in situ* characterization of the structural variation of the organic transistors cast by the doctor-blading coating process through microbeam Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) at D-line in CHESS, Cornell University. The crystallization process is monitored for various coating speeds to control the evolution from anisotropic to isotropic films, which provides a full characterization of the nucleation evolution in the doctor-blading coating process. The results reveal the relationship between the microstructure, morphology and the device performance and direct fine tuning of coating parameters for future roll-to-roll processing of organic electronics devices.

WK8

A Novel *in situ* Planar Biaxial Experiment

Aaron Stebner

Colorado School of Mines, Golden, CO 80401

Advanced alloys, such as lightweight metals and shape memory alloys, are becoming increasingly important to the advancement of many industries. They often possess complex microstructures that result in anisotropic and asymmetric behaviors, often due to twinning and phase transformation of low symmetry crystal structures. Because of this, their three-dimensional mechanical properties and mechanisms of deformation cannot be fully understood through uniaxial characterization and processing studies. To elucidate these behaviors, a custom planar biaxial load frame capable of *in situ* x-ray and neutron diffraction experimentation has been built. The instrument was designed to study any arbitrary plane-stress loading condition, in addition to load path change events. Thus, the micromechanics of full plane stress yield and transformation loci may be quantified in addition to path-dependent behaviors. We will review the new experimental capabilities, sample designs, and discuss implications for improving processing models of advanced alloys.



Wednesday, May 13

Facility-specific Workshops

APS Workshop 9

Workshop on Sn-119 Nuclear Resonant Scattering at the APS

Location: Bldg. 402, Room E1100/E1200

Organizers: Michael Hu and Bogdan Leu (APS)

The purpose of this workshop is to inform the broader general user community about the development of a new capability at Sector 30 regarding the use of the ^{119}Sn nuclear resonance. The workshop will bring together experts in the field with potential new users to identify specific needs and develop plans to implement those requirements.

The nuclear resonant scattering studies performed at Sector 3 and Sector 16 in the last two decades have proved valuable in studying diverse materials, including porphyrins, proteins, enzymes and inorganic catalysts, superconductors, clathrates, thermoelectrics, metallic alloys, and earth-bound minerals under extreme pressures. Measurement of element-selective phonon density of states and extraction of numerous thermal and elastic constants motivated many new areas of research.

Similarly, measurement of nuclear forward scattering in the time domain with nanosecond resolution led to better understanding of electronic properties, such as valence and magnetism, in samples and under conditions that render these measurements impossible in the laboratory. For example, magnetism has been measured in monolayers or under pressures exceeding 1 Mbar.

Thus, the interest in nuclear resonant studies has grown to a point where it is necessary to optimize beamlines for different isotopes and to create more opportunities. One such opportunity presents itself at Sector 30. The working energy of the HERIX spectrometer at Sector 30 (23.7 keV) and the ^{119}Sn nuclear resonance (23.88 keV) can be reached with the same monochromator. The combination of this cryogenically cooled, high-resolution monochromator with 1 meV resolution and a newly installed short-period undulator (1.72 cm) creates an ideal condition for such measurements. The available flux is better by almost an order of magnitude than at similar facilities around the world. Recent tests and scientific output [1] have demonstrated this capability at Sector 30.

Tin-based nuclear resonance studies are of interest to a variety of groups working with such materials as newly discovered superconductors, thermoelectric materials, clathrates, Sn-halides, porphyrins, and organometallic compounds. The combination of access to the ^{119}Sn resonance with capabilities such as microfocusing for nanomaterial studies and infrastructure for high-pressure measurements should make the new technique highly attractive for new users.

Reference

[1] B.M. Leu et al., "Vibrational dynamics of the host framework in Sn clathrates," *Phys. Rev. B* **90**, 104304 (2014), DOI: <http://dx.doi.org/10.1103/PhysRevB.90.104304>.

8:30 – 8:35 Welcome & Introductory Remarks

8:35 – 9:05 Ercan Alp (Argonne National Laboratory)
Sn-based Nuclear Resonant Scattering Studies: Past and Present

9:05 – 9:45	John Tse (University of Saskatchewan) <i>Chemical Bonding and Lattice Dynamics of Sn Compounds from 119-Sn Mossbauer</i>
9:45 – 10:25	Raphael Hermann (Forschungszentrum Juelich) <i>Highly Anisotropic Lattice Dynamics in $[(\text{SnSe})_{1.04}]_m\text{-}[\text{MoSe}_2]_n$ Ferrecrystals</i>
10:25 – 10:35	Break
10:35 – 11:15	Mathieu Roskosz (Univ. des Science et Tech. de Lille) <i>Tin Isotopes: The Next Probe of Planetary Differentiation and Core Formation</i>
11:15 – 11:55	W. Robert Scheidt (University of Notre Dame) <i>Tin Porphyrins 1969–2014</i>
11:55	Wrap-up and concluding remarks

WK9

Sn-based Nuclear Resonant Scattering Studies: Past and Present

E.E. Alp, W. Bi, J. Zhao, M.Y. Hu, T.S.Toellner, and B. Leu

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

^{119}Sn is the second most popular Mössbauer isotope after ^{57}Fe . This is partly due to long lifetime of its parent isotope $^{119\text{m}}\text{Sn}$ (250 days), relatively simple M1 transition from 3/2 to 1/2 state, reasonably long lifetime (18.3 nsec or 25.7 neV), and low transition energy (23.88 keV). Sn was among the first metals extracted (around 3500 BC). In modern times, Sn has found wider use in organotin compounds, transparent conductors, catalysis, protective coatings, float-glass production, and more recently in dye-sensitized solar cells, perovskites, Li-ion batteries, and tin chalcogenides as thermoelectric materials. Sn is also shown to be amenable to form two-dimensional topological insulators.

In this talk, I will introduce the Sn-based Mössbauer work done at the synchrotron radiation sources, their information content, and give a description of the new capability at Sector 30 beamline.

This work is supported by U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences under contract DE-AC02-06CH11357.

WK9

Chemical Bonding and Lattice Dynamics of Sn compounds from 119-Sn Mossbauer

John S. Tse

University of Saskatchewan, Department of Physics and Engineering Physics, Saskatoon, Saskatchewan, Canada

In this presentation, I will present a general introduction on how 119-Sn Mossbauer spectroscopy can provide useful chemical information and lattice dynamics of Sn nuclei in a variety compounds. Special emphases will be on system that cannot be easily amenable to laboratory Mossbauer spectrometers, such as thin films and under extreme conditions.



WK9

Highly Anisotropic Lattice Dynamics in $((\text{SnSe})_{1.04})_m\text{-(MoSe}_2)_n$ Ferecrystals

Raphaël P. Hermann

Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

The highly anisotropic lattice dynamics properties in SnSe based ferecrystals obtained from nuclear resonance inelastic x-ray scattering by the ^{119}Sn Mössbauer resonance will be discussed. Ferecrystals and related misfit layered compounds exhibit extremely low lattice thermal conductivity. These materials multilayer materials exhibit turbostratic disorder between the two constituent layers stacked in the direction perpendicular to the substrate, here m unit-cells of SnSe and n of MoSe_2 . By measuring the density of phonon states for Sn with the beam in plane with the layers and perpendicular to the layers, highly contrasting speed of sound and force constants are found for the $(m,n)=(1,1)$ system. Further, a comparison of systems with $(m,n)=(1,1)$ and $(4,1)$ reveals the importance of interface effects in determining the lattice dynamics properties. Overall the ferecrystals are ideal in revealing properties of phonons under confinement.

Benedikt Klobes, Michael Hu, Matt Beekman, and David C. Johnson are acknowledged for the fruitful collaboration. The Advanced Photon Source at Argonne National Laboratory is acknowledged for provision of synchrotron radiation facilities at Sector 3.

WK9

Tin Isotopes: The Next Probe of Planetary Differentiation and Core Formation

Mathieu Roskosz

UMET, CNRS, University of Lille, France

Terrestrial planets (including Mars and the Moon) are differentiated into metallic cores and silicate mantles and crusts. This layered structure provides some of the most important properties of these planets such as a magnetic field that deflects the solar wind and plate tectonics. Understanding the thermodynamical conditions (P, T, $f\text{O}_2$) that prevailed during this differentiation is thus a major question in Earth sciences. The elemental concentrations of siderophile (iron-loving) elements in the Earth's mantle have been intensively studied. Based on this approach, it is now widely accepted that the upper mantle abundances have been set by metal-silicate equilibrium in an early magma ocean. However, the redox conditions and their evolution during planetary formation are still highly controversial.

A new approach of this question is based on the isotopic composition of siderophile elements (mainly Si and Fe). However, a quantitative analysis of data collected on natural samples requires knowing accurately the way isotopes partition between coexisting phases (iron-based metal alloys, silicates and sulfides in particular). The so-called *fractionation factor* can be determined experimentally but it requires drastic equilibrium conditions that are barely achievable at the high pressures and temperatures of interest. In the case of iron and tin these experimental difficulties can be overcome if fractionation factors are indirectly measured using a synchrotron-based inelastic spectroscopy. The determination of these factors is achieved by measuring phonon excitations using a kind of inelastic x-ray scattering based on special Mössbauer nuclei (NRIXS).

In this context the recent analytical developments make possible to analyze the isotopic compositions of tin in natural samples. So far, this system has never been successfully explored from a geochemical point of view. Though some attempts were made in the past, the chemical separation of tin from other elements present in rocks was a real issue that is being solved these days. Now, we have a unique opportunity to develop the tin isotope geochemistry. There are very few places in the world with sufficient x-ray intensity, proper high-resolution optics, and nanosecond time resolved detectors with high efficiency to measure ^{119}Sn -specific properties of materials. The APS beamlines (Sector 3 and Sector 30) have developed proper crystal optics suitable for this purpose.

Workshop Agendas and Abstracts

Here I will present known aspects of the physical and coordination chemistry of tin in geomaterials, how they should control tin isotopes fractionation and how Sector 30 will help us, in the coming years, to provide the mandatory fractionation factors to make Sn isotopes the new probe of the early evolution of the Moon, the Earth and Mars.



Wednesday, May 13

Facility-specific Workshops

APS Workshop 10

Application of Synchrotron X-ray Scattering Techniques to Nuclear Materials

Location: Bldg. 401, Room A5000

Organizers: Don Brown (Los Alamos National Laboratory) and Maria Okuniewski (Idaho National Laboratory)

The heyday of research into nuclear energy materials predated the modern model of the national user facility in the United States, which essentially was pioneered at Intense Pulsed Neutron Source at Argonne National Laboratory in the 1980s. As a result, many of the advanced characterization techniques that have been developed at neutron and synchrotron x-ray sources have not been brought to bear on nuclear materials.

The recent renewed interest in nuclear power, spurred by increased energy costs and concerns about climate change, has meant a resurgence in nuclear materials research, including work at user facilities. However, barriers to the study of naturally radioactive and activated materials still exist, in particular at synchrotron sources, which often do not have the infrastructure to deal with radioactive material that neutron sources inherently possess. The purpose of this proposed workshop is to gather those scientists currently utilizing the APS to study nuclear materials, as well as scientists whose programs could benefit from the advanced tools available at the APS.

The workshop will begin with several talks about cutting-edge nuclear material science to expose non-APS users to the possibilities for this type of work. It will conclude with a discussion of the current policies that govern the study of nuclear materials at the APS, including design of containment, shipping and local transport, sample handling, and completion of the experiment. Here again, participants who are not APS users will add valuable input as they can comment on best practices at universities and other government laboratories. The goal of this workshop is to produce a white paper compiling the expressed needs of the user community regarding radioactive sample handling at the APS and recommendations about how to accommodate those needs.

1:30 – 1:40	Welcome & Introductory Remarks
1:40 – 2:10	Jim Stubbins (University of Illinois Urbana-Champaign) <i>Analysis of Nuclear Fuels, Cladding, and Structural Materials</i>
2:10 – 2:40	Meimei Li (Argonne National Laboratory) <i>Synchrotron Radiation Characterization of Materials for Nuclear Energy Applications</i>
2:40 – 3:10	Mohamed Elbakhshwan (Brookhaven National Laboratory) <i>Synchrotron X-ray Diffraction of Nuclear Materials</i>
3:10 – 3:20	Break
3:30 – 3:50	APS Radiation Safety Officer
3:50 – 4:50	Panel Discussion
4:50	Wrap Up

WK10

Analysis of Nuclear Fuels, Cladding and Structural Materials

James Stubbins

University of Illinois Urbana-Champaign, Urbana, IL 61801

The APS has provided substantial new understanding of the bulk effects that govern the performance of materials for nuclear applications. Much of this understanding is due to the fact that prior to very bright light sources, the performance of materials for nuclear application was determined on pre- and post-irradiated samples where only a “before and after” picture could be obtained. Current work with the APS has provided the opportunity to understand the active processes involved during the deformation of metallic alloys, which were previously not known. In particular, the role of various strengthening mechanisms was not fully characterized or appreciated. In this talk, the effects of various strengthening mechanism on nuclear materials performance will be discussed with particular attention to the new understanding of dynamic deformation processes.

WK10

Synchrotron Radiation Characterization of Materials for Nuclear Energy Applications

Meimei Li

Argonne National Laboratory, Argonne, IL 60439

The use of synchrotron radiation offers new opportunities to advance the fundamental understanding of nuclear reactor materials in extreme conditions of irradiation, temperature, stress and corrosion. This presentation will highlight recent studies using synchrotron x-ray scattering, spectroscopy and imaging techniques to understand the dynamic behavior of nuclear reactor materials and radiation damage over a wide range of length scales. The presentation will also discuss a recently-developed new capability for *in situ* characterization of irradiated specimens under thermal-mechanical loading using combined techniques of far-field high-energy diffraction microscopy (ff-HEDM)/tomography/wide-angle x-ray scattering (WAXS)/small-angle x-ray scattering (SAXS). The containment design for safe handling of an irradiated specimen at an open beamline at the APS will also be discussed.

WK10

Synchrotron X-ray Diffraction of Nuclear Materials

Mohamed Elbakhshwan¹, David J. Sprouster¹, Simerjeet K. Gill¹, Sanjit Ghose², Eric Dooryhee², and Lynne E. Ecker¹

¹Nuclear Science and Technology Department, Brookhaven National Laboratory, Upton, NY 11973

²National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973

Structural materials for nuclear energy systems are required to withstand radiation and corrosion at high pressure and temperature during reactor operation. Zirconium alloys used for cladding experience corrosion reactions with the coolant as well as the fuel during normal and accident conditions. Austenitic stainless steels, such as 304 and 347, are frequently used for core internals such as core barrels, bolts and support plates. Ferritic-martensitic steels such as T91 and HT9 are being considered as structural materials in advanced nuclear reactors. Exposure to radiation in a nuclear reactor can cause changes in the microstructure of the zirconium alloys or steels that can lead to brittle fracture, fatigue or irradiation-assisted stress-corrosion cracking. Radiation induced segregation can make the material prone to phase-transformations and the creation of new phases. In addition, the accumulation of defects (vacancy clusters) or helium can lead to void formation and swelling.

Synchrotron radiation sources can play an essential role in providing quantitative characterization of the atomic structure of complex materials; not just carefully prepared ideal systems, but materials that are actually used in nuclear reactors. The presentation will focus on the early oxidation states of fuel cladding alloys and the characterization of irradiated materials that was performed at the new state-of-the-art National Synchrotron Light Source II (NSLS II).



First, a sample environment was developed to perform *in situ* x-ray diffraction and x-ray fluorescence to understand the behavior of zirconium alloys under high pressure and temperature steam environment. Second, a robot has been developed at the X-ray Powder Diffraction (XPD) Beamline to automatically acquire high-resolution x-ray diffraction data, high energy (high Q) data for Pair Distribution Function Analysis, and small-angle x-ray scattering data for large number of samples of reactor pressure vessel steels or structural materials with varying chemistries, grain sizes, cold-work conditions and irradiation conditions. This tool provides safe, unmanned manipulation of relatively large numbers of radioactive samples for statistically representative, high-throughput measurements.

Wednesday, May 13

Facility-specific Workshops

APS Workshop 11

Tracking Electronic and Structural Dynamics in Proteins and Materials at Sector 14

Location: Bldg. 402, Room E1100/E1200

Organizers: Robert Henning (CARS, University of Chicago) and Anthony DiChiara (APS and CARS, University of Chicago)

The major upgrade to the BioCARS 14-ID beamline [1] produced unprecedented time-resolved capabilities that have been exploited for x-ray science spanning biology, chemistry, materials science, and physics. More recently, a new area detector (Rayonix MX340-HS, a 60-megapixel high-readout-rate integrating area detector) and secondary Kirkpatrick-Baez focusing mirrors were installed. The new equipment expands opportunities for time-resolved x-ray diffraction and solution scattering at 14-ID even further, by providing $\sim 15 \times 15 \mu\text{m}^2$ focused pink or monochromatic beam.

The workshop will bring together current practitioners and prospective new users of time-resolved pump-probe x-ray techniques from both biological and physical sciences. The goal of the workshop is to provide an overview of current capabilities and to discuss future challenges, needs, and opportunities, especially as they relate to brighter and smaller spots offered by the reduced-emittance APS MBA-lattice upgrade. The scientific emphasis will be on our new/current focal capability and the recent advances in serial crystallography, microcrystallography, x-ray excited warm dense matter, and time-resolved Laue diffraction and solution scattering.

Reference

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

- | | |
|-------------|--|
| 1:30 – 1:40 | Robert Henning (University of Chicago/BioCARS)
<i>Introduction</i> |
| 1:40 – 2:10 | Hyun Sun Cho (National Institutes of Health)
<i>Watching a Signaling Protein Function in Real Time via 150-picosecond Time-resolved Solution Scattering</i> |
| 2:10 – 2:40 | Xiaoshan Xu (University of Nebraska-Lincoln)
<i>Structural Dynamics in Improperly Multiferroic Hexagonal Ferrites</i> |
| 2:40 – 3:10 | Marius Schmidt
<i>Time-resolved Macromolecular Crystallography at the Synchrotron and at the X-ray FEL</i> |
| 3:10 – 3:30 | Break |
| 3:30 – 4:00 | Stephen Durbin (Purdue University)
<i>Interaction of X-ray and Laser Pulses in GaAs</i> |
| 4:00 – 4:30 | Sebastian Westenhoff (University of Gothenburg, Sweden)
<i>Signal Transduction in Phytochrome Photosensors Visualized by Time-resolved X-ray Scattering</i> |



4:30 – 5:00	Aaron Lindenberg (Stanford University/SLAC) <i>Ultrafast Studies of Interlayer Coupling in Transition Metal Dichalcogenide ReS₂</i>
5:00	Concluding remarks

WK11

Watching a Signaling Protein Function in Real Time via 150-picosecond Time-resolved Solution Scattering

Hyun Sun Cho, Friedrich Schotte, and Philip Anfinrud

Laboratory of Chemical Physics, NIDDK, NIH, Bethesda, MD 20892

To understand how signaling proteins function, it is crucial to know the time-ordered sequence of events that lead to the signaling state. Using the time-resolved infrastructure we helped develop on the BioCARS beamline, we tracked the reversible photocycle of photoactive yellow protein following trans-to-cis photoisomerization of its p-coumaric acid (pCA) chromophore. Briefly, a picosecond laser pulse photoexcites pCA and triggers a structural change in the protein, which is probed with a suitably delayed picosecond x-ray pulse. When the protein is studied in a crystalline state, this “pump-probe” approach recovers time-resolved diffraction “snapshots” whose corresponding electron density maps can be stitched together into a real-time movie of the structural changes that ensue. However, the actual signaling state is not accessible in the crystalline state due to crystal packing constraints. This state is accessible in time-resolved small- and wide-angle x-ray scattering studies, which probe changes in the size, shape, and structure of the protein. The mechanistically detailed, near-atomic resolution description of the complete PYP photocycle developed from these studies provides a framework for understanding signal transduction in proteins, and for assessing and validating theoretical/computational approaches in protein biophysics. Thanks to an NIH-funded 2014 upgrade of the BioCARS beamline, the x-ray flux achievable and the rate at which images can be acquired has been boosted significantly, benefitting both time-resolved Laue crystallography and time-resolved SAXS/WAXS studies. This research was supported in part by the Intramural Research Program of the NIH, NIDDK.

WK-11

Structural Dynamics in Improperly Multiferroic Hexagonal Ferrites

Xiaoshan Xu

University of Nebraska-Lincoln, Lincoln, NE 68588

Hexagonal ferrites, as a new family of multiferroic materials, exhibit ferromagnetism and ferroelectricity simultaneously. The improper ferroelectricity appears below 1050 K, driven by a non-polar structural distortion, while the weak ferromagnetism occurs below 130 K resulting from a competition between a couple of structural distortions. Since both the ferroelectricity and ferromagnetism have structural origins, a structurally mediated magnetoelectric coupling may be possible, as proposed by theory. As a key step, understanding the structural response to an electric field is crucial to understanding the magnetoelectric couplings in hexagonal ferrites. Using time-resolved x-ray diffraction, we probe the structural response to an effective electric field generated by the photo-induced charge carriers. By comparing the results with temperature-dependent structural refinements, dramatic responses of non-polar structural distortion are revealed, with the same time-scale of the charge carrier decay. The pattern of the lattice constants change indicates complex nature of the structural response. These results suggest that the structural response to the electric field may be a route for the magnetoelectric effect.

WK11

Time-resolved Macromolecular Crystallography at the Synchrotron and at the X-ray FEL

Marius Schmidt

UW-Milwaukee, Physics Department, Milwaukee, WI 53211

Time-resolved crystallography unifies structure with kinetics. A time-series of difference maps is required to extract the molecular structures of reaction intermediates as well as the temporal evolution of the associated concentrations. Powerful synchrotron beamlines such as BioCARS at the Advanced Photon Source (APS) make the collection of these movies possible. *Multiple* time-series of photoactive yellow protein (PYP) can be collected rapidly. An additional experimental parameter such as the temperature can be varied. New, hitherto inaccessible, information can be extracted. Crystallography becomes five-dimensional [1,2]. At an x-ray free-electron laser, however, time-resolved serial femtosecond crystallography (TR-SFX) has several advantages: (i) due to the diffraction before destruction principle, radiation damage is negligible although enormous doses are deposited, (ii) small nano- and micro-crystals are utilized that can be easily and uniformly excited. Reactions in photo-reactive proteins such as PYP can be started by an optical laser pulse, and reactions in enzymes may be started by diffusion of substrate, (iii) cyclic reactions as the one in PYP and non-cyclic reaction such as those catalyzed by enzymes are conceptually on the same footing, (iv) the ultra-short, femtosecond x-ray pulses provide access to ultrafast time-scales beyond the pulse-limitations at the synchrotron. We present difference maps determined from TR-SFX [3] at beamline CXI at the LCLS. These results will pave the way to exciting, new experiments with photoreceptors and enzymes with serial crystallography at synchrotrons at the x-ray FELs.

- [1] Schmidt, M., Srajer, V., Henning, R., Ihee, H., Purwar, N., Tenboer, J., and Tripathi, S., (2013), Protein energy landscapes determined by five-dimensional crystallography, *Acta Crystallogr D* **69**, 2534–2542.
- [2] Schmidt, M., Graber, T., Henning, R., and Srajer, V., (2010), Five-dimensional crystallography, *Acta crystallographica. Section A, Foundations of crystallography* **66**, 198–206.
- [3] Tenboer, J., Basu, S., Zatspein, N., Pande, K., Milathianaki, D., Frank, M., Hunter, M., Boutet, S., Williams, G.J., Koglin, J.E., Oberthuer, D., Heymann, M., Kupitz, C., Conrad, C., Coe, J., Roy-Chowdhury, S., Weierstall, U., James, D., Wang, D., Grant, T., Barty, A., Yefanov, O., Scales, J., Gati, C., Seuring, C., Srajer, V., Henning, R., Schwander, P., Fromme, R., Ourmazd, A., Moffat, K., Van Thor, J.J., Spence, J.C., Fromme, P., Chapman, H.N., and Schmidt, M., (2014), Time-resolved serial crystallography captures high-resolution intermediates of photoactive yellow protein, *Science* **346**, 1242–1246.

WK11

Interaction of X-ray and Laser Pulses in GaAs

Stephen Durbin

Purdue University, Physics Building, West Lafayette, IN 47906

Unusual excited states of matter can now be created with x-ray pulses at the APS Sector 14, a unique synchrotron source, creating energy densities comparable to optical laser pulses but with unique properties driven by the greater penetration depth and an energetic spectrum of electrons and fluorescence. An x-ray-induced excited state can be further excited by a laser pulse, or an x-ray pulse can excite a previously laser-pumped material. Combining the strikingly different interaction with materials of x-rays and optical photons can lead to new metastable states with unique dynamical properties, such as x-ray induced optical transparency. We report here on a double pump study of GaAs, using an x-ray pump with photons energetic enough to eject *K* electrons in GaAs, and an optical laser pump tuned for exciting valence electrons into the conduction band. Optical probes reveal that defect states surprisingly play a critical role in mediating strong interactions between the x-rays and the optical photons.



WK11

Signal Transduction in Phytochrome Photosensors Visualized by Time-resolved X-ray Scattering

A. Björling¹, H. Takala¹, O. Berntsson¹, S. Niebling¹, J.A. Ihalainen², and S. Westenhoff¹¹Department of Chemistry and Molecular Biology, University of Gothenburg, 40530 Gothenburg, Sweden²Nanoscience Center, Department of Biological and Environmental Science, University of Jyväskylä, 40014 Jyväskylä, Finland

Sensory proteins must relay structural signals over large distances from the sensory site to regulatory output domains. Phytochromes are a major family of sensor proteins that control diverse cellular functions in plants, bacteria and fungi.

We study the structural dynamics of signal transduction in the photosensory core of the phytochrome form *Deinococcus radiodurans*. Our crystal and solution structures show an open and closed form of the dimeric protein for the activated and resting states, respectively [1]. This nanometer-scale rearrangement is controlled by refolding of an evolutionarily conserved ‘arm’, which is in contact with the chromophore. Time-resolved x-ray solution scattering data confirms that the opening movement is conserved in many bacterial phytochromes [2].

To arrive at these conclusions, x-ray crystallography was paired with time-resolved solution scattering. I will discuss two approaches to extract structural information from the latter data set. Firstly, structures are selected from many frames in unbiased molecular dynamics simulations [1,3]. Secondly, we have programmed a GROMACS-based molecular dynamics tool, in which the molecules are driven towards states that agree with the experimental scattering data [4]. I will discuss how these tools open up for studying the structural changes of proteins in solution.

[1] Takala, H. et al., Signal amplification and transduction in phytochrome photosensors. *Nature* **509**, 245–248 (2014).

[2] Björling, A. et al., Ubiquitous structural signalling in bacterial phytochromes. Unpublished.

[3] Arnlund, D. et al., Visualizing a protein quake with time-resolved x-ray scattering at a free-electron laser. *Nat. Methods* **11**, 923–926 (2014).

[4] Björling, A., Niebling, S., Marcellini, M., van der Spoel, D., and Westenhoff, S. Deciphering solution scattering data with experimentally guided MD simulations. *J. Chem. Theory Comput.* **11**, 150113180629009 (2015).

WK11

Ultrafast Studies of Interlayer Coupling in Transition Metal Dichalcogenide ReS₂

Aaron M. Lindenberg

Stanford University/SLAC, Stanford, CA 94305

I will describe recent experiments probing ultrafast structural dynamics in quasi-2D transition metal dichalcogenides. Time-resolved x-ray scattering measurements carried out at Sector 14 at the APS and at the Stanford Synchrotron Radiation Laboratory (SSRL) allow for direct probes of interlayer coupling phenomena in these materials, a key aspect of their functionality. Measurements reveal ultrafast acoustic responses and induced out-of-plane disorder following above-gap photo-excitation. If time allows, I will also describe recent complementary studies using time-resolved electron diffraction.

