DRIVING **DISCOVERY**

2017 APS/CNM USERS MEETING

WORKSHOP AGENDAS AND ABSTRACTS

Tuesday, May 09

APS Workshop 1
High-energy Resolution Inelastic X-ray Scattering Workshop

Location: Bldg. 402, Room E1100/1200

Organizers: Ayman H. Said (APS), Ercan E. Alp (APS), Michael Y. Hu (APS), and Ahmet Alatas (APS)

Inelastic x-ray scattering is making an increasing impact in addressing lattice dynamics related issues in wide range of scientific areas including condensed matter physics, geophysics and chemistry. The workshop is intended to provide a forum for presenting new research and exchanging ideas about new applications and technical developments for IXS users. Diverse areas of research, including superconductivity, geophysics, charge density waves, and quantum phase transitions, will be covered, as well as theoretical approaches to IXS and NRS techniques.

8:30–8:35	Stephen Streiffer (Argonne National Laboratory) *Opening Remarks*
8:35–8:40	Ahmet Alatas (Argonne National Laboratory) *HERIX Update at Sectors 3 and 30*
8:40–8:50	Michael Hu (Argonne National Laboratory) *Sn-NRS Program at Sector 30*
8:50–9:25	Frank Weber (Karlsruhe Institute of Technology) *High Pressure, Anomalous Line Shapes and High Precision Phonon Spectroscopy at the HERIX Spectrometer at ID-30, APS*
9:25–10:00	Sofia Michaela Souliou (European Synchrotron Radiation Facility) *High Energy Resolution Inelastic X-ray Scattering under High Pressure Conditions*
10:00–10:20	Break/Workshop Picture
10:20–10:55	Olivier Delaire (Duke University) *Anharmonic Phonon Dispersions and Scattering Rates across the Brillouin Zone with Inelastic X-ray Scattering and First-principles Simulations*
10:55–11:30	Felix Flicker (University of California, Berkeley) *Charge Order in $NbSe_2$*
11:30–12:05	Dipanshu Bansal (Oak Ridge National Laboratory) *Lattice Dynamics and Thermal Transport in Multiferroic $CuCrO_2$*
12:05–1:30	Lunch
1:30–2:05	Mathieu Roskosz (Muséum National d'Histoire Naturelle) *Tin Isotopes: The Next Probe of Planetary Differentiation and Core Formation*
2:05–2:40	Daniel Pérez Lozano (KU Leuven-Instituut voor Kern- en Stralingsfysic) *The Role of Phonons in the Critical Temperature Enhancement of Sn Nanowires*
2:40–3:15	Jennifer Jackson (California Institute of Technology) *Phonon Dispersion Measurements of (Mg,Fe)O at High Pressures: Implications for Earth's Interior*
3:15–3:35	Break
3:35–4:10	Jason Hancock (University of Connecticut) *Negative Thermal Expansion in Two Incipient Ferroelastics*
4:10–4:45	Dmitry Reznik (University of Colorado – Boulder) *Electronic Nematic Fluctuations in Fe-based Superconductors Investigated by Inelastic Neutron and X-ray Scattering*

4:45–5:20 Riccardo Comin (Massachusetts Institute of Technology)
Lattice Dynamics in Organometallic Lead Halide Perovskites

5:20–5:30 Ercan Alp (Argonne National Laboratory)
Concluding Remarks

WK-1

High Pressure, Anomalous Line Shapes and High Precision Phonon Spectroscopy at the HERIX Spectrometer at ID-30, APS

Frank Weber
Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

I will review recent work, which we performed at the HERIX spectrometer at ID-30:

(1) In a high-pressure–low-temperature study of *1T*-$TiSe_2$ [1] we investigated the soft phonon mode of the charge-density-wave (CDW) transition up to nearly 10 GPa and down to 5 K as well as for intercalated Cu_xTiSe_2 at ambient pressure. We find that the intercalation-induced superconductivity can be explained by a solely phonon-mediated pairing mechanism, while this is not possible for the superconducting phase under pressure. We argue that a hybridization of phonon and exciton modes in the pairing mechanism is necessary to explain the full observed temperature-pressure-intercalation phase diagram. These results indicate that *1T*-$TiSe_2$ under pressure is close to the elusive state of the excitonic insulator.

(2) *2H*-$NbSe_2$ is one of the few compounds where CDW order and superconductivity co-exist without doping or other tuning parameters. We observe [2] changes of the phonon line shape that are characteristic for systems with strong electron-phonon coupling in the presence of a superconducting energy gap $2\Delta_c$ and from which we can demonstrate an *l* dependence of the superconducting gap. Reversely, our data imply that the CDW energy gap is strongly localized along the *l* direction. The confinement of the CDW gap to a very small momentum region explains the rather low competition and easy coexistence of CDW order and superconductivity in *2H*-$NbSe_2$.

(3) We investigated the soft mode behavior of the structural phase transition common to the 122 iron-based superconductors in hole-doped systems. Achieving a precision in determining the phonon energy of ±0.03 meV we can demonstrate the clear response of lattice dynamical properties to the magnetic phase transitions in various systems and compare them to neutron scattering work performed in $Ba(Fe_{1-x}Co_x)_2As_2$ [3] where a large softening below superconducting T_c contrasts the hardening observed in zero-momentum techniques [4,5].

[1] Maschek, M., et al. (2016). "Superconductivity and hybrid soft modes in 1T-$TiSe_2$." *Physical Review B* **94**: 214507.

[2] Weber, F., Rosenkranz, S., Heid, R., and Said, A.H. (2016). "Superconducting energy gap of 2H–$NbSe_2$ in phonon spectroscopy." *Physical Review B* **94**: 140504(R).

[3] Weber, F., et al. (2016). "Enhancement of finite wavevector nematic fluctuations in the superconducting state of $Ba(Fe_{1-x}Cox)_2As_2$." arXiv:1610.00099.

[4] Böhmer, A.E., et al. (2014). "Nematic Susceptibility of Hole-Doped and Electron-Doped $BaFe_2As_2$ Iron-Based Superconductors from Shear Modulus Measurements." *Physical Review Letters* **112**: 047001.

[5] Yoshizawa, M., et al. (2012). "Structural Quantum Criticality and Superconductivity in Iron-Based Superconductor $Ba(Fe_{1-x}Cox)_2As_2$." *Journal of the Physical Society of Japan* **81**: 024604.

WK-1

High Energy Resolution Inelastic X-ray Scattering under High Pressure Conditions

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Synchrotron-based high resolution inelastic x-ray scattering (IXS) is nowadays routinely combined with pressure generating diamond anvil cells (DACs), often cryogenically cooled or resistively/laser-heated, for the study of lattice dynamics (acoustic and optical phonon dispersions as well as phonon density of states) under extreme thermodynamic conditions.

In the first part of the talk, I will give an overview of the high pressure instrumentation and experimental activity in the IXS beamline of the ESRF, as well as of new capabilities arising in combination with the recently commissioned thermal diffuse scattering side-station. In the second part of the talk, I will present recent IXS results on (1) elemental antimony upon approaching the pressure-induced structural transition from the rhombohedral *A*7 structure

towards an incommensurate host-guest structure, (2) the high-pressure superconducting phase of the mineral calverite $AuTe_2$, and (3) the interplay between the superconducting and charge density wave state in $YBa_2Cu_3O_{6+x}$ under pressure.

WK-1

Anharmonic Phonon Dispersions and Scattering Rates across the Brillouin Zone with Inelastic X-ray Scattering and First-principles Simulations

Olivier Delaire[1,2], Dipanshu Bansal[2], Jennifer Niedziela[2], Chen Li[2], Jiawang Hong[2], Tyson Lanigan-Atkins[1], Shan Yang[1], Ahmet Alatas[3], Michael Hu[3], and Ayman Said[3]

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A detailed understanding of phonon anharmonicity (phonon-phonon interactions), electron-phonon coupling, and spin-phonon coupling is of broad interest for the design of novel energy materials, for example to establish reliable microscopic models of thermal transport and thermodynamics. For example, the contribution of phonons to thermal conductivity in thermoelectrics needs to be suppressed to enhance the conversion efficiency, but little is known about the respective contributions of different phonon modes. As illustrated in our recent studies [1–5], inelastic x-ray scattering (IXS) and inelastic neutron scattering (INS) measurements can be used to map phonon dispersions and linewidths throughout the Brillouin zone. In particular, IXS/NRIXS can probe phonons in small crystals <100 μm, as function of temperature and pressure (in diamond anvil cells). In addition, we perform density functional theory (DFT) simulations of the phonon dispersions, linewidths, and experimental cross-sections, in order to rationalize measurements. Our studies provide critical insights into the dominant phonon scattering mechanisms, including anharmonic phonon-phonon scattering, electron-phonon coupling, spin-fluctuation scattering, and scattering by defects or nanostructures. In this presentation, I will illustrate how our approach, combining x-ray/neutron measurements on single-crystals with detailed DFT simulations, has achieved novel insights into the microscopic underpinnings of thermal conductivity in a number of materials, such as PbTe, SnTe, $AgSbTe_2$, SnSe, Mo_3Sb_7, $CuCrO_2$, FeS [1–6]. In particular, we identified the importance of anharmonic lattice instabilities in achieving low thermal conductivities in PbTe, SnTe [1,3] and more recently in SnSe [4], and traced the origin of anharmonicity to the underlying electronic bonding with DFT. Using first-principles simulations of phonon-phonon interactions, we also show how anomalous satellite peaks in the phonon spectral function of the TO mode in rocksalt chalcogenides arises from a resonance in the phonon self-energy [3]. This deeper understanding of anharmonic phonon quasiparticles opens new avenues to tailor microscopic thermal transport and design new materials.

O.D. acknowledges funding from the U.S. DOE, Office of Basic Energy Sciences, Materials Science and Engineering Division, through the Office of Science Early Career program (DE-SC0016166), and as part of the S3TEC EFRC.

[1] O. Delaire, J. Ma, K. Marty, A.F. May, M.A. McGuire, M.-H. Du, D.J. Singh, A. Podlesnyak, G. Ehlers, M. Lumsden, and B.C. Sales (2011). *Nature Materials* **10**: 614.

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[3] C.W. Li, O. Hellman, J. Ma, A.F. May, H.B. Cao, X. Chen, A.D. Christianson, G. Ehlers, D.J. Singh, B.C. Sales, and O. Delaire (2014). *Physical Review Letters*.

[4] C. Li, J. Hong, A.May, D. Bansal, S. Chi, T. Hong, G. Ehlers, and O. Delaire (2015). *Nature Physics* **11**: 1063.

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WK-1

Charge Order in $NbSe_2$

Felix Flicker

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Niobium diselenide has long served as a prototype of two-dimensional charge ordering, believed to arise from an instability of the electronic structure analogous to the one-dimensional Peierls mechanism. Despite this, various anomalous properties have recently been identified experimentally which cannot be explained by Peierls-like weak-coupling theories. We consider instead a model with strong electron-phonon coupling, taking into account both the full momentum and orbital dependence of the coupling matrix elements. We show that both are necessary for a consistent description of the full range of experimental observations. We argue that $NbSe_2$ is typical in this sense, and that any charge-ordered material in more than one dimension will generically be shaped by the momentum and orbital dependence of its electron-phonon coupling as well as its electronic structure. The consequences will be observable in many charge-ordered materials, including cuprate superconductors.

WK-1

Lattice Dynamics and Thermal Transport in Multiferroic $CuCrO_2$

D. Bansal[1], J.L. Niedziela[1], A. Said[2], A. May[1], G. Ehlers[3], D.L. Abernathy[3], Ashfia Huq[3], Melanie Kirkham[3], H. Zhou[4], and O. Delaire[1,5]

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The co-existence and interplay of ferroelectricity and magnetism in multiferroic materials is of both fundamental and technological importance. We report extensive x-ray and neutron scattering measurements of lattice dynamics in delafossite $CuCrO_2$ ($7 \leq T \leq 530$ K) across the concomitant magnetic and ferroelectric transition ($T_N \sim 24$ K). These experiments are complemented by first-principles simulations of the phonons. Our phonon dispersions and density of states measurements reveal very anisotropic vibrations of Cu atoms, which exhibit low-frequency modes of large amplitude parallel to the basal plane of the layered delafossite structure. The anisotropic vibrations are also supported by atomic displacement parameters from neutron diffraction. While little overall change in phonon frequencies is observed across T_N, the low frequency in-plane modes also show a systematic temperature dependence of neutron and x-ray scattering intensities. Furthermore, we find that spin fluctuations persist up to ~300 K, far above T_N. Modeling of the thermal conductivity indicates that these spin fluctuations above T_N constitute a strong source of phonon scattering, significantly suppressing thermal transport.

This research was supported by the Office of Science Early Career Research Program under Award No. DE-SC0016166. The use of Oak Ridge National Laboratory's Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. DOE. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Theoretical calculations were performed using resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under contract No. DE-AC02-05CH11231.

WK-1

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

Mathieu Roskosz
MNHN, IMPMC, CNRS, UPMC, 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, fO_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.

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.

WK-1

The Role of Phonons in the Critical Temperature Enhancement of Sn Nanowires

Daniel Pérez Lozano
KU Leuven, Oude Markt 13, 3000 Leuven, Belgium

Tin is a weak-coupling superconductor whose critical temperature (Tc) is 3.72 K. Nanostructuring Sn in the form of nanowires leads to a Tc enhancement as its diameter is reduced. However, the mechanism behind the enhancement is not well understood and it is normally attributed to either phonon softening or to quantum size effects. The phonon density of states (F(E)) is determined for Sn nanowires with diameters of 18 nm, 35 nm and 100 nm. Using F(E) to calculate the nanowires Tc and comparing it with resistance measurements, we demonstrate that the modification of F(E) explains the Tc enhancement.

WK-1

Phonon Dispersion Measurements of (Mg,Fe)O at High Pressures: Implications for Earth's Interior

Jennifer M. Jackson[1], Gregory J. Finkelstein[1], Ayman Said[2], Ahmet Alatas[2], Bogdan M. Leu[2], and Thomas S. Toellner[2]
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The large chemical, density, and dynamical contrast associated with the juxtaposition of a liquid iron-dominant alloy and an intimate mixture of silicates and oxides at Earth's core–mantle boundary is associated with a wide range of complex seismological features. Seismic observations in this region have detected patches that are about 5–20 km thick in which the seismic wave velocities are reduced by up to 30%. These ultralow-velocity zones (ULVZs) have been interpreted as aggregates of partially molten material or as solid, iron-enriched assemblages, typically based on proposed sources of velocity reduction. Interpretation of these features and the dynamic processes that formed them requires, in part, knowledge of the elastic tensors of candidate phases.

In this contribution, we will present phonon dispersion relations of single-crystal (Mg,Fe)O at high pressures using high energy resolution inelastic x-ray scattering. The single crystal was hydrostatically loaded with a helium pressure medium, and the experiments were conducted at Sector 30 of the Advanced Photon Source. Analysis of the phonon dispersion relations as a function of crystallographic direction, in combination with *in situ* volume (density) measurements, permits the determination of the single crystal elastic modulus tensor of (Mg,Fe)O. We will present results obtained at high pressures and discuss the implications for the Earth's core-mantle boundary region.

WK-1

Negative Thermal Expansion in Two Incipient Ferroelastics

Jason Hancock
University of Connecticut, Storrs, CT 06269

Recent discoveries of materials displaying negative thermal expansion (NTE), a substance's tendency to shrink when heated, have rejuvenated research interest in this unusual phenomenon. In recent work at the APS, we have found that the robust NTE spanning over 1000 K in ScF3 occurs as excited states above a structural quantum phase transition. This discovery permits classification of ScF3 as an incipient ferroelastic (IF) in a stoichiometric compound and suggests there may be a generic connection between the IF state and NTE behavior. To test this, we have again used inelastic x-ray scattering at the APS to investigate another stoichiometric incipient ferroelastic Hg2I2 and find remarkable similarities in the dynamical response. In addition we report, for the first time, NTE behavior in the mercury halides, strongly suggesting an intricate link between (clean) structural quantum phase transitions and NTE, providing a beacon for further discoveries of NTE materials.

WK-1

Electronic Nematic Fluctuations in Fe-based Superconductors Investigated by Inelastic Neutron and X-ray Scattering

Dmitry Reznik
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Nematic order is ubiquitous in liquid crystals and is characterized by a preferred direction in an otherwise uniform liquid. Recently a similar symmetry breaking has been observed in some electronic phases in quantum materials related to high temperature superconductors. We investigated the prototypical Fe-based high-temperature superconductor $Ba(Fe_{1-x}Co_x)_2As_2$ where the interplay of electronic nematic order and superconductivity is well

established. Previous measurements found a strong suppression of nematic fluctuations at zero momentum in the superconducting state, but what happens at nonzero momentum is unknown. We found that fluctuations at small momenta, which correspond to wavelengths of as much as 25 unit cells, do not compete with superconductivity. Instead they continue to grow below superconducting Tc. This result contrasts the conventional picture where the behavior at the ordering wavevector (*q=0*) and nearby (small) wavevectors should be similar. Our results imply the existence of a length scale larger than 25 unit cells that is important for understanding of the interplay between nematicity and superconductivity. The talk will discuss these results as well as new inelastic neutron and x-ray experiments on other Fe-based superconductors.

This work was supported by the DOE, Office of Basic Energy Sciences, Office of Science, under Contract No. DE-SC0006939

WK-1
Lattice Dynamics in Organometallic Lead Halide Perovskites

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In recent years, light-harvesting devices based on a new class of organometallic lead iodide perovskites (CH3NH3PbI3) were found to exhibit power conversion efficiencies beyond 20.1%, rapidly approaching the performance of commercial Silicon-based modules. Similar breakthroughs were reported in other area of optoelectronics, such as light-emitting devices, light sensing, and photocatalysis. While major challenges remain regarding the stability and durability of the active material and corresponding devices, several avenues are being explored that could revolutionize the field of semiconductors by offering a new cost-effective platform for high-performance devices fabricated using room-temperature, wet chemistry techniques.

In this talk, I will present inelastic x-ray scattering insights on the nature of the near-room-temperature cubic-to-tetragonal transitions of the perovskite structure in methylammonium lead bromide and iodide. The measurement of the lowest energy phonon branches as a function of momentum confirm the presence of zone-edge instabilities in these systems. Further, and most notablty, I will show how the quasielastic scattering above the structural transition reveals the persistence of low-symmetry structures in the form of nanodomains with short range order. These results underscore the absence of a bona fide cubic phase and expose the inability of existing structural models to describe what appears to be a dynamical rather than a static lattice above room temperature, in a regime critically relevant for photovoltaic applications.

Tuesday, May 9

APS Workshop 2
Even Small Wavelengths, When Bright Enough, Have Big Data Problems

Location: Bldg. 401, Room A5000

Organizers: Reeju Pokharel and Turab Lookman (LANL)

Non-destructive characterization of new classes of challenging materials has been made possible with the advent of third-generation synchrotron light sources, such as the Advanced Photon Source (APS) at Argonne National Laboratory, and x-ray free electron lasers (XFEL), such as the Linac Coherent Light Source (LCLS) at Stanford. The high energy and brilliance of the x-rays produced by these light sources can probe high Z, 3D polycrystalline samples at the mesoscale (~0.1-10 μm). While providing previously inaccessible data, the increasing average brightness of these light sources also creates new challenges, such as the generation of extremely large data sets (GBs to TBs). These unconventionally large data sets are overwhelming the experimentalists. Furthermore, the fact that data is generated from multi-modal techniques such as high-energy x-ray diffraction microscopy (HEDM), computed micro-tomography (μ-CT), and coherent x-ray diffraction imaging (CXDI), makes data registration and analysis even more challenging, as multiple length and time scale information from different techniques must be combined to gain physical insight into materials behavior. Current data analysis tools are still in their infancy, resulting in a significant amount of time and resources spent on manual processing with brute force and inefficient, home-brew scripts. Moreover, this big data problem will only worsen with a growing user base. Increasing data collection rates with 4th generation light sources (APS upgrade, LCLS-II repetition rate of 2 MHz compared to 120 Hz at LCLS, EuXFEL 3000 pulses/shot at 10 Hz, etc.) are creating an urgent need for the development of efficient, fast, and user-friendly (as little as possible user intervention during reconstruction) software, which has the potential to change how experiments and data mining are performed in the field of 3D materials science.

The main topics of this workshop will be:

- Identify and explore the range of datasets that are currently being produced from experiments at various light sources to solve materials science problems.
- Discuss the latest developments in advanced data analysis tools.
- Encourage collaborations between experimentalists, modelers, and data scientists across national labs, academia, and industry.

The overall workshop goal is to improve information extraction capability from high-dimensional data and design a real-time feedback framework for driving experiments.

8:30–8:40	Reeju Pokharel (Los Alamos National Laboratory) *Opening Remarks*
8:40–9:30	Charles A. Bouman (Purdue University) *Statistical Approaches to High-quality 3-D Tomographic Reconstruction from Sparse Views*
9:30–10:20	Edwin Fohtung (New Mexico State University/Los Alamos National Laboratory) *Big Data Requirements in Tracking Vortex Dynamics in a Single Ferroic Nanoparticle*
10:20–10:40	Break/Workshop Picture
10:40–11:30	Kevin Yager (Brookhaven National Laboratory) *Towards an Autonomous X-ray Scattering Beamline*
11:30–12:20	Shiu Fai Frankie Li (DITTO Technologies, Inc.) *Reconstructing and Analyzing 3D Multi-view Geometric Data, from Material Science to Computer Vision*
12:20–1:30	Lunch

1:30–2:20	Stephen R. Niezgoda (Ohio State University) *Does Materials Science Have a Big Data Problem or Something Much Worse*
2:20–3:00	Hemant Sharma (Argonne National Laboratory) *Solving Big Data and Big Computer Problems in X-ray Microscopy*
3:00–3:20	Break
3:20–4:10	Jan Ilavsky and Peter R. Jemian (Argonne National Laboratory) *Enabling World-leading Collaborative Science Using SAXS at Light Sources, the Role of Common Data Analysis Tools and the NeXus NXcanSAS Data Format for SAXS and SANS*
4:10–4:50	Sven C. Vogel (Los Alamos National Laboratory) *Real-time Adaptive Acceleration of Dynamic Experimental Science*
4:50–5:00	Turab Lookman (Los Alamos National Laboratory) *Concluding Remarks*

WK-2

Big Data Requirements in Tracking Vortex Dynamics in a Single Ferroic Nanoparticle

Dmitry Karpov[1], Ross Harder[2], Lookman Turab[3], and Edwin Fohtung[1,3]

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Three-dimensional (3D) image reconstruction using Bragg coherent diffraction imaging (BCDI) has recently opened new vistas in understanding of fundamental mechanisms of condensed matter physics and materials science. In Bragg coherent diffraction, when a spatially coherent beam of x-rays illuminates a material, so that scattering from all crystal extremities interfere, the diffraction patterns collected contain enough information to be inverted to real space images. We shall discuss the role of big data in BCDI experiments from 3rd and 4th generation light sources in tracking a single vortex within a ferroelectric nanocrystal under external electric field. We demonstrate improved success rate (computation time, cost function and convergence) in reconstructing real space images of oxide nanostructures aided by *ab initio* computational methods.

This work was supported by the Air Force Office of Scientific Research (AFOSR) under Award No. FA9550-14-1-0363. (Program Manager: Dr. Ali Sayir). Edwin Fohtung also acknowledges support, in part from the LANSCE Professorship sponsored by the National Security Education Center at Los Alamos National Laboratory under Subcontract No. 257827.

WK-2

Towards an Autonomous X-ray Scattering Beamline

Kevin G. Yager

Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973

This talk will discuss preliminary work in building an autonomous x-ray scattering beamline, wherein sample handling, data analysis, and experimental decision-making are all automated. In particular, machine-learning methods are being investigated as a means of automatically analyzing, clustering, and tagging x-ray scattering images. The use of machine vision and deep learning neural networks methods will be discussed, including how these can be adapted to scientific problems.

Research at Center for Functional Nanomaterials and National Synchrotron Light Source II, Brookhaven National Laboratory, is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012704.

WK-2

Reconstructing and Analyzing 3D Multi-view Geometric Data, from Material Science to Computer Vision

S.F. Li

DITTO Technologies, Inc.

Non-destructive 3D measurements, structure from motion (SfM), and analysis-by-synthesis all fundamentally comes from the same class of multi-view geometrical inverse problems. Their applications range from 3D model reconstruction, microstructure mapping, 3D facial recognition, to even glasses fitting in e-commerce applications. Solution methods ranged widely from non-linear robust fitting (e.g., bundle adjustment) to stratified Monte Carlo sampling method. The resulting dataset from are often high dimensional and sparse in

nature, making analysis extremely problem dependent. In this talk, I'll discuss some of the dimensional reduction and robustification techniques common in volumetric mapping of polycrystalline materials and 3D reconstructions of human faces.

WK-2

Does Materials Science Have a Big Data Problem or Something Much Worse

Stephen R. Niezgoda[1,2], Mengfei Yuan[1], and Nicholas Galbincea[1]

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It is commonly stated that materials science is undergoing a transformation from a data-limited to data-driven field, and we are entering the big-data age of materials science. However, while individual materials datasets can be very large (i.e., 4-D diffractions) the data is still sparse in the sense that often we only have a very limited number of observations. Or while the number of points in the dataset are large the number of features captured may be small (number of grains in near-field HEDM). This is the opposite of traditional big data problems, where the datasets are lower dimensional but contains hundreds of thousands or millions of observations, and big data analysis approaches common in other fields break down when applied to materials science. This talk will focus approaches to make meaningful statistical estimates from sparsely sampled systems, including crystallographic texture estimation and spatial statistics. Also highlighted will be methods for comparing datasets and describing how different or similar different observations of materials structures. As a final point, the description or quantification of materials variance and how to include this variance in formal uncertainty quantification for performance modeling and design.

WK-2

Solving Big Data and Big Computer Problems in X-ray Microscopy

Hemant Sharma

Argonne National Laboratory, Argonne, IL 60439

At Sector 1 of the Advanced Photon Source, ~1TB of data per day is generated with compute times in the order of ~10^5 CPU h/day. With developments in x-ray beam, detectors, and optics, these are expected to increase by three orders of magnitude. This talk will focus on the MIDAS package for reduction of high-energy diffraction microscopy data, which employs novel data compression, transfer, and analysis techniques to provide real time feedback to experiments.

WK-2

Enabling World-leading Collaborative Science Using SAXS at Light Sources, the Role of Common Data Analysis Tools and the NeXus NXcanSAS Data Format for SAXS and SANS

Jan Ilavsky and Pete Jemian

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

Small-angle scattering community is one of the larger communities of synchrotron users and extends to even larger number of desktop small-angle scattering community and to smaller, but important, small-angle neutron community. The size of the community and wide range of instrumentation designs and capabilities pose highly variable challenges in data handling. This was recognized by users utilizing combination of instruments and facilities as barrier to their productivity relatively long time ago. Similar challenge was seen in the lack of cross-facility/instrument applicable data reduction and analysis software for users. Since 1998, canSAS organization ("Collective Aid for Nomadic Small-Angle Scatterers") has been working to establish common standards in production of data – instrumentation, reproducibility and reliability of data, data formats for raw and reduced data, and software for data reduction and analysis. Members of canSAS are mostly facility staff and well-established users of numerous facilities. Recent achievement of the group is the NXcanSAS standard for reduced SAXS and SANS data, part of larger NEXUS effort. This talk will present short historical summary and discuss the challenges, achieved results, and future plans.

This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

WK-2

Real-time Adaptive Acceleration of Dynamic Experimental Science

Sven C. Vogel[1], Cindy Bolme[2], and James P. Ahrens[3]

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Analyzing and extracting scientific knowledge from modern science experiments has become the rate-limiting step in the scientific process. We propose to accelerate knowledge-discovery from experimental scientific facilities by combining computer and statistical science to produce an adaptive methodology and toolset that will

analyze data and augment a scientist's decision-making so that the scientist can optimize experiments in real time. We will develop this capability in the context of dynamic compression experiments, an area of core mission importance for LANL and an area that is currently in the midst of substantial increases in the rate of data generation. This project will result in a data science focused information science and technology (IS&T) toolset that is optimized for and will revolutionize dynamic compression science experiments using x-ray user facilities. Furthermore, this work will produce many reusable components that can be applied to multiple scientific domains. When achieved, our approach will allow scientists to elevate their focus above the mundane tasks required for experiment completion to that of making strategic scientific decisions.

Funding from LANL LDRD-20170029DR is greatfully acknowledged. This abstract was approved for unlimited release as LA-UR-16-25299.

Tuesday, May 9

CNM Workshop 3
Transient Spectroscopy and Non-equilibrium Dynamics of 2D Materials

Location: Bldg. 401, Room A1100

Organizers: Gary Wiederrecht (CNM) and Goran Karapetrov (Drexel University and MSD)

The unique optical and electronic properties of 2D materials enable important new opportunities in applications such as energy and heat transport, quantum information, sensing, and energy conversion. These opportunities continue to grow with the rapidly expanding number of elements and compounds that form single-crystal 2D materials and fabrication of hybrid 2D layered systems. The relatively high optical extinction of even a single layer of many of the materials (particularly transition metal dichalcogenides such as MoS2 or WSe2) enables many of these opportunities, as well as the optical characterization of important phenomena such as correlated electron behavior. Time-resolved absorption and emission spectroscopies such as transient absorption spectroscopy and time-correlated single photon counting, are particularly valuable for establishing the dynamics and spectral signatures of the collective responses.

Transient spectroscopy also opens a new window of opportunities to study coexisting phases in solid state materials as well as explore the mechanisms of phase transitions (both thermally induced and quantum). Many systems undergo phase transitions that take place in conditions out of equilibrium, guiding the system into a metastable state. With advent of new nanoscience tools one could engineer the material in order to control these states and arrive to the desired functionality of the system. Layered 2D materials offer a rich set of correlated electron phases that can be utilized for this purpose and lead to breakthroughs in applications. Thus exploring the non-equilibrium dynamics in these materials could lead to new states of matter containing metastable states of interest.

8:30–8:45	Welcome and Introductory Remarks
8:45–9:25	Richard Schaller (Argonne National Laboratory) *Energy and Electron Transfer Processes in 2D Semiconductor Nanoplatelets*
9:25–10:05	Aaron Lindenberg (Stanford University, SLAC) *Ultrafast Structural Dynamics in Monolayer and Multilayer 2D TMDC Materials*
10:05–10:35	Break
10:35–11:15	Xiaodong Xu (University of Washington) *Monolayer Magnets*
11:15–11:55	Ken Kuno (University of Notre Dame) *Single-layer Graphene Oxide Photoreduction Explained*
12:00–1:30	Lunch
1:30–2:10	Xiaoyang Zhu (Columbia University) *Charge Transfer Excitons at van der Waals Interfaces*
2:10–2:50	Tong Zhu (Purdue University) *Charge Transfer Excitons at 2D Inorganic-organic Interfaces*
2:50–3:20	Break
3:20–4:00	Elaine Li (University of Texas at Austin) *Valley Dynamics in Monolayer Transition Metal Dichalcogenides*
4:00–4:40	Michael Man (Okinawa Institute of Science & Technology, Japan) *Imaging Electron Motions in 2D Semiconductor Heterojunctions*
4:40–5:00	Wrap-up and Concluding Remarks

WK-3

Energy and Electron Transfer Processes in 2D Semiconductor Nanoplatelets

Benjamin T. Diroll[1], Clare E. Rowland[2], Peijun Guo[1], Igor Fedin[3], Pierre Darancet[1], Stephen Gray[1], Dmitri V. Talapin[1,3], and Richard D. Schaller[1,2]

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Colloidally prepared, two-dimensional semiconductor nanostructures offer advantages for numerous classes of application including energy capture and conversion, detection, and biolabeling. We perform photophysical characterizations of these systems to obtain thorough understanding of fundamental desired and undesired processes of energy and heat transport and interconversion. I will present studies using time-resolved optical methods such as absorption and emission as functions of sample temperature and photon energy that aim to arrive at insights regarding energy transfer, electron transfer, and electron-phonon and phonon-phonon scattering events in these systems.

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.

WK-3

Ultrafast Structural Dynamics in Monolayer and Multilayer 2D TMDC Materials

Aaron M. Lindenberg

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

Novel characterization techniques developed over the past two decades have revolutionized our ability to visualize the microscopic, atomic-scale processes that determine the functional properties of materials. The overarching challenge here is that the relevant time-scales and length-scales for these processes are typically 10^{-13} seconds (100 femtoseconds) and 10^{-10} m (1 Å) such that our view of how a material functions is often blurred out in time or in space. In this talk, I will describe recent experiments using femtosecond x-ray, electron, and optical pulses as a means of probing and manipulating the optoelectronic and structural properties of materials on ultrafast time-scales, as they transform and *in situ*. In this talk, I will focus in particular on two main topics: 1) I will discuss experiments probing dynamic deformations of multilayer transition metal dichalcogenide films on femtosecond and picosecond time-scales. These studies reveal a surprising light-induced nonlinear modulation in the interlayer bonding which can be viewed as a modulation in the Casimir/van der Waals interaction between quasi-2D layers. 2) I will discuss new experiments using femtosecond electron diffraction to probe doped MoWTe2 alloys, investigating their dynamical response in both 2H and 1T' phases.

WK-3

Monolayer Magnets

Xiaodong Xu

Department of Physics, Department of Materials Science and Engineering, University of Washington, Seattle, WA 98105

Since the discovery of graphene, the family of two-dimensional (2D) materials has grown to encompass a broad range of electronic properties. However, until recently 2D crystals with intrinsic magnetism were still lacking. Such crystals would enable new ways to study 2D magnetism by harnessing the unique features of atomically-thin materials, such as electrical control for magnetoelectronics and van der Waals engineering for novel interface phenomena. In this talk, I will describe our recent magneto-optical spectroscopy experiments on van der Waals magnets, chromium(III) iodide CrI_3. I will first demonstrate the existence of isolated monolayer semiconductor with intrinsic Ising ferromagnetism. I will then show the layer number-dependent magnetic phases. The magnetic ground state evolves from being ferromagnetic in a monolayer, to antiferromagnetic in a bilayer, and back to ferromagnetic in a trilayer and thin bulk. Lastly, I will discuss the emerging spin phenomena in monolayer WSe_2/CrI_3 ferromagnetic semiconductor heterostructures, including ferromagnetic control of valley pseudospin in WSe_2 via large magnetic exchange field, and optical analog of giant magnetoresistance effect.

WK-3

Single-layer Graphene Oxide Photoreduction Explained

Masaru Kuno

University of Notre Dame, Notre Dame, IN 46556

Single layer graphene oxide (GO) is an important precursor in the production of chemically-derived graphene. During reduction, GO's electrical conductivity and band gap change gradually. Doping and chemical functionalization are also possible, illustrating GO's immense potential in creating functional devices through control of its local hybridization. Here we show that laser irradiation controllably reduces individual single-layer GO sheets. The reaction can be followed in real time through dramatic enhancements of GO's photoluminescence efficiency along with large spectral redshifts. Both are captured through movies of its reduction kinetics. Rate maps

illustrate sizable spatial and temporal heterogeneities in sp^2 domain growth and reveal how reduction "flows" across GO sheets. The observed heterogeneous reduction kinetics provides mechanistic insight into GO's conversion to chemically-derived graphene and highlights opportunities for overcoming its dynamic, chemical disorder.

WK-3

Charge Transfer Excitons at van der Waals Interfaces

X.-Y. Zhu
Columbia University, New York, NY 10027

The van der Waals interfaces of molecular donor/acceptor or graphene-like two-dimensional (2D) semiconductors are central to concepts and emerging technologies of light-electricity inter-conversion. Examples include, among others, solar cells, photo-detectors, and light emitting diodes. A salient feature in both types of van der Waals interfaces is the poorly screened Coulomb potential that can give rise to bound electron-hole pairs across the interface (i.e., charge transfer (CT) or inter-layer excitons). Here we address common features of CT excitons at both types of interfaces. We emphasize the competition between localization and delocalization in ensuring efficient charge separation. At the molecular donor/acceptor interface, electronic delocalization in real space can dictate charge carrier separation. In contrast, at the 2D semiconductor heterojunction, delocalization in momentum space due to strong exciton binding may assist in parallel momentum conservation in CT exciton formation.

WK-3

Charge Transfer Excitons at 2D Inorganic-organic Interfaces

Tong Zhu, Long Yuan, Yan Zhao, Jianguo Mei, and Libai Huang
Department of Chemistry, Purdue University, West Lafayette, IN 47907

Fabrication of van der Waals (vdW) heterostructures based on two-dimensional transition metal dichalcogenides (2D-TMDs) has proven to be effective for the applications in optoelectronic devices, photovoltaics and light emitting devices. Like these 2D building blocks, molecular and polymeric organic solids are also free of dangling bonds, offering potential to be integrated with 2D materials to form vdW heterostructures. 2D inorganic-organic vdW heterostructure which involves a 2D material and layers of small organic molecular thin film offer flexibility of manipulating interlayer excitonic states because the momentum matching requirement could be relieved. The intriguing yet less exploited questions for 2D inorganic-organic vdW heterostructures include the optoelectronic behaviors such as charge transfer (CT) and the nature of interfacial states following CT. In this study, a type II heterojunction is designed by interfacing monolayer WS_2 with tetracene to fabricate 2D inorganic-organic vdW heterostructure with the conduction band minimum lying in tetracene and valence band maximum resides on WS_2. The emission of long-lived, spatially indirect CT excitons is directly observed at the heterostructure interface. Electron and hole transfer are found to occur on a sub-picosecond time scale. Transient Absorption Microscopy technique is employed to study the transport of interfacial CT exciton. Understanding the nature and behavior of this interfacial CT state in such 2D inorganic-organic VdW heterostructures offers considerable potential to enable novel devices for optoelectronics and light harvesting.

WK-3

Valley Dynamics in Monolayer Transition Metal Dichalcogenides

Kai Hao[1], Akshay Singh[1], Fengcheng Wu[1], Philipp Nagler[2], Kha Tran[1], Christian Schüller[2], Tobias Korn[2], Dennis Pleskot[3], Nathaniel M. Gabor[3], Sophia Helmrich[4], Nina Owschimikow[4], Ulrike Woggon[4], Allan H. MacDonald[1], Galan Moody[5], and Xiaoqin Li[1]

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The emerging field of valleytronics aims to exploit the valley pseudospin of electrons residing near Bloch band extrema as an information carrier. Using ultrafast nonlinear optical spectroscopy methods such as two-dimensional Fourier transform spectroscopy and two-color pump/probe, we investigate the ultrafast valley dynamics of excitons, trions, and valley pseudo-spins in monolayer $MoSe_2$ and WSe_2.

If one present valley degree of freedom using a Bloch vector, the valley polarization and valley coherence refers the longitudinal and transverse relaxation time, respectively. Valley polarization time describes the classical information storage time while valley coherence is relevant for optically and coherently manipulating such information. In $MoSe_2$, we found that valley dynamics associated with excitons valley polarization is lost after ~1 ps while valley decoherence occurs within ~100 fs due to electron-hole exchange interaction. Interestingly, trion valley dynamics can be significantly extended. In WSe_2, we observe no decay of a near-unity valley polarization associated with

the intra-valley trions during ~25 ps, while the valley polarization of the inter-valley trions exhibits a fast decay of ~4 ps. Furthermore, we show that resonant excitation is a prerequisite for observing the long-lived valley polarization associated with the intra-valley trion.

WK-3
Imaging Electron Motions in 2D Semiconductor Heterojunctions

Michael K.L. Man

Femtosecond Spectroscopy Unit, Okinawa Institute of Science and Technology Graduate University, 904-0495 Japan

Technological progress since the late 20th century has centered on semiconductor devices, such as transistors, diodes, and solar cells. At the heart of these devices, is the internal motion of electrons through semiconductor materials due to applied electric fields or by the excitation of photocarriers. Imaging the motion of these electrons would provide unprecedented insight into this important phenomenon, but requires high spatial and temporal resolution. Current studies of electron dynamics in semiconductors are generally limited by the spatial resolution of optical probes, or by the temporal resolution of electronic probes. In this talk, we combine femtosecond pump-probe techniques with spectroscopic photoemission electron microscopy to image the motion of photoexcited electrons from high-energy to low-energy states in a type-II 2D InSe/GaAs heterostructure [1]. At the instant of photoexcitation, energy-resolved photoelectron images reveal a highly non-equilibrium distribution of photocarriers in space and energy. Thereafter, in response to the out-of-equilibrium photocarriers, we observe the spatial redistribution of charges, thus forming internal electric fields, bending the semiconductor bands, and finally impeding further charge transfer. By assembling images taken at different time-delays, we make a movie lasting a few tens of picoseconds of the electron transfer process in the photoexcited type-II heterostructure—a fundamental phenomenon in semiconductor devices like solar cells. Quantitative analysis and theoretical modeling of spatial variations in the video provide insight into future solar cells, electron dynamics in 2D materials, and other semiconductor devices.

[1] Michael K.L. Man et al. (2017). *Nature Nanotechnology* **12**: 36–40.

Tuesday, May 9

CNM Workshop 4
Machine Learning and Data Science in Materials Modeling, Imaging and Applications

Location: APCF Auditorium

Organizers: Subramanian Sankaranarayanan (CNM), Mathew Cherukara (XSD), Badri Narayanan (MSD), and Tom Peterka (MCS)

The advent of big data analytics in computing science community along with the reduction in computing and memory costs over the last few years have brought powerful machine learning techniques to the forefront; such methods are now routinely used in business, transactional and social media applications. These machine learning methods hold tremendous promise to advance various facets nanoscale materials research, particularly via successfully combining them with first-principles physics, atomic simulations and experimental characterization. This workshop aims to facilitate and strengthen the synergistic approach to experimental and theoretical works of experts from academia, national labs and industries to discuss the latest developments in machine learning tools and techniques to develop new methods that enable (a) accelerated discovery, characterization and (b) design of hybrid materials and novel device architectures for a range of different emerging energy applications and technologies.

The Center for Nanoscale Materials and Advanced Photon Source at Argonne have expertise and state-of-the-art facilities in the synthesis, characterization and theoretical modeling of nanoscale materials. There are several strong research programs focused on fundamental studies of material behavior across different length scales, which employ these world-class user facilities. Such programs will greatly benefit from a platform to discuss the successes of various machine learning strategies, algorithms, and their applications to materials synthesis/design/characterization with leading experts from various material science and applied math disciplines.

The dramatic improvements in computational efficiencies, availability and cost have resulted in increased impact of informatics in today's science, technology and business. This workshop is expected to provide an opportunity for academics, R&D scientists at industry, and students to exchange ideas, think creatively about new avenues for collaborations with user facilities at Argonne and to work on developing and applying machine learning and data science techniques into development and implementation of new frontiers in nanotechnology.

Workshop topics:

- Machine learning and data science in materials modeling with emphasis on bridging modeling techniques with disparate length and time scales.
- Machine learning algorithms for integrated imaging of nanoscale materials
- Machine learning and data mining for property prediction and inverse design of materials
- Data driven discovery and design of hybrid materials for energy applications

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8:30–8:40	Subramanian KRS Sankaranarayanan (Argonne National Laboratory) *Introductory Remarks*
8:40–9:20	Aidan Thompson (Sandia National Laboratory) *Automated Generation of High-accuracy Interatomic Potentials Using Quantum Data*
9:20–10:00	Andrew Ferguson (University of Illinois, Urbana-Champaign) *Nonlinear Machine Learning in Soft Materials Engineering and Design*
10:00–10:20	Break
10:20–11:00	Charles A. Bouman (Purdue University) *Integrating Physical and Learned Models in Imaging Science*

11:00–11:40	Youssef Nashed (Northwestern University) *Learning Ptychographic Reconstruction with Backpropagation*
11:40–1:00	Lunch
1:00–1:40	Aggelos Katsaggelos (Northwestern University) *Machine Learning Approaches for Solving Inverse Problems*
1:40–2:20	Rafael Jaramillo (Massachusetts Institute of Technology) *Why and How to Continuously Publish Experimental Workflow in Materials Science*
2:20–2:40	Break
2:40–3:20	James Rondinelli (Northwestern University) *Learning from Data to Design Functional Noncentrosymmetric Complex Oxides*
3:20–4:00	Turab Lookman (Los Alamos National Laboratory) *From Data to Materials Discovery: Challenges in Learning and Design*
4:00–4:30	Closing Remarks and Discussion

WK-4

Automated Generation of High-accuracy Interatomic Potentials Using Quantum Data

Aidan Thompson

Center for Computing Research, Sandia National Laboratories, Albuquerque, NM 87123

Molecular dynamics simulation is a powerful computational method for bridging between macroscopic continuum models and quantum models treating a few hundred atoms, but it is limited by the accuracy of the interatomic potential. Sound physical and chemical understanding have led to good potentials for certain systems, but it is difficult to extend them to new materials and properties.

The solution is obvious but challenging: develop more complex potentials that reproduce large quantum datasets. The growing availability of large data sets has made it possible to use automated machine-learning approaches for interatomic potential development. In the SNAP approach, the interatomic potential depends on a very general set of atomic neighborhood descriptors, based on the bispectrum components of the density projected onto the surface of the unit 3-sphere. Previously, this approach was demonstrated for tantalum, reproducing the screw dislocation Peierls barrier. In this talk, it will be shown that the SNAP method is capable of reproducing a wide range of energy landscapes relevant to diverse material science applications: i) point defects in indium phosphide, ii) stability of tungsten surfaces at high temperatures, and iii) formation of intrinsic defects in uranium.

WK-4

Nonlinear Machine Learning in Soft Materials Engineering and Design

Andrew Ferguson

Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Champaign, IL 61820

The inherently many-body nature of molecular folding and colloidal self-assembly makes it challenging to identify the underlying collective mechanisms and pathways governing system behavior, and has hindered rational design of soft materials with desired structure and function. Fundamentally, there exists a predictive gulf between the architecture and chemistry of individual molecules or colloids and the collective many-body thermodynamics and kinetics. Integrating machine learning techniques with statistical thermodynamics provides a means to bridge this divide and identify emergent folding pathways and self-assembly mechanisms from computer simulations or experimental particle tracking data. I will discuss our applications of this framework that illustrate the value of nonlinear machine learning in understanding and engineering soft materials: the non-equilibrium self-assembly of Janus colloids into pinwheels, clusters, and archipelagos; engineering reconfigurable “digital colloids” as a novel high-density information storage substrate; probing hierarchically self-assembling π-conjugated asphaltenes in crude oil; and determining macromolecular folding funnels from measurements of single experimental observables. I will close with an outlook and some personal perspectives on the future of machine learning in soft materials engineering.

WK-4

Integrating Physical and Learned Models in Imaging Science

Charles A. Bouman
Purdue University, West Lafayette, IN 47907

Model-based imaging methods have been demonstrated to offer enormous potential in solving difficult inverse problems with sparse or noisy data. The key to their success has been the ability to model both subtle aspects of imaging sensors (i.e., the forward model) along with accurate characteristics of the images being formed (i.e., the prior model). In particular, model-based methods can incorporate accurate well-established forward models of complex sensing systems such as x-ray CT systems, transmission electron microscopes, and optical sensors. However, it is less clear how model-based methods can leverage the recent advances in machine learning, particularly with large data sets.

In this talk, we discuss some of these challenges and present some ideas and results that demonstrate how machine learning methods can be combined with model-based imaging to achieve unprecedented results. In particular, we present some recent results in three areas: statistical learning for dynamic sampling (SLADS), plug-and-play priors for super-resolution EM imaging, and plug-and-play priors for adaptive optics phase retrieval. A key thesis of our talk is that machine learning methods can be successfully merged with traditional analytical models, thus exploiting the strengths of both approaches.

WK-4

Learning Ptychographic Reconstruction with Backpropagation

Youssef Nashed
Northwestern University, Evanston, IL 60208

Synchrotron radiation light source facilities are leading the way to ultrahigh resolution x-ray imaging. High resolution imaging is essential to understanding the fundamental structure and interaction of materials at the smallest length scale possible. Diffraction based methods achieve nanoscale imaging by replacing traditional objective lenses by pixelated area detectors and computational image reconstruction. Among these methods, ptychography is quickly becoming the standard for sub-30 nanometer imaging of extended samples, but at the expense of increasingly high data rates and volumes.

In this talk, I will present our work for solving the ptychographic image reconstruction problem through fitting a physics based model to the measured data. The model parameters are learned in a similar manner to deep neural networks, utilizing the backpropagation method as implemented in Google's TensorFlow package. I will also show results from simulated and real data acquired at the Advanced Photon Source (APS), and reconstructed using up to 192 GPUs on Argonne Leadership Computing Facility (ALCF) resources.

WK-4

Machine Learning Approaches for Solving Inverse Problems

Aggelos K. Katsaggelos
Department of EECS, Northwestern University, Evanston, IL 60208

In this talk, I will present some of our recent results in solving inverse problems, such as, the image recovery, super-resolution, and compressive sensing problems. I will present both analytical and learning approaches for solving such problems. More specifically, I will first present hierarchical Bayesian approaches for blind deconvolution and image super-resolution. I will then present dictionary approaches for solving the video super-resolution problem as well as the problem of fusing visible and x-ray fluorescence images. Finally, I will present some of our results using deep neural networks for fusion and temporal compressive sampling. I will conclude the talk by discussing the impact of learning approaches in solving inverse problems.

WK-4

Why and How to Continuously Publish Experimental Workflow in Materials Science

Rafael Jaramillo
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

The body of published literature contains only a small subset of existing experimental results. To draw a common analogy, publications are only the tip of the iceberg and are based on a large quantity of unseen results. Publishing the complete experimental record—making it discoverable, accessible, and persistent—would constitute a substantial challenge, but the benefits would be tremendous. Complete publishing would create an expandable resource of data for use by multiple communities, such as researchers developing machine-learning approaches to predictive computational materials science.

I will describe a vision for continuous publishing in experimental materials science. Our approach is grounded in the central role of workflow tracking, both for organizing day-to-day research and for facilitating sharing. We envision a tiered, flexible ecosystem of software that divides labor according to existing institutional structures, and avoids recreating existing cyberinfrastructure. We would establish libraries as an essential partner, allowing researchers to innovate on data collection while

maintaining high confidence in data integrity and in the implementation of permissions. I will highlight the many existing resources that could be leveraged to realize this vision, and describe ongoing efforts such as a workflow tracker that is being evaluated by several research groups at MIT.

WK-4

Learning from Data to Design Functional Noncentrosymmetric Complex Oxides

James M. Rondinelli[1], Prasanna V. Balachandran[2], Joshua Young[3], and Turab Lookman[2]

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[3] Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104

Accelerating the search for functional materials is a challenging problem. Here we develop an informatics-guided *ab initio* approach to accelerate the design and discovery of noncentrosymmetric (NCS) materials. The workflow integrates group theory, informatics and density-functional theory to uncover design guidelines for predicting noncentrosymmetric compounds, which we apply to layered Ruddlesden-Popper oxides. Group theory identifies how configurations of oxygen octahedral rotation patterns, ordered cation arrangements and their interplay break inversion symmetry, while informatics tools learn from available data to select candidate compositions that fulfil the group-theoretical postulates. Our key outcome is the identification of 242 compositions after screening ~3,200 that show potential for NCS structures, a 25-fold increase in the projected number of known Ruddlesden-Popper oxides without inversion symmetry. We validate our predictions for 19 compounds using phonon calculations, among which 17 have noncentrosymmetric ground states including two potential multiferroics. Our approach enables rational design of materials with targeted crystal symmetries and functionalities.

P.V.B. and T.L. acknowledge funding support from the Los Alamos National Laboratory (LANL) LDRD No. 20140013DR on Materials Informatics and the Center for Nonlinear Studies (CNLS). J.M.R. and J.Y. were supported by NSF under grant nos. DMR-1454688 and DMR-1420620, respectively.

WK-4

From Data to Materials Discovery: Challenges in Learning and Design

Turab Lookman

Los Alamos National Laboratory, Los Alamos, NM 87545

Next generation experimental facilities will offer unprecedented access to understanding *in situ* bulk materials behavior and generate large amounts of data at higher rates than possible today. A key aspect is learning from the data. Needed are tools that will seamlessly integrate data with theory and inference in a codesign loop for prediction and understanding, including discovery of new materials. I will review initiatives, including our own, to address some of these challenges.

Tuesday, May 9

APS Symposium
Structure-based Drug Discovery: The Next 25 Years

Location: Bldg. 402, APS Lecture Hall

Organizers: Lisa Keefe (IMCA-CAT / Hauptman-Woodward Medical Research Institute)
Barry Finzel (University of Minnesota)

This symposium will bring together researchers in the pharmaceutical industry and experts in multiple aspects of structural biology to explore strategies that are effective for challenging projects and accelerating drug discovery.

Industry and academic researchers will showcase innovative drug discovery successes, highlight complementary and synchrotron-based techniques, and explore multi-faceted approaches to acquiring protein-ligand structural information.

Attendees will engage in open forum discussions to assess opportunities for incorporating emerging strategies into structural biology research programs.

Following the symposium, there will be a no-host dinner at the Argonne Guest House.

Session Chair:	**Anne Mulichak (IMCA-CAT / Hauptman-Woodward Medical Research Institute)**
8:30–8:40	Lisa Keefe (IMCA-CAT / Hauptman-Woodward Medical Research Institute) *IMCA-CAT: 25 Years of Shining a Light on Drug Discovery*
8:40–8:50	Vincent Stoll (AbbVie) *Why has the Pharmaceutical Industry Invested in IMCA for 25 Years?*
8:50–9:05	Suresh Sunderrajan (Science & Technology Partnerships and Outreach, Argonne National Laboratory) *Argonne and Industry: A Partnership Built on Science and Technology*
9:05–9:15	Stephen Streiffer (Advanced Photon Source, Argonne National Laboratory) *Welcome from the Advanced Photon Source*
9:15–10:00	Vadim Cherezov (University of Southern California) *Keynote – Toward Structure-based Drug Design for GPCRs Using Synchrotrons and XFELs*
10:00–10:15	Break
10:15–11:00	Clint Potter (New York Structural Biology Center and NanoImaging Services, Inc.) *Keynote – CryoEM from Academia to Industry*
11:00–11:30	Stephen Soisson (Merck Research Laboratories) *Structurally Enabling Membrane Proteins to Accelerate Drug Discovery*
11:30–12:00	Vincent Stoll (AbbVie) *Driving Innovation and Turning Failure to Success for Patients, the Bcl-2 Story*
12:00–1:15	Lunch
Session Chair:	**Kevin Battaile (IMCA-CAT / Hauptman-Woodward Medical Research Institute)**
1:15–1:45	Steven Sheriff (Bristol-Myers Squibb Research & Development) *Structure of the Kinase Domain of TGFβR2*
1:45–2:15	Richard Alexander (Janssen Pharmaceuticals) *Opportunities in Industrial Crystallography: Fragment Based Crystallography as a Screening Tool*

2:15–2:45	Matt Calabrese (Pfizer) *Flipping a New Switch on an Old Enzyme: AMPK Activators for Diabetic Nephropathy*
2:45–3:00	Break
3:00–3:30	Sarah L. Perry (University of Massachusetts Amherst) *Graphene Microfluidics for Room Temperature Crystallography*
3:30–4:00	Artem Evdokimov (HarkerBIO LLC) *Macromolecular Crystallization: The Old, The New, and The Inconvenient*
4:00–4:30	Clemens Schulze-Briese (DECTRIS Ltd.) *Pushing the Limits of Protein Crystallography with EIGER*
4:30–5:00	Srinivas Chakravarthy (BioCAT / Illinois Institute of Technology) *An Overview of the SAXS Program at the Biophysics Collaborative Access Team (BioCAT)*
5:00–5:05	Lisa Keefe (IMCA-CAT / Hauptman-Woodward Medical Research Institute) *Concluding Remarks*

SYMP

Toward Structure-based Drug Design for GPCRs Using Synchrotrons and XFELs

Vadim Cherezov
Department of Chemistry, Bridge Institute, University of Southern California, Los Angeles, CA 90089

G protein-coupled receptors act as the cellular gatekeepers, regulating majority of physiological processes in the human body, and thus represent primary therapeutic drug targets. Rational Structure-based Drug Design studies rely heavily on the availability of co-crystal x-ray structures to characterize the ligand binding site and help optimize ligand design. Tens to hundreds of ligand-bound structures are normally determined in the course of a drug design program prior to clinical trials. While SBDD represents a routine protocol in case of soluble protein targets, such as kinases and proteases, the application of this approach to membrane proteins based on experimentally determined structures, particularly of GPCRs, has been very limited. The primary challenge in attempting the structure determination of GPCRs is the inherent flexibility of these receptors essential for their activity given their physiological role of signal transduction. In this talk, I will outline recent developments toward enabling SBDD for GPCRs using third generation synchrotron sources and x-ray free electron lasers.

This work is funded in parts by the National Institutes of Health grants R01 GM108635, P01 DA035764 and by the GPCR Consortium.

SYMP

CryoEM from Academia to Industry

Clint Potter
New York Structural Biology Center and NanoImaging Services, Inc., New York, NY 10027

CryoEM methodology has seen dramatic technical advances over the past 5 years and 3 to 4 Å resolution is now routinely being achieved. This “resolution revolution” has been largely driven by advances in camera technology and computational methods. The field has rapidly moved from “blobology” to high resolution structure determination of important targets. There is now a growing interest from the pharmaceutical industry in adopting these methods and the expectations are high. This talk will provide an overview of the methodology, technical advances, current limitations and prospects of the technique.

SYMP

Structurally Enabling Membrane Proteins to Accelerate Drug Discovery

Stephen M. Soisson
Biochemical Engineering and Structure, Merck Research Laboratories

The use of x-ray crystallography to drive the structure-based design of small molecules has significantly impacted the drug discovery over the past 20 years. Unfortunately, this impact has been predominantly limited to the realm of drugs targeting soluble proteins or their sub-domains, while higher complexity targets, such as membrane proteins, have largely remained out of reach on the timescales required for drug discovery. Relatively recent advances in the field’s abilities to produce larger quantities of membrane proteins, coupled with concomitant advances in crystallization technologies and high intensity x-ray sources, are increasing our optimism

that membrane proteins can be structurally enabled on a fast enough time-scale it impact drug discovery. This talk will cover some of the challenges to membrane protein structural biology and some of the approaches that our group has taken to overcome these difficulties. Several recent examples of membrane protein structures with small molecules bound will help illustrate the opportunities that such structural information can provide to drug discovery efforts. Possible future directions for membrane protein work will be discussed, including the critical role that synchrotrons and next generation sources will play moving forward.

SYMP

Driving Innovation and Turning Failure to Success for Patients, the Bcl-2 Story

Vincent Stoll
AbbVie

In this presentation you will see how data collected at IMCA were used to drive innovation on an unprecedented approach to drug discovery by blocking a protein/protein interaction with a small molecule drug. The main focus will be on how the dose limiting toxicities of our early clinical candidate, were rapidly overcome through structure-based drug design. From a very novel and unexpected finding in a crystal structure of Bcl-2 in complex with an inhibitor we turned a clinical candidate that was limited, into a break through therapy for cancer patients. This work highlights the critical importance of the work we do at IMCA and how it can directly impact patients.

SYMP

Structure of the Kinase Domain of TGFβR2

Steven Sheriff
Bristol-Myers Squibb Research & Development, New York, NY 10154

The cytokine TGF-β consists of three isoforms that act pleiotropically on epithelial, endothelial, and hematopoietic cells to promote hemostasis, immunomodulation, extracellular matrix deposition, and tumor suppression through differentiation, activation, and regulation of proliferation. TGF-β becomes a tumor promoter when cancer cells become insensitive to TGF-β growth suppression and overexpress TGF-β, which creates a microenvironment where tumor cells can grow unchecked, but surrounding and immune cells are inhibited. TGF-β signals through two transmembrane serine/threonine kinase receptors, TGFβR1 and TGFβR2. While the structure of the kinase domain of TGFβR1 has been known for over 15 years, to date no structure of the TGFβR2 kinase domain has been reported. The TGFβR2 kinase domain is extremely soluble and we found that a surface entropy reduction strategy was necessary to obtain crystals. A construct that yielded crystals that diffract to high resolution (<2 Å) contains mutations to Ala of 6 charged residues in a patch on the surface of the C-lobe of the TGFβR2 kinase domain. The apo structures and structures of staurosporine and another compound binding are compared for TGFβR1 kinase domain, TGFβR2 kinase domain, and a chimeric TGFβR1 kinase domain, where 7 active site residues have been mutated to their TGFβR2 equivalents.

SYMP

Flipping a New Switch on an Old Enzyme: AMPK Activators for Diabetic Nephropathy

Matthew Calabrese
Pfizer WRD, New York, NY 10017

AMP activated protein kinase (AMPK) is a master metabolic regulator with impact on a range of catabolic and anabolic processes. As such, modulating AMPK has emerged as an attractive approach toward disease intervention. Here, we describe the identification and optimization of a novel allosteric activator of AMPK.

SYMP

Graphene Microfluidics for Room Temperature Crystallography

Sarah L. Perry
Department of Chemical Engineering, University of Massachusetts Amherst, Amherst, MA 01003

The advent of serial crystallography has opened up new possibilities for the collection of protein structural information at room temperature. However, the advantages of room temperature data are paired with increased potential for radiation damage and the likelihood of needing to merge data from a number of crystals. We have developed a graphene-based fixed-target platform for efficiently mounting a large number of crystals for room temperature analysis. The use of graphene facilitates the collection of high quality x-ray diffraction data with excellent signal-to-noise while also minimizing water loss from the device. Expansion of this technology has the potential to enable the reproducible growth of a large number of crystals, ligand screening experiments, and dynamic structural studies of protein targets that have been resistant to single-crystal strategies. Furthermore, these technologies show strong promise to enable the room temperature collection of diffraction data from oxygen-sensitive proteins.

SYMP

Macromolecular Crystallization: The Old, The New, and The Inconvenient

Artem Evdokimov
HarkerBIO, LLC, Buffalo, NY 14203

Protein crystallography has earned its privileged position in the structural biologist's arsenal. Over the past several decades this powerful technology has become a mainstay method for the determination of macromolecular structure. The speed and success rate of protein structure determination received a massive boost from the developments in expression and purification of recombinant macromolecules and the meteoric advancements in data collection and structure determination. In contrast with the above, the progress made in practical improvement of protein crystallization is relatively sedate and the field of protein crystallization is laden with challenges and opportunities, some of which are the subject of this presentation.

SYMP

Pushing the Limits of Macromolecular Crystallography with EIGER

Clemens Schulze-Briese
DECTRIS, Ltd., 5405 Baden-Dättwil, Switzerland

Drug development relies on structural information about the biological target to model ligands and optimize interactions. To obtain best x-ray diffraction data, DECTRIS has developed the EIGER family of Hybrid Photon Counting pixel detectors to be effectively noise-free and remarkably fast. Direct detection of single x-ray photons in 75 µm pixels ensures highly accurate data.

Experiments at the Swiss Light Source have demonstrated that EIGER X series detectors record data of higher quality than does PILATUS3, the previous gold standard for data quality [1]. The key to the higher quality lies in the smaller pixel size, which increases the signal to noise of small reflections, and the continuous read-out technology, which increases the benefit of ultrafine-phi slicing. A discussion of these findings will be followed by a few examples of recent results from synchrotrons [2–4].

EIGER R 1M and 4M are mega-pixel HPC detectors that turn diffractometers into versatile platforms for virtually any laboratory application. First results show the benefit of the high spatial resolution of the detectors and indicate that data quality is comparable to that acquired at synchrotrons.

EIGER allows crystallographers to make the best use of precious beam time at synchrotrons and laboratory x-ray sources. The detectors can lead to better x-ray structures more quickly and provide optimal starting points for drug development projects.

[1] Casanas et al. (2016). *Acta D.* **72**: 1036.

[2] Barba-Spaeth et al. (2016). *Nature* **536**: 48.

[3] Yamano et al. (2016). *Cell* **165**: 949.

[4] Z.Q. Fu (2017), personal communication.

SYMP

An Overview of the SAXS Program at the Biophysics Collaborative Access Team (BioCAT)

Srinivas Chakravarthy, Weikang Ma, and Thomas Irving
Biophysics Collaborative Access Team / Illinois Institute of Technology, APS, Argonne National Laboratory, Argonne, IL 60439

Small angle x-ray scattering (SAXS) is widely considered a powerful biophysical tool to investigate structural characteristics of biological macromolecules. The adoption of in-line size exclusion chromatography (SEC-SAXS) as the default data acquisition strategy at BioCAT has resulted in a palpable increase in the reliability with which high quality data can be obtained for even the most biochemically challenging samples. This has provided unprecedented access to a wider variety of biomedical projects. I will discuss some examples that illustrate the enhanced utility of this technique. In addition, we are exploring structural changes during key biological processes such as protein and nucleic acid folding, enzyme-substrate binding, and ligand binding using time-resolved SAXS. I will discuss the results of recent developmental efforts at BioCAT in this field and exciting future prospects.

Wednesday, May 10

CNM Workshop 5
Materials with Unique Nano-architectures: Fabrication, Theory, and Characterization

Location: Bldg. 440, Room A105/106

Organizers: Xiao-Min Lin (CNM), Subramanian Sankaranarayanan (CNM), and Zhang Jiang (CNM)

Recent developments in nanoscience see significant growth of materials with unique nano-architectures, using nanoparticles, 2D materials and polymer to create inorganic-organic hybrid materials. These advanced materials have lead to many applications in the area of flexible electronics, filtration, bio-separation, nanophotonics, sensors and actuators. The purpose of this workshop is to bring expertise from areas in fabrication, theory modeling and characterization, and exchange ideas how to push this field forward, and discuss what capability the DOE nanocenter user facility should develop to facilitate the progress in this field.

9:15–9:30	Opening Remarks
9:30–10:00	Joselle McCracken (University of Illinois at Urbana-Champaign) *Bio-compliant 4D Printing: Cell Dynamics and Aquatic Actuators*
10:00–10:30	HongYou Fan (Sandia National Laboratory) *Revealing Nanoparticle Assembly under High Pressure*
10:30–10:45	Break
10:45–11:15	Sanket Deshmukh (Virginia Tech) *PSO-assisted Development of Elastomechanically Stable Coarse-grained Models*
11:15–11:45	Chengde Mao (Purdue University) *Programmed DNA Self-assembly*
12:00–1:30	Lunch
1:30–2:00	Yongfeng Mei (Fudan University) *Rolled-up Nanomembranes for Novel Applications*
2:00–2:30	David H. Gracias (John Hopkins University) *3D Self-folding Nanostructures for Electronic, Optical, and Biomedical Applications*
2:30–2:45	Break
2:45–3:15	Byeongdu Lee (Argonne National Laboratory) *SAXS Studies on the Interaction Potentials of Duplex DNA Grafted Nanoparticles*
3:15–3:45	Arthi Jayaraman (University of Delaware) *Using Theory and Molecular Simulations to Link Molecular Design to Morphology and Function in Polymeric Materials*
3:45–4:00	Closing Remarks
4:00	Adjourn (Tour of CNM and APS)

WK-5

Bio-compliant 4D Printing: Cell Dynamics and Aquatic Actuators

Joselle McCracken
University of Illinois Urbana-Champaign, Champaign, IL 61820

Direct-Ink Writing (DIW) is a facile form of additive manufacturing that elevates 3D printed structures into materials regimes whose chemistries enable them to be temporally dynamic (4D). Here we describe several dynamic material systems that apply DIW methodologies and design principles for the fabrication of specifically bio-compliant 4D printed structures. These include the integration of ionotropic hydrogel, nanocomposite, and iron oxide nanoparticle materials into soft aquatic actuator devices that are compositionally tuned for ideal printing and post-printing performance in hydrated environments. Additionally, we incorporate a silicate nanodisc within a 2-hydroxyethyl methacrylate (HEMA) hydrogel matrix, which allows for composition-based micro-patterning that is in turn predictive of preosteoblast attachment and differentiation outcomes. These underlying system chemistries can then be leveraged in a materials-centric way into additional 4D biomimetic forms. The temporally dynamic functions of these device classes are necessary for the continued development of additive manufacturing capabilities and suggest deep ramifications for the fields of synthetic biology and tissue engineering.

WK-5

Revealing Nanoparticle Assembly under High Pressure

Hongyou Fan
Sandia National Laboratories and University of New Mexico, Albuquerque, NM 87123

Precise control of structural parameters through nanoscale engineering to improve optical and electronic properties of functional nanoparticles continuously remains an outstanding challenge. Previous work on nanoparticle assembly has been conducted largely at ambient pressure. Here I will present a new stress-induced fabrication method in which we applied high pressure or stress to nanoparticle arrays to induce structural phase transition and to consolidate new nanomaterials with precisely controlled structures and tunable properties. By manipulating nanoparticle coupling through external pressure, a reversible change in their assemblies and properties can be achieved and demonstrated. In addition, over a certain threshold, the external pressure will force these nanoparticles into contact, thereby allowing the formation and consolidation of one- to three-dimensional nanostructures. Through stress induced nanoparticle assembly, materials engineering and synthesis become remarkably flexible without relying on traditional crystallization process where atoms/ions are locked in a specific crystal structure. Therefore, morphology or architecture can be readily tuned to produce desirable properties for practical applications.

Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

WK-5

PSO-assisted Development of Elastomechanically Stable Coarse-grained Models

Sanket A. Deshmukh
Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061

Accuracy of a Molecular Dynamics (MD) simulation strongly depends on a set of parameters, called as a force-field, that defines the intra- and inter-molecular interactions between atoms/molecules. In this talk, I will discuss utilization of the particle swarm optimization (PSO) method in expediting the search for optimized force-field parameters for the development of elastomechanically stable coarse-grained (EM CG) models. We have employed PSO to develop new CG water models. These new models could reproduce the experimentally observed physical, chemical, and thermodynamic properties of water. Our work demonstrates the potential of PSO method in accelerating the search for optimized force-field parameters and thus fast-track the discovery of new hybrid materials.

WK-5

Programmed DNA Self-assembly

Chengde Mao
Department of Chemistry, Purdue University, West Lafayette, IN 47907

Polyhedra are a class of geometric structures containing regular polygons (e.g., triangles, squares, pentagons, and hexagons). Buckminsterfullerene C_{60} is a probably the most famous example of molecular polyhedra. However, it remains challenging to develop a rational strategy to assemble molecular polyhedra in a systematic way. Solutions to this problem are relevant to the self-assembly of spherical virus particles as well. A virus contains a protein shell (capsid), which is often a polyhedra structure and consists of many copies of identical proteins. Here, we will discuss a rational approach for self-assembly of regular polyhedra from branched DNA/RNA motifs. The DNA/RNA polyhedra have similar sizes to most viruses (tens of nanometers). The assembly process also superficially resembles the assembly of spherical viral capsids: the structures contain many copies of identical units that

are related with each other by symmetries. We have further explored potential applications of the resulting polyhedral cages.

WK-5

Rolled-up Nanomembranes for Novel Applications

Yongfeng Mei
Department of Materials Science, Fudan University, Shanghai 200433, China

Rolled-up nanomembranes can take advantage of strain-engineering and form into three dimensional (3D) tubular structures for various applications including lab-on-a-chip, micro-/nanomachines, optical microcavity, sensors and actuators. In this talk, we will introduce the method and process of rolled-up nanotech. With specified materials adopted, several new demonstration will be presented ranging from nanocrystalline diamond optical microcavity to stimuli-responsive nanomembrane rolls. We believe that nanomembrane origami (e.g., rolling, bending and stretching) could offer an exciting platform for 3D mesostructures and their applications.

WK-5

3D Self-folding Nanostructures for Electronic, Optical and Biomedical Applications

David H. Gracias
Johns Hopkins University, Baltimore, MD 21218

Self-folding of patterned thin films provides a convenient, and high throughput strategy to mass- produce 3D nanostructures. In this talk, I describe strategies to pattern and manipulate strain in graphene and thin metal or silicon based films to form functional devices for applications in electronics, optics and medicine. Films are patterned using photo, e-beam or nanoimprint lithography and strain mismatch, capillary or swelling induced forces are used to curve and bend the thin films. Importantly, self-folding can tune the optical spectrum and band gap of materials and provides a means to create isotropic sensors or novel transistor devices. I will also discuss the creation of shell-based sensors for single cell recording as well as hydrogel actuators. Our studies highlight the importance of 3D thin film geometries and architectures both from a fundamental and applied perspective.

WK-5

SAXS Studies on the Interaction Potentials of Duplex DNA Grafted Nanoparticles

Soyoung E. Seo[1], Tao Li[2], Andrew J. Senesi[2], Chad A. Mirkin[1,3,4], and Byeongdu Lee[2]
[1] Department of Chemistry, Northwestern University, Evanston, IL 60208
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[4] International Institute for Nanotechnology, Northwestern University, Evanston, IL 60208

Hybridization interactions between DNA-functionalized nanoparticles (DNA-NPs) can be used to program the crystallization behavior of superlattices, yielding access to complex three-dimensional structures with over 30 different lattice symmetries. While the role of attractive interactions is well-understood, the role of repulsive interactions in such crystallization processes is still largely unexplored. Here, a comprehensive approach is taken to study the role of repulsive interactions in the assembly behavior of DNA-NPs that enables the calculation of interparticle interaction potentials based on experimental results. We used two different means to assemble DNA-NPs—Watson-Crick base pairing interactions and depletion interactions—and systematically varied the salt concentration to study the repulsive interactions in DNA-NP superlattices. A comparison between two systems allows us to decouple the repulsive forces from the attractive hybridization interactions that are sensitive to the ionic environment. The result suggests that the gap distance between adjacent DNA-NPs follows a simple power law dependence on solution ionic strength regardless of the type of attractive force present. We developed a simple mean-field theory based on classical polymer brush theory and determined that the observed trend is due to the variation in effective cross sectional diameter of DNA duplex and thickness of DNA shell as a function of salt concentration. Based on this theory, we established an empirical formula with which we determined the dielectric constant of the DNA duplex to be within the range of 5 and 12.

WK-5

Using Theory and Molecular Simulations to Link Molecular Design to Morphology and Function in Polymeric Materials

Arthi Jayaraman

Department of Chemical and Biomolecular Engineering, and Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716

In my research group we develop molecular models, theory and simulation techniques to connect molecular features of macromolecular materials, specifically polymers, to their morphology and macroscopic properties, thereby guiding synthesis and characterization of these materials for various applications in the energy and biomedical fields. In this talk, I will present our work understanding ways to tune morphology in polymer functionalized nanoparticles containing polymer nanocomposites. One way to tailor polymer nanocomposite morphology is by functionalizing nanoparticle surfaces with polymers, and systematically tuning the design features of these grafted polymers. We use Polymer Reference Interaction Site Model (PRISM) theory and molecular simulations to study polymer grafted nanoparticles in polymer matrix, and to understand the effect of monomer chemistry, monomer sequence, and polydispersity, in the polymer functionalization on the effective interactions, and dispersion/assembly of functionalized nanoparticles in a polymer matrix. We validate our computational predictions through direct comparisons with experimental work involving polymer nanocomposite synthesis and small angle neutron and x-ray scattering based characterization. Lastly, time permitting, I will also present highlights of other recent atomistic and coarse-grained molecular simulation work we have been conducting to predict thermal transitions and stability in biologically relevant macromolecular materials.

Wednesday, May 10

APS/CNM Workshop 6
Nanodiffraction in Materials, Chemistry, and Physics: Scientific Opportunities

Location: Bldg. 401, Room A5000

Organizers: Paul G. Evans (University of Wisconsin-Madison), Martin V. Holt (CNM), and Zhonghou Cai (APS)

The development of x-ray nanobeam instrumentation at synchrotron x-ray light sources has created a wide range of opportunities in understanding nanoscale phenomena in materials science, chemistry, and condensed matter physics. Such instruments, including Argonne's Hard X-ray Nanoprobe produce highly brilliant x-ray beams with focal spot sizes on the order of tens of nanometers and sufficient phase-coherent intensity to produce high-dynamic range scattering patterns from individual nanoscale objects. The far higher brilliance of the upgraded APS promises to enable new classes of nanodiffraction experiment and to bring new challenges in the management and predictive analytic interpretation of large nanodiffraction datasets. The scientific use of these instruments has required the creation of advanced x-ray analysis techniques based on combinations of coherent diffraction and ptychography with the unique optical conditions of tightly focused x-ray beams. This workshop intends to explore the next level of scientific questions that will be addressed by the recent development of frontier nanoscale x-ray diffraction microscopy techniques.

Invited speakers include experts in nanobeam applications in materials research, chemical synthesis and structure of nanomaterials, and condensed matter physics. In addition to these application areas, talks will highlight how recent developments in Bragg ptychography, time-domain experiments, and dynamical diffraction simulations enable new directions in nanodiffraction characterization. Finally, talks will highlight opportunities associated with the use of advanced computational and numerical analysis in the large datasets generated in structural and chemical x-ray nanoprobe imaging.

8:30–8:45	Zhonghou Cai (Argonne National Laboratory), Paul Evans (University of Wisconsin-Madison), and Martin Holt (Argonne National Laboratory) *Welcome and Introductory Remarks*
8:45–9:20	Felix Hofmann (University of Oxford) *Bragg Coherent Diffraction Imaging of Ion Bombardment Damage*
9:20–9:55	Lincoln Lauhon (Northwestern University) *Towards Total Tomography: Correlation of Nanoscale Strain and Composition in Nonplanar Heterostructures*
9:55–10:10	Break
10:10–10:45	Joseph Heremans (Argonne National Laboratory) *The Importance of Strain on Spin Defects in Quantum Materials*
10:45–11:20	Vincent Jacques (Université Paris-Saclay, Orsay) *Coherent X-ray Nanodiffraction: A Powerful Way to Study Phase Defects in Condensed Matter Physics*
11:20–12:00	Panel Discussion (Hofmann, Lauhon, Heremans, Jacques) *Scientific Questions Driving Capabilities in Nanoscale X-ray Microscopy*
12:00–1:30	Lunch
1:30 - 2:05	Ian Robinson (Brookhaven National Laboratory) *Challenges for Bragg Coherent Diffractive Imaging at Future Light Sources*
2:05–2:40	Virginie Chamard (Institut Fresnel) *Bragg Ptychography: When Crystallography Meets Microscopy*
2:40–3:00	Break

3:00–3:35	Haidan Wen (Argonne National Laboratory) *Tracking the Evolution of Structural Heterogeneities by Time-resolved X-ray Diffraction Microscopy*
3:35–4:10	Anastasios Pateras (University of Wisconsin-Madison) *Dynamical Scattering Effects in Coherent Bragg X-ray Nanodiffraction*
4:10–4:40	Panel Discussion (Robinson, Chamard, Wen, Pateras) *Future of Nanoscale X-ray Science: Novel Methods, Bright Sources, and Big Data*
4:40–4:55	Zhonghou Cai (Argonne National Laboratory), Paul Evans (University of Wisconsin-Madison), and Martin Holt (Argonne National Laboratory) *Concluding Remarks*

WK-6

Bragg Coherent Diffraction Imaging of Ion Bombardment Damage

F. Hofmann[1], E. Tarleton[2], R.J. Harder[3], N.W. Phillips[4, 5], J.N. Clark[6], I.K. Robinson[7], B. Abbey[4], W. Liu[3], Y. Zayachuk[2], and C.E. Beck[2]

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[6] Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA 94025
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Focussed Ion Beam (FIB) milling is a mainstay of nano-scale machining. Using a tightly focussed ion beam, often gallium (Ga^+), FIB can sculpt nanostructures via localized sputtering. This ability to cut solid matter on the nano-scale revolutionized sample preparation across the life-, earth- and materials sciences. However, despite its widespread usage, detailed understanding of the functional consequences of FIB-induced damage, intrinsic to the technique, remains elusive.

Here, we study the nano-scale strain fields brought about by FIB-exposure of initially pristine gold nano-crystals. Using Bragg Coherent Diffraction Imaging (BCDI), we measure the full, 3D-resolved lattice strain tensor within each nano-crystal. Even low gallium ion doses, typical of FIB imaging and previously thought negligible, cause substantial lattice distortions. At higher doses extended self-organised defect structures appear. Combined with detailed numerical calculations, these observations provide fundamental insight into the nature of the damage created, and the defects that lead to a surprisingly inhomogeneous morphology.

Our findings show that the effects of FIB-machining reach far beyond the defects in the ion-implanted layer visible by TEM. They highlight the urgent need for the development of new strategies to control damage in FIB-nanofabricated devices, and hint at the potential of FIB for nano-scale strain engineering. The ability to probe these complex distortions in 3D illustrates the tremendous potential of coherent diffraction for nano-scale defect analysis.

WK-6

Towards Total Tomography: Correlation of Nanoscale Strain and Composition in Nonplanar Heterostructures

Lincoln Lauhon

Northwestern University, Evanston, IL 60208

I will describe a new project correlating strain and composition in InGaAs-based nanowires to understand and improve their growth and optical properties. InGaAs-based nanowires are promising compact near-IR light sources for realizing on-chip photonic information transfer. Capping layers or “shells” are necessary to confine carriers and passivate surface states, and such shells can be lattice matched or intentionally mismatched to modify electronic band structure and suppress non-radiative recombination. However, interface strain and higher In contents (for longer wavelengths) can lead to composition fluctuations, which in turn modify strain. The complex three-dimensional nature of the strain and composition variations at the nanoscale present a major challenge to characterization that we are addressing by correlating coherent x-ray diffraction imaging (CXDI) and atom probe tomography (APT) of single nanowires. Prior published work correlating APT and XRD on continuous and discontinuous InGaN quantum wells will first be presented. I will then discuss preliminary work using focused hard x-rays at APS/CNM 26-ID and NSLS II, in which strain modulations induced by stacking faults and coherently grown core-shell structures are analyzed with nanoscale resolution in three dimensions.

WK-6

The Importance of Strain on Spin Qubits in Quantum Materials

F. Joseph Heremans[1,2], Stephan O. Hruszkewycz[1], Martin V. Holt[3], Samuel J. Whiteley[2], and David D. Awschalom[1,2]

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Point defects in wide-bandgap semiconductors are promising candidates as solid-state qubits for quantum information processing due to their long spin coherence times, fast manipulation rates, and optical initialization and readout. These spin qubits, such as the nitrogen vacancy (NV) center in diamond or the divacancy (VV) in silicon carbide (SiC), can be manipulated using a number of different techniques including microwave driving, all-optical control, as well as electrical and mechanical manipulation [1]. As localized, molecule-like states trapped within their semiconductor host, these spin qubits are very sensitive to their local environment. While this sensitivity has enabled nanoscale metrology, including sensing magnetic, electric fields and temperature, it also exposes spin qubits to local sample inhomogeneities. These effects are dominated by the crystal strain in the lattice, making materials growth and characterization critical for these spin qubits in quantum materials. For example, inhomogeneous distributions in strain cause different defects to emit at slightly different wavelengths, which means their emitted photons are not indistinguishable [2], a requirement for spin-photon quantum entanglement schemes. Here in this talk, I will detail a few methods to help understand and mitigate the effects of strain on spin qubits in both nanoscale and bulk crystals, using x-ray diffraction techniques.

Commercial nanoparticles, used for nanoscale quantum sensing are often made with highly damaging techniques, such as milling or detonation, creating highly strained particles which obfuscates some of the effects used for nanoscale sensing and ultimately limiting the sensitivity of measurements. While fabricating high-quality, engineered nano-diamonds have been demonstrated [3], these efforts are time-consuming and not scalable. Using Bragg coherent diffraction imaging, we are studying how much annealing techniques help 'heal' some of the damage found in commercial diamond nanoparticles [4]. In a parallel effort in understanding strain in these materials, we are exploring the use of surface acoustic wave devices on piezoelectric, hetero-layered materials such as AlN on SiC to mechanically couple our spin qubits to other quantum systems such as superconducting qubits. Using imaging techniques at coherent x-ray diffraction instruments such as the CNM/APS Hard X-ray Nanoprobe we can probe the material properties and internal strains of our devices, and by synchronizing our surface acoustic waves to the bunch structure of the APS storage ring we can use these microscopy tools to understand the mechanics of the spin-phonon coherent coupling at the crystallographic level. Beyond these current experiments, we would like to utilize other possible XRD techniques to help understand and solve the materials challenges facing spin defects in quantum materials.

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

[1] F.J. Heremans et al. (2016). *Proc. IEEE* **104**: 2009.

[2] L.C. Bassett, et al. (2011). *Phys. Rev. Lett.* **107**: 266403.

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WK-6

Coherent X-ray Nanodiffraction: A Powerful Way to Study Phase Defects in Condensed Matter Physics

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The continuous development of large scale facilities like synchrotrons has allowed getting x-ray beam characteristics that contributed to develop new experimental techniques. Amongst them, coherence properties are always improving, and nanoscale x-ray beam sizes are now routinely used. These technical improvements were made possible thanks to machine improvements in terms of stability, source sizes and lower emittance, and, as a consequence, to the possibility to extend the lengths of beamlines to hundreds of meters. The combination of coherence and nanobeam properties for hard x-rays has opened new ways of studying hard condensed matter, in particular to get information about phase defects at the nanoscale in various kinds of structures.

In this talk, I will present two topics of condensed matter physics that benefited from this combination. The first one is the study of plastic defects appearing in micro-objects submitted to an external force [1]. The technique allows detecting a single dislocation in a sample [2], which makes it very powerful and complementary to other local probes. I will also illustrate the strength of combining coherence and nanobeam in the study of charge density waves submitted to an external current [3]. In such systems, the electron density is spatially modulated periodically, and the CDW can slide when an external field is applied in the case of incommensurate systems. The coherent x-ray nanodiffraction studies reveal the different steps of sliding that depend on the dimensionality of the system, through the behavior of the CDW phase.

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WK-6

Challenges for Bragg Coherent Diffractive Imaging at Future Light Sources

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The Bragg Coherent Diffraction Imaging (BCDI) method is a powerful method of imaging nanostructure inside materials in three dimensions with resolution appropriate for seeing nanoscale structure [1]. The future directions of the technique are illustrated in this talk by recent preliminary results involving technical advances in BCDI. We have recently extended the method to soft x-rays where the challenges are i) the limited penetration of x-rays into the material, ii) limited reciprocal space and iii) the need for a windowless, all-vacuum setup. Soft x-ray BCDI at NSLS-II has been used to address the pinning of stripes in the cuprate HTSC material $La_{2-x}Ba_xCuO_4$ (LBCO) at x=0.125 [2]. The resonant signal level at CSX-1 was sufficient to record coherent diffraction at the charge-density wave (CDW) vector (0.24,0,1.5) on resonance at the Cu L_3-edge, for which preliminary images of the stripe domains have been obtained. The resonance is needed to couple to the Cu-d orbitals to enhance an otherwise weak signal.

The second technical advance we have made is to design a suitable cryostat for hard x-ray BCDI at existing beamlines, namely 34-ID-C at APS. This is challenging because of the need to control vibrations. BCDI is a particularly favorable technique in this situation, as will be explained. We used the new cryostat at 34-ID-C to image the 235K "LTO-HTT" structural transition of LBCO, x=0.125 to test the idea that the pinning sites above are the orthorhombic grain boundaries which are rearranged by crossing it. We are attempting to image the pattern of domains by inversion of the Bragg coherent diffraction pattern, but this is also challenging [3].

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[2] X.M. Chen, V. Thampy, C. Mazzoli, A.M. Barbour, H. Miao, G.D. Gu, Y. Cao, J.M. Tranquada, M.P.M. Dean, and S.B. Wilkins (2016). "Remarkable Stability of Charge Density Wave Order in $La_{1.875}Ba_{0.125}CuO_4$." *Phys. Rev. Letts.* **117**: 167001.

[3] X.M. Chen, V. Thampy, H. Miao, Y. Cao, M.P.M. Dean, C. Mazzoli, A.M. Barbour, W. Hu, S.B. Wilkins, G.D. Gu, J.M. Tranquada, and I.K. Robinson (to be published).

WK-6

Bragg Ptychography: When Crystallography Meets Microscopy

V. Chamard

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Imaging complex crystalline materials at the nanoscale is a major challenge of nanoscience, which calls for a microscopy method combining sensitivity to the crystalline properties, 3D imaging capability, *in situ* compatibility and high spatial resolution. In this context, the recent advents of x-ray lensless imaging methods, based on Bragg coherent diffraction, have opened promising perspectives [1] filling the gap between direct microscopies (AFM, SEM, TEM) and reciprocal-space based x-ray Bragg diffraction analysis.

3D Bragg ptychography microscopy [2] is a coherent diffraction imaging method developed at third generation synchrotron sources, and which merges concepts developed in inverse microscopy and crystallography. This modality is based on the acquisition of far-field Bragg coherent intensity patterns; It exploits the partially redundant information obtained by scanning a finite beam spot size transversally to the sample, while measuring the corresponding 3D far-field intensity diffraction pattern by scanning angularly the sample along the rocking curve. Instead of lenses, numerical tools are employed to retrieve the lost phase [3] and hence the complex-valued sample scattering contrast. Thereby, it ensures access to truly quantitative information, such as the crystalline displacement field, from which the 3D strain component and crystalline plane rotations can be derived, with nanoscale spatial resolution. 3D imaging of extended crystalline samples is then possible [2,4], opening Bragg coherent diffraction microscopy to a large range of applications.

In this presentation, the general concepts of Bragg ptychography will be detailed, illustrated by recently proposed developments [2–7]. Finally, we will show how Bragg ptychography can be exploited to bring new insights on the hierarchical crystalline structure of biominerals and promotes thereby the understanding of the mechanisms underlying biomineralization [8].

This project has received funding from the European Research Concil (ERC) under the European Union's Horizon H2020 research and innovation program grant agreement no. 695093.

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[6] V. Chamard et al., *Scientific Reports* **5**: 9827 (2015).

[7] S.O. Hruszkewycz et al., *Nature Materials* (2016).

[8] F. Mastropietro et al., submitted.

WK-6

Tracking the Evolution of Structural Heterogeneities by Time-resolved X-ray Diffraction Microscopy

Haidan Wen

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

Heterogeneities in condensed matter systems play important roles in determining their functionalities. Although heterogeneities have been intensively studied in equilibrium, the evolution of heterogeneities driven out of equilibrium has not been well understood due to technical challenges of probing ultrasmall on ultrafast time scales. Visualizing dynamical interaction among heterogeneities is critical for understanding and subsequently harnessing materials with new or enhanced functionalities. In this talk, I will present several examples of studying the evolution of structural heterogeneities by time-resolved x-ray diffraction microscopy with 100 ps temporal resolution, including dynamical structural phase separation in photoexcited VO_2, optically activated domain dynamics in $BaTiO_3$, and engineering nanoscale energy transport by local THz-field excitation. Looking into future, I will update the on-going effort for a new *in situ* multimodal imaging platform by integrating near-field optical and x-ray diffraction microscopes.

WK-6

Dynamical Scattering Effects in Coherent Bragg X-ray Nanodiffraction

A. Pateras[1], J. Park[1], J.A. Tilka[1], Y. Ahn[1], M.V. Holt[2], C. Reichl[3], J.P. Dehollain[4], L.M.K. Vandersypen[4], and P.G. Evans[1]

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The investigation of nanoscale structural effects in nearly perfect crystal heterostructures is a challenging diffraction problem that requires including dynamical diffraction effects. The kinematical description of diffraction does not adequately reproduce the experimental results because the relevant thicknesses are considerably larger than the x-ray extinction depth. The importance of these effects is apparent in scanning hard x-ray nanodiffraction experiments on GaAs/AlGaAs heterostructures, which produce sharp features in diffraction patterns, intense signals outside the nominal cone of the zone plate, and splittings of the diffraction intensity maxima due to lattice tilts. We report numerical methods for incorporating dynamical scattering theory in previously developed coherent Bragg diffraction kinematical modeling. By including dynamical effects, we quantitatively describe the diffraction of tightly-focused x-ray nanobeams with the substrate and the thick layers of the epitaxial heterostructure. By comparing the simulations with experimental results, we provide insight into important problems. First, we reproduce x-ray nanodiffraction data from a buried GaAs quantum well layer in an AlGaAs heterostructure which is epitaxially grown on a GaAs substrate, using kinematical diffraction for the thin overlayers and the Darwin theory of dynamical diffraction for the scattering from the substrate. This study serves as a first step for verifying the simulation methods with experimental data on a relatively simple system. Second, in a quantum electronic system consisting of quantum dots defined by metal electrodes, we employ nanodiffraction to measure the lattice distortions in the overlayers and at the depth of the GaAs/AlGaAs interface. This study allows the distortion within the volume occupied by the two-dimensional electron gas to be probed, and indicates that the distortions play an important role in the definition of the quantum dot. Such distortions can modify the electron energetics by shifting the energy levels of confined states.

Wednesday, May 10

APS Workshop 7
High-resolution Fluorescence Detection: Advanced X-ray Emission and Absorption Spectroscopy Studies Towards an Upgraded APS (APS-U)

Location: Bldg. 401, Room A1100

Organizers: Chengjun Sun (APS) and Mali Balasubramanian (APS)

High-energy resolution fluorescence detection is an important route for improving the utility of advanced x-ray emission and absorption spectroscopies. With increases in brightness, flux, and sub-micro focusing by APS-U, it will become easier to apply high-resolution detection methods to a wider variety of experiments, such as x-ray emission for ultra-diluted samples, high-pressure x-ray emission spectroscopy, time–resolved x-ray emission/XANES, high-resolution x-ray absorption spectroscopy, and spin-resolved x-ray absorption spectroscopy. This symposium will consider the prospects of instrumentation and applications for improved higher energy resolution fluorescence detection by utilizing the miniature x-ray emission spectrometers (miniXES), a high-resolution crystal spectrometer, and x-ray spectrometers using polycapillary optics. Furthermore, the latest developments of theory and superconducting detectors will be discussed.

Session 1: Chair, Chengjun Sun (Argonne National Laboratory)

8:25–8:30	Assemble
8:30–8:50	Steve Heald (Argonne National Laboratory) *Present and Future Applications of High Resolution Fluorescence Detection at Sector 20*
8:50–9:15	Jenny Lockard (Rutgers University–Newark) *Probing Metal Spin States in Metal-organic Frameworks with K-beta X-ray Emission Spectroscopy*
9:15–9:40	Yuming Xiao (HPCAT, Advanced Photon Source) *High Pressure X-ray Emission Spectroscopy at HPCAT*
9:40–10:05	Yulia Pushkar (Purdue University) *Natural and Artificial Water Oxidation Mechanisms Revealed by X-ray Spectroscopy*
10:05–10:30	Break

Session 2: Chair, Mali Balasubramanian (Argonne National Laboratory)

10:30–11:00	Kenneth Finkelstein (Cornell High Energy Synchrotron Source, CHESS) *XES and Spectrometer Developments at CHESS*
11:00–11:30	Niranjan Govind (PNNL) *Exploring Electron Delocalization on the Femtosecond Timescale*
11:30–11:55	Antonino Miceli (Argonne National Laboratory) *Recent Advances in Superconducting X-ray TES Spectrometers*
11:55–12:00	Closing remarks

WK-7

Present and Future Applications of High Resolution Fluorescence Detection at Sector 20

Steve Heald
X-ray Science Division, Advanced Photon Source, Argonne, IL 60439

There have been a number of applications of high resolution fluorescence detection at Sector 20 at the Advanced Photon Source. For many years we have used high resolution crystal based detectors such as a WDX or a bent Laue type to separate closely spaced fluorescence lines. For example, separating the U L_α line from the K lines of Rb and Sr. This allowed mapping and XANES of dilute concentrations of U in sediments with a large background of other fluorescence lines. More recently we performed a number of x-ray emission studies (non-resonant and resonant) using the miniXS style spectrometers. MiniXS detectors can also be used for high energy resolution fluorescence detection (HERFD), but their efficiency is low. To better carry out HERFD measurements we have a six crystal analyzer based on spherically bent crystals. In the future, the APS upgrade will open up new possibilities. For example, the miniXS spectrometers can be combined with sub-micron microprobes to provide chemically sensitive imaging using x-ray emission spectroscopy on time scales similar to our current fluorescence mapping. Also, it may become possible to detect single atoms with a microprobe, using a detector with similar resolution as the fluorescence line width.

This research used resources of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, and was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357, and the Canadian Light Source and its funding partners.

WK-7

Probing Metal Spin States in Metal-organic Frameworks with K-beta X-ray Emission Spectroscopy

Jenny V. Lockard
Rutgers University–Newark, Newark, NJ 07102

Metal organic frameworks are hybrid materials that are composed of metal ions or clusters connected by organic molecules to form crystalline microporous networks. These materials have great potential for adsorption-based functions since their intrinsic porosity and tunable architecture allows bandgap manipulation, gas/substrate selectivity and the incorporation of other synergistic characteristics. Synthetic strides in developing new frameworks with these properties have, however, far outpaced the progress in advancing the fundamental understanding of their adsorption-based processes and reaction mechanisms. Consequently, there are often significant ambiguities in the structure/function relationships that give rise to their utility. Our research aims to make those connections by producing molecular level understanding of metal organic framework behavior. To accomplish this goal, a targeted set of vibrational, optical, and x-ray spectroscopy methods are utilized, by both *ex situ* and *in situ* means. This talk will focus specifically on the application of K-beta x-ray emission spectroscopy to garner information on the important roles of host-guest interactions and framework pore size restrictions for a series of MOF material under different guest environments.

WK-7

High Pressure X-ray Emission Spectroscopy at HPCAT

Yuming Xiao, Paul Chow, Eric Rod, Rich Ferry, Curtis Kenney-Benson, Arunkumar Bommmannavar, Stanislav Sinogeikin, and Guoyin Shen
HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, IL 60439

The structural, electronic and magnetic properties of materials under high pressure are of fundamental interest in physics, chemistry, materials science, and earth sciences. Among several hard x-ray based techniques, x-ray emission spectroscopy (XES) provides a powerful tool to probe element specific information for understanding the electronic and magnetic properties of materials under high pressure. In this presentation, we discuss on the particular requirements and instrumentation used in high pressure XES experiments [1,2]. We then present several examples to illustrate the recent progress in high pressure XES studies at High Pressure Collaborative Access Team (HPCAT) at Advanced Photon Source, followed by an outlook toward future development in high pressure XES with new diffraction-limited storage rings (APS-U, etc.) and technologies for making better x-ray focus mirrors and detectors [2].

[1] Xiao, Y., P. Chow, G. Boman, L.G. Bai, E. Rod, A. Bommannavar C. Kenney-Benson, S. Sinogeikin, and G.Y. Shen (2015). *Rev. Sci. Instrum* **86**: 072206

[2] Xiao, Y., P. Chow, and G.Y. Shen (2016). *High Press. Res.* **36**(3): 315–331.

WK-7

Natural and Artificial Water Oxidation Mechanisms Revealed by X-ray Spectroscopy

Yulia Pushkar[1], Scott C. Jensen[1], Katherine M. Davis[2], Brendan Sullivan[1], and Gerald T. Seidler[3]

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[3] Department of Physics, University of Washington, Seattle, WA 98195

Electronic structure of metal centers in materials and proteins can be studied by x-ray emission spectroscopy. X-ray emission spectroscopy (XES) is an emerging technique with a growing application to biological and biomimetic systems. Dispersive detection of high resolution x-ray fluorescence is best suited for ultra-fast applications as instant snapshots of electronic structure are obtained with single pulse of x-rays.

Here, we report an improved, cost effective spectrometer used to analyze biomimetic coordination compounds such as $[Mn^{IV}(OH)_2(Me_2EBC)]^{2+}$ and $[Mn^{IV}(O)(OH)(Me_2EBC)]^{+}$, the second of which contains a key Mn^{IV}=O structural fragment implicated in a range of chemical reactivities. The formal oxidation state (Mn^{IV}) is identical in the two compounds but their electronic structure is different, as reflected in the reported x-ray emission spectra. Experimental measurements and DFT calculations show that the localized spin density on Mn is different for the two complexes and is a result of a single chemical bond change: Mn-OH conversion to Mn=O. The relevance of the observed spectroscopic changes is discussed for applications in analysis of complex biological systems such as photosystem II.

In photosystem II laser pump x-ray probe time resolved measurements allowed us to follow evolution of electronic structure in the oxygen evolving complex (Mn4Ca– cluster) within few microseconds. DFT analysis of PS II was conducted to predict changes in the Gibbs energies of catalytic steps and search for structure and/or activity relationships. To aid interpretation of the Mn Kbeta x-ray emission spectra of the Mn4Ca cluster model Mn-compounds have been analyzed. Atomistic model for the S_3 state of the OEC reported by us in 2015 [1] is the same (within the XRD resolution) as recently reported by Shen and co-workers [2].

Transition of these experiments to free electron laser require re-evaluation of the damage threshold. Our preliminary Mn Kbeta emission spectroscopy data show that Mn ions in solution are subjected to multi-photon excitations / multiple ionizations within single 10–40 fs pulse of the LCLS source.

[1] K.M. Davis, B.T. Sullivan, M. Palenik, L. Yan, V. Purohit, G. Robison, I. Kosheleva, R. W. Henning, G.T. Seidler, and Y. Pushkar (2015), arXiv:1506.08862.

[2] Suga et al. (2017), *Nature* **543**(7643): 131–135.

WK-7

XES and Spectrometer Developments at CHESS

Kenneth Finkelstein[1], Christopher J. Pollock[2], and Zachary Porter[3]

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Our beamline divides available beamtime between programs supporting emission spectroscopy and single crystal diffraction. We have both missions in mind when developing analyzer optics and the associated instrumentation. Work on curved crystal pixelated analyzers benefits from Bosch process deep-Reactive Ion Etching (d-RIE) available at Cornell Nanofabrication Facility.

The talk will focus on: the range of crystal analyzers being used at CHESS, challenges and opportunities associated with their fabrication, the science motivating this development, novel analyzer instrumentation, and plans for a new spectroscopy beamline, coming in 2019, as part of the CHESS-U undulator upgrade.

Research conducted at the Cornell High Energy Synchrotron Source (CHESS) is supported by National Science Foundation and the National Institutes of Health/National Institute of General Medical Sciences under NSF Award DMR-1332208.

WK-7

Exploring Electron Delocalization on the Femtosecond Timescale

Niranjan Govind[1], Amity Andersen[1], Zachary Fox[3], Yu Zhang[2], Shaul Mukamel[2], and Munira Khalil[3]

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[3] University of Washington, Seattle, WA 98105

The overall goal of this project is to understand valence electron and vibrational motion following metal-to-metal charge transfer (MMCT) excitation in the following mixed valence dimer and trimer transition metal complexes dissolved in aqueous solution. The project objectives are (i) to observe the time-dependent re-arrangement of *d* electrons across two transition metal sites and the bridging ligand following photoinduced MMCT excitation on a sub-50 fs timescale using femtosecond x-ray pulses generated at LCLS (ii) to simulate femtosecond x-ray absorption and emission spectra of solvated, photo-excited, transition metal mixed valence complexes

(iii) to determine the role of coupled electronic and vibrational motions during ultrafast photoinduced charge transfer. This talk will focus on our theoretical efforts to interpret the experimentally observed spectra and to simulate and predict transient spectroscopic signatures on the femtosecond timescale.

WK-7

Recent Advances in Superconducting X-ray TES Spectrometers

Antonino Miceli

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

While semiconductor pair-breaking detectors (e.g., silicon-drift detectors) are currently the workhorse for most spectroscopic applications at x-ray synchrotron beamlines, their resolution is fundamentally limited by the statistics of electron-hole pair creation. An increasing number of synchrotron experiments require energy resolution far beyond (i.e., $E/\Delta E > 1{,}000$) what is achievable with these types of detectors. For these applications, wavelength-dispersive spectrometers are generally used and they provide excellent energy resolution, but are inefficient in the collection of the x-rays emitted from the sample. Superconducting detectors represent the best viable alternative that can overcome the limitations of both these technologies. The very low noise levels and energy-dispersive nature of superconducting detectors make efficient use of every single x-ray photon. In this talk, we present recent developments in superconducting x-ray transition edge sensors (TES) spectrometers for light source facilities.

Wednesday, May 10

APS Workshop 8
Advances in Chemical Interpretation of Signals in Macromolecular Crystallography

Location: Bldg. 401, Room A1100

Organizers: Dominika Borek (University of Texas Southwestern Medical Center), Karolina Michalska (Structural Biology Center, Advance Photon Source), and Diana R. Tomchick (University of Texas Southwestern Medical Center)

Very fast photon-counting detectors, high-capacity computing and beamline automation which has been introduced at most APS macromolecular beamlines has expanded the range of applicability of crystallographic methods such that many data sets from multiple, nearly isomorphous crystals can be analyzed and compared simultaneously to extract chemical and physical signals. These signals, which are otherwise undetectable or barely reach the level of statistical significance, provide unique information about systems under investigation. For instance, data from multi-crystal experiments may be analyzed simultaneously to identify the presence and identity of weakly bound ligands or to characterize conformational transitions and disorder with changing chemical and physical conditions.

To take full advantage of the rapid technical progress at the APS, novel experimental strategies, data analysis methods and approaches to validation must be developed and implemented. Data mining methods that reduce the dimensionality of the space in which the signal is analyzed and quantified have been available, but historically their use in macromolecular crystallography was limited due to the scale of the necessary computations.

This half-day workshop will review advances in approaches to detection, quantification and validation of electron density changes resulting from chemical reactions and physical processes induced in macromolecular crystals by light, electric fields, x-rays, and other external stimuli. The topics will include: (1) new experimental techniques to generate differential signals, (2) novel methods for detecting and validating the presence of ligands, and (3) newly developed dimensionality reduction approaches to quantify structural variability.

1:00–1:15	Dominika Borek (UT Southwestern Medical Center) *Assembly and Introduction*
1:15–1:45	Kristopher White (Stanford University) *Characterizing Protein Mechanics with Electric Fields at BioCARS*
1:45–2:15	Ana Gonzalez (SSRL, SLAC National Accelerator Laboratory) *Conformational Variation of Proteins and Radiation Damage*
2:15–2:45	Zbyszek Otwinowski (UT Southwestern Medical Center) *Decomposition of Electron Density Maps Corresponding to a Single Crystal Form to Chemical Signals*
2:45–3:15	Break
3:15–3:45	David Akey (University of Michigan) *Massively Multiple Merged Data for Low-resolution Native SAD Phasing*
3:45–4:15	Diana Tomchick (UT Southwestern Medical Center) *Strategies to Address Macromolecular/Ligand Complex Structures in the Context of an Academic Service Laboratory*
4:15–4:45	Wladek Minor (University of Virginia) *Reproducibility in Biomedical Sciences Big Data Perspective*
4:45–5:00	Karolina Michalska (Argonne National Laboratory) and Diana Tomchick (UT Southwestern Medical Center) *Discussion and Concluding Remarks*

WK-8

Characterizing Protein Mechanics with Electric Fields at BioCARS

Kristopher White
Stanford University, Stanford, CA 94305

The mechanics of proteins connect their structure and function. We have developed a new method, called EFX, which allows us to directly explore this connection. EFX combines the use of electric fields exerting precise patterns of force on crystalline proteins with time-resolved crystallography to read out the resulting dynamics. I will introduce the principles underlying the method and describe its realization at BioCARS 14 ID. Finally, I will show that subtle, diverse motions can be induced throughout a protein structure, including at likely functional sites.

WK-8

Conformational Variation of Proteins and Radiation Damage

Ana Gonzalez
SSRL, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

Protein crystallography data collection at synchrotrons is routinely carried out at cryogenic temperatures to mitigate radiation damage. This practice results in an increase of approximately 100-fold in the lifetime of the crystals. However, it has been observed that the structures from flash-cooled crystals have a reduced conformational variety. This effect can hide important functional mechanisms from observation and is a main motivation for experiments to be carried out at room temperature, but the trade-offs between the increased risk of radiation damage and the increased number alternative conformations at room temperature relative to cryogenic temperature have not been studied. A study of the effects of radiation damage on the conformational landscapes of three different proteins (T. danielli thaumatin, hen egg white lysozyme, and human cyclophilin A) was carried out at room (278 K) and cryogenic (100 K) temperatures. Increasingly damaged datasets were collected at each temperature, up to a maximum dose of the order of 10^7 Gy at 100 K and 10^5 Gy at 278 K. Although it was not possible to discern a clear trend between damage and multiple conformations at either temperature, disorder was seen to increase with higher absorbed dose for the three proteins at 100 K. At 278 K, however, the total increase in this disorder was only statistically significant for thaumatin. This analysis suggests that, at the doses and dose rates typically used for experiments, elevated conformational heterogeneity is nor caused by radiation damage.

S. Russi, A. González, L.R. Kenner, D.A. Keedy, J.S. Fraser, and H. van den Bedem (2017). "Conformational variation of proteins at room temperature is not dominated by radiation damage." *J. Synchrotron Rad.* **24**: 73–82.

WK-8

Decomposition of Electron Density Maps Corresponding to a Single Crystal Form to Chemical Signals

Zbyszek Otwinowski[1,2], Raquel Bromberg[1], and Dominika Borek[1,2]
[1] Department of Biophysics, University of Texas Southwestern Medical Center, Dallas, TX 75390
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We performed a set of x-ray experiments on the same crystal form of glucose isomerase. Experiments were done at multiple temperatures, with different time-dose regimes, and with variations in the composition of the crystallization milieu. The crystals were highly isomorphous, which allowed us to investigate how specific radiation damage is affected by variable experimental conditions. To facilitate the analysis, we applied a novel data mining approach to decompose electron density difference maps into statistically independent components. Then we imaged these components in real space as difference electron density maps and analyzed distributions of statistically significant peaks to identify possible chemical events resulting in a particular pattern.

We will present the results of this analysis, which show a very high diversity of chemical changes induced by x-ray radiation. The analysis allowed for decoupling the temperature-dependent components of radiation-induced changes from the temperature-independent components, so that the reactions resulting from electron tunneling could be analyzed. We were also able to observe the radiation-induced changes due to time-dose effects, as well as the variation due to changes in the composition of the crystallization and cryo-stabilization conditions. The range of chemical variability provides yet another indication that radiation-induced changes are highly dependent on experimental conditions and proceed through multiple pathways on time scales comparable to the time scales of data collection. These observations affect not only the structural interpretation of models obtained with x-ray crystallography, but also provide insight into factors that affect diffraction data quality.

We will discuss our current work, which stemmed from these observations and which will facilitate better approaches to diffraction data acquisition and analysis.

WK-8

Massively Multiple Merged Data for Low-resolution Native SAD Phasing

David L. Akey and Janet L. Smith

Life Sciences Institute, University of Michigan, Ann Arbor, MI 48109

A challenge for determination of the structure of a novel protein is solving the phase problem. Historically, this has been accomplished by incorporation of non-native heavy atoms into the protein crystals and measurement of the small differences between modified and non-modified crystals (isomorphous replacement) or of the small anomalous difference measured between Bijvoet pairs (anomalous diffraction). Use of native anomalously scattering atoms (predominately Sulfur and Phosphorous) can help to solve the phase problem, but anomalous differences for these scatterers are typically only 1–2% of the overall diffraction and are thus very difficult to measure accurately. Accurate measurement of these differences can be accomplished by using exceptionally high multiplicity data measured from many individual samples. We present a case in which anomalous differences were measured accurately enough to phase using only low (5.2 A) resolution data. The phases determined were sufficiently accurate to extend useful data to 3.0 A for initial model building. Strategies for assessing and merging data from many samples were essential for successful completion of this project. An analysis of different strategies for combining data for substructure determination will also be presented.

WK-8

Strategies to Address Macromolecular/ Ligand Complex Structures in the Context of an Academic Service Laboratory

Diana R. Tomchick

Structural Biology Laboratory, Department of Biophysics, University of Texas Southwestern Medical Center, Dallas, TX 75390

The mission of the University of Texas Southwestern Medical Center's Structural Biology Laboratory (SBL) is to provide education and access to campus researchers to macromolecular x-ray crystallography and related biophysical techniques. A critical role of the SBL is to provide mentoring and assistance to graduate and postdoctoral students through all stages of a structural project, from cloning to structure determination and model analysis. Since the establishment of the SBL in 2000, collaborations with more than 60 research groups on the UT Southwestern campus on over 120 projects, resulting in over 130 peer-reviewed publications and over 200 x-ray crystal structures deposited in the Protein Data Bank to date. Many of the most biologically interesting structural projects pursued through the SBL have also proven to be quite challenging ones, with difficulties ranging from protein production to structure validation and all the steps in-between. In addition to the challenges presented by working with students with little knowledge or experience in single-crystal x-ray crystallography, interpretation of protein/ligand complex structures are often complicated by sub-optimal crystal quality or data collection, low data resolution or completeness, severe radiation damage, high data anisotropy, poor phasing signal, partial merohedral twinning, incorrect sequence assignment and over-optimistic electron density interpretation. Strategies employed to cope with various non-ideal x-ray crystallographic structures of protein/ligand complexes will be presented.

Results shown in this report are derived from work performed at Argonne National Laboratory, Structural Biology Center at the Advanced Photon Source. Argonne is operated by UChicago Argonne, LLC, for the U.S. Department of Energy, Office of Biological and Environmental Research under contract DE-AC02-06CH11357.

WK-8

Reproducibility in Biomedical Sciences Big Data Perspective

W. Minor

University of Virginia, Charlottesville, VA 22908

Experimental reproducibility is the cornerstone of scientific research, upon which all progress rests. The veracity of scientific publications is crucial because subsequent lines of investigation rely on previous knowledge. Several recent systematic surveys of academic results published in biomedical journals reveal that a large fraction of representative sets of studies in a variety of fields cannot be reproduced in another laboratory. Big Data approach and especially NIH Big Data to Knowledge (BD2K) program is coming to the rescue.

The goal of the presented research is to provide the biomedical community with a strategy to increase the reproducibility of reported results for a wide range of experiments by building a set of "best practices," culled by extensive data harvesting and curation combined with experimental verification of the parameters crucial for reproducibility. Experimental verification assisted by the automatic/semi-automatic harvesting of data from laboratory equipment into the already developed sophisticated laboratory information management system (LIMS) will be presented. This data-in, information out paradigm will be discussed.

Wednesday, May 10

APS Workshop 9
X-ray Characterization of Materials Evolution: The State-of-the-Art

Location: Bldg. 402, Room E1100/E1200

Organizers: Ashwin J. Shahani (University of Michigan) and Xianghui Xiao (APS)

The kinetic pathways of materials during processing and service ultimately determine their properties and performance. Due to the advent of high-energy and *in situ* x-ray characterization techniques (e.g., tomography, topography, and diffraction) researchers have the unique opportunity to uncover the fundamental mechanisms underlying the evolution of technologically relevant materials during solidification, deformation, shock, and related materials processing.

The focus of this workshop is to bring together experts in technique development and applications to assess the current state-of-the-art in probing the evolution of materials over a broad range of length and time scales. Particular emphasis will be given to understanding the dynamics of defects and interfaces in metals and semiconductors (e.g., Ti-based superalloys and Si polycrystals) via *in situ* observations. Invited speakers will be asked to highlight explicitly the societal or industrial importance of their research findings (e.g., additive manufacturing) within their presentations.

8:30–8:35	Ashwin Shahani (University of Michigan) *Opening Remarks*
8:35–9:10	Tao Sun (Argonne National Laboratory) *High-speed X-ray Imaging and Diffraction at the 32-ID-B Beamline of the Advanced Photon Source*
9:10–9:45	Lianyi Chen (Missouri University of Science and Technology) *Characterizing the Dynamics of Laser Powder Bed Fusion Additive Manufacturing Processes by High-speed X-ray Imaging*
9:45–10:20	Robert Suter (Carnegie Mellon University) *Tomographic Studies for Reliable Additive Manufacturing of Metals*
10:20–10:50	Break/Workshop Picture
10:50–11:25	Nikhilesh Chawla (Arizona State University) In situ *Materials Science: Probing Microstructural Evolution of Metallic Materials in Real Time*
11:25–12:00	Peter Voorhees (Northwestern University) *Creating Materials Databases Using X-ray Tomography*
12:00–1:00	Lunch
1:00–1:35	Amy Clarke (Los Alamos National Laboratory) In situ *Imaging of Metallic Alloy Solidification Dynamics for Advanced Manufacturing*
1:35–2:10	Ashwin Shahani (University of Michigan) *Probing the Growth Dynamics of Periodic Crystals and Quasicrystals in Real-time*
2:10–2:45	Michael Dudley (Stony Brook University) *Evolution of Defects During the Growth of SiC Substrates and Epilayers*
2:45–3:15	Break
3:15–3:50	Zonghai Chen (Argonne National Laboratory) *Unveiling Failure Mechanism of Lithium-ion Batteries*
3:50–4:25	Jordi Cabana (University of Illinois at Chicago) *Visualization of Electrochemical Reactions in Battery Materials with X-ray Microscopy*

4:25–5:00 Feng Lin (Virginia Tech)
Understanding the Surface Chemistry of Battery Materials Using Synchrotron X-ray Spectroscopy

5:00–5:15 Xianghui Xiao (Argonne National Laboratory)
Concluding Remarks

WK-9

High-speed X-ray Imaging and Diffraction at the 32-ID-B Beamline of the Advanced Photon Source

Tao Sun, Kamel Fezzaa, and Cang Zhao
Advanced Photon Source Imaging Group, Argonne National Laboratory, Argonne, IL 60439

Many scientifically and/or technologically significant phenomena are transient in nature, such as interaction of water droplet with hydrophobic surfaces, atomization of fuel spray out of high-pressure engineer nozzles, reactions of highly energetic materials, fracture of materials on impact, rapid melting and solidification of metals in laser additive manufacturing, material phase transformation induced by thermal or mechanical shocks. At the 32-ID-B beamline of the Advanced Photon Source, scientists have been using the high-speed hard x-ray imaging technique to solve critical problems involved in various highly dynamic processes in hard and soft condensed matters. High-energy x-ray photons possess great penetration power, which allows one to see though the samples and capture the internal structure evolution in relatively thick or dense materials. Through years' of efforts, 6.5 MHz frame rate, 100 ps temporal resolution, and 1 μm spatial resolution have been achieved for imaging. Recently, high-speed x-ray diffraction technique and instrument have been developed at our beamline, which well complements the imaging technique by providing sample structure information in the reciprocal space. Different from conventional pump-probe x-ray scattering techniques, our approach aims at understanding the physics in irreversible and/or non-repeatable dynamic processes (like those aforementioned) by collecting multiple frames of scattering data from a single event. In the presentation, I will introduce our current beamline capabilities and user programs, and specifically highlight the application of high-speed x-ray imaging and diffraction techniques in studying the metal additive manufacturing.

WK-9

Characterizing the Dynamics of Laser Powder Bed Fusion Additive Manufacturing Processes by High-speed X-ray Imaging

Lianyi Chen
Missouri University of Science and Technology, Rolla, MO 65409

Laser powder bed fusion is a major additive manufacturing technique for producing complex-shaped metal parts by selective melting successive layers of metal powders using a laser beam. Understanding the physics of laser powder bed fusion (LPBF) processes is critical for establishing location-specific processing-microstructure-property relationships. The non-transparency of metals to visible light and the highly localized (tens of micrometers) and very short (tens of microseconds) interaction of a laser beam with metal powders during LPBF pose a huge challenge to the characterization and understanding of this process. The detailed physics of the LPBF process and the mechanisms of defect formation and microstructure evolution are still not clear. In this talk, I will present our ongoing research on characterizing the dynamics of laser powder bed fusion additive manufacturing processes by high-energy high-speed x-ray imaging, with a focus on the dynamics of laser-powder interaction. The physics governing powder moving and spattering during laser melting will be discussed. The results obtained in this work are important for establishing the location-specific processing-microstructure relationships in LPBF of metals.

WK-9

Tomographic Studies for Reliable Additive Manufacturing of Metals

R. Cunningham[1], H. Liu[1], Y. Shen[1], C. Zhao[2], T. Sun[2], A.D. Rollett[1], and R.M. Suter[1]
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Additively manufactured (AM) metals are known to contain a variety of defect structures that can lead to undesirable properties. We study powder bed systems in which the materials undergo complex thermal cycling during laser or electron beam melting of successive layers; this processing leads to heterogeneities on multiple length scales. We are using a combination of synchrotron based x-ray probes to characterize these structures and to attempt to elucidate

steps that can reduce or eliminate their deleterious effects. Absorption contrast tomography measurements at 2-BM study preexisting pore structures in the starting powder material and correlate these structures with pores in the AM samples. While hot isostatic pressing is able to reduce or remove some of these structures, we observe that some regrow during subsequent high temperature treatments. These measurements are being correlated with high energy diffraction microscopy measurements at 1-ID that study stress/strain distributions and crack formation around the defect features including internal pores and surface roughness. We also study the dynamics of laser melting using the high-speed radiography facility at 32-ID. Here we are able to visualize laser-powder interactions and phase transformation dynamics at milli- to microsecond time scales. These dynamics are correlated with processing parameters such as laser power and scanning speed to clarify the cross-over from lack of fusion on the one hand (low power/high speed) and keyhole formation on the other (high power/low speed); these observations clarify the constraints on the process parameter space that yield optimized structures. These results demonstrate that the diverse set of tomographic and diffractive probes available at the APS holds great promise for determining the path towards reliable additive manufactured materials and parts.

WK-9

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

N. Chawla

Fulton Professor of Materials Science and Engineering, Center for 4D Materials Science, Arizona State University, Tempe, AZ 85287

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

X-ray synchrotron micro and nano-tomography provides a wonderful means of characterization damage in materials non-destructively. In this talk, I will describe experiments and simulations that address the critical link between microstructure and deformation behavior of metallic materials, by using a three-dimensional (3D) virtual microstructure obtained by x-ray synchrotron tomography. The approach involves capturing the microstructure by novel and sophisticated *in situ* testing in an x-ray synchrotron, followed by x-ray tomography and image analysis, and 3D reconstruction of the microstructure. Case studies on fundamental precipitation evolution and deformation phenomena in aluminum alloys under cyclic loading and in a corrosive environment will be presented and discussed. New opportunities for x-ray microtomography, including lab-scale diffraction contrast tomography (DCT) will be highlighted.

WK-9

Creating Materials Databases Using X-ray Tomography

Jin Zhang[1], Stefan O. Poulsen[2], John W. Gibbs[3], Peter W. Voorhees[2], and Henning F. Poulsen[1]

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The materials design process rests on a foundation of materials data. These data can be of many forms. For example, CALPHAD and density function theory methods are commonly employed to determine phase diagrams in the multicomponent alloys of engineering interest and the free energies needed for kinetic models. However, there are many parameters that are central to a design effort and are quite challenging to measure, such as liquid diffusivities and interfacial energies. We outline a method to determine materials parameters using 4D x-ray tomography. The approach uses the microstructure measured at one time as an initial condition in a phase field simulation. Then by comparing the computed and measured microstructures at a later time, we show that it is possible to determine difficult-to-measure materials parameters, such as the solute diffusivity in a liquid metal. The generalization of this approach to other materials parameters will be discussed.

WK-9

In situ Imaging of Metallic Alloy Solidification Dynamics for Advanced Manufacturing

A.J. Clarke[1], D. Tourret[2], S.D. Imhoff[2], J.W. Gibbs[2], P.J. Gibbs[2], J.C.E. Mertens[2], A. Stokes[1], D. Diercks[1], Y. Song[3], K. Fezzaa[4], T. Sun[4], J.F. Hunter[2], M.A. Espy[2], F.E. Merrill[2], F.G. Mariam[2], C.H. Wilde[2], B.M. Patterson[2], R.A. Lebensohn[2], J.K. Baldwin[2], J.T. McKeown[5], J.D. Roehling[5], T.M. Rodgers[6], J.D. Madison[6], and A. Karma[3]

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Solidification is critical to processes like casting and additive manufacturing and the manufacture of metallic alloy components we use in our everyday lives. State-of-the-art characterization techniques, now available at U.S. DOE User Facilities and in the laboratory, are not only enabling fundamental studies of metallic alloy solidification dynamics, but also *in operando*, *in situ* deformation, and manufacturing studies. Here we use x-ray, proton, and electron imaging to study solidification dynamics from the micro-scale to the macro-scale, at times ranging from microseconds to minutes. Our experimental results are used to inform, develop, and validate computational models at the same length and time-scales. Integrating *in situ* characterization and modeling will yield the prediction and control of metallic alloy solidification dynamics and the creation of microstructures and properties by design with advanced manufacturing.

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

WK-9

Probing the Growth Dynamics of Periodic Crystals and Quasicrystals in Real-time

Insung Han[1], Saman Moniri[1], Xianghui Xiao[2], and Ashwin J. Shahani[1]

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

The solidification pathways of metals and semiconductors continue to be a phenomenon of great interest to scientists and engineers, involving a complex interplay of many physical effects. Various interfacial morphologies with pronounced orientational order have been observed, several of which remain unexplained by existing models. Here, we have used synchrotron-based x-ray microtomography to peer into the interfacial dynamics underlying this complex phase transformation. Our studies would not be possible without the great strides in data sampling and reconstruction, computer hardware and storage, and algorithms for processing Big Data in a massively parallel environment. Using this approach, we have gained new insights on the growth mechanisms of crystals (both periodic and quasicrystalline) from a featureless liquid, as will be presented and discussed. In particular, our results on the decagonal quasicrystal (d-QC) show that the interfacial velocities vary strongly with crystallographic orientation, such that the d-QC resembles a faceted rod-like structure.

WK-9

Evolution of Defects During the Growth of SiC Substrates and Epilayers

Michael Dudley

Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY 11794

A review is presented of recent monochromatic and white beam synchrotron topography based studies of the evolution of defects during the growth of SiC substrates and epilayers. For the substrates, details of the evolution of the three-dimensional defect configurations in the PVT-grown substrate boules is presented. Analysis of the distribution, character and origins of grown-in c-axis screw dislocations (both hollow and closed-core), deformation induced basal plane dislocations (BPDs), and grown-in threading edge dislocations is discussed. Detailed topography analysis is also presented of the deflection onto the basal plane of c-axis threading dislocations of Burgers vector 1/3<11-20>, 1/3<11-23>, and [0001] which produces new types of dislocation sources [1] as well as some novel faulted defect configurations [2]. For the epilayers, a review is presented of Synchrotron X-ray Topography and KOH etching studies carried out on *n* type 4H-SiC offcut substrates before and after n^- homo-epitaxial growth to study defect replication and strain relaxation processes and identify the nucleation sources of both interfacial dislocations (IDs) and half-loop arrays (HLAs) which are known to have a deleterious effect on device performance [3,4]. In addition the value of *in situ* studies is demonstrated by a preview of the results of some recent high temperature deformation studies in SiC.

[1] H. Wang, F. Wu, S. Byrappa, S. Sun, B. Raghothamachar, M. Dudley, E.K. Sanchez, D. Hansen, R. Drachev, S.G. Mueller, and M.J. Loboda (2012). *Appl. Phys. Lett.* **100**: 172105-1–172105-4.

[2] M. Dudley, F. Wu, H. Wang, S. Byrappa, B. Raghothamachar, G. Choi, S. Sun, E.K. Sanchez, D. Hansen, R. Drachev, S.G. Mueller, and M.J. Loboda (2011). *Appl. Phys. Lett.* **98**: 232110-1.

[3] H. Wang, F. Wu, Y. Yang, J. Guo, B. Raghothamachar, M. Dudley, J. Zhang, G. Chung, B. Thomas, E.K. Sanchez, S.G. Mueller, D. Hansen, and M.J. Loboda (2014). "Gallium Nitride and Silicon Carbide Power Technologies 4," K. Shenai, M. Bakowski, M. Dudley, and N. Ohtani (Eds.), *ECS Tansactions* **64**(7): 213–222.

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WK-9

Unveiling Failure Mechanism of Lithium-ion Batteries

Zonghai Chen

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

Lithium-ion batteries have been the dominant energy storage devices for portable electronics, and are under serious development for emerging applications in transportation systems. However, the safety of lithium-ion batteries remains the major technological barrier for both applications. It is of our great interest to unveil the reaction pathways that can lead to the thermal runaway of lithium-ion batteries, and hence to provide insights to enhance the safety characteristics of lithium-ion batteries at the material level. Bearing this urgent need, *in situ* high energy x-ray diffraction (HEXRD) was utilized to investigate the thermal decomposition reaction of electrode materials with the presence of the non-aqueous electrolyte. In this talk, several unique applications of HEXRD for battery safety will be discussed.

WK-9

Visualization of Electrochemical Reactions in Battery Materials with X-ray Microscopy

Jordi Cabana

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

In this talk, I will discuss examples of the visualization of electrochemical phase transformations using a variety of modes within the general family of x-ray microscopy, tailored to suit the scales and phenomena to be probed, but focusing on single particles. The focus will be placed on emphasizing recent developments that bring about advances in spatial, chemical and temporal resolution. A brief discussion of the tradeoffs created by each advance will be presented. The ability to probe phenomena at increasing temporal resolution will be framed in the context of *operando* measurements. Because thermodynamic pathways can be controlled by the presence of electrical potential, the harvesting of a sample from a cycled battery, while providing a useful preliminary insight, can lead to misleading results due to the relaxation of components into a different state that is more stable under open circuit conditions. Therefore, measurements performed during the electrochemical reaction will be leveraged in this discussion. The mechanisms of transformation will be related to their impact on material and architecture properties.

WK-9

Understanding the Surface Chemistry of Battery Materials Using Synchrotron X-ray Spectroscopy

Feng Lin

Departments of Chemistry and MSE, Virginia Tech, Blacksburg, VA 24061

Chemical evolution and structural transformations at the surface of an electrode material influence greatly the key performance metrics of lithium batteries, including energy density, power capability, safety and cycle life. This presentation will discuss how we bridge the design principles of surface chemistry in electrode materials with advanced characterization tools, in pursuit of safer and durable lithium batteries. A high-throughput analytical method, based on synchrotron x-ray spectroscopy and transmission electron microscopy, is developed to investigate the surface phase irreversibility of lithium ion battery materials, a phenomenon that has been widely observed yet poorly understood. It is found that, in layered cathode materials, surface reconstruction from a layered to a rock-salt structure is commonly observed under a variety of battery operating conditions, particularly in high energy Ni-rich NMC compositions. This phenomenon, together with electrolyte decomposition and formation of a cathode electrolyte interphase, result in poor high-voltage cycling performance, impeding attempts to improve the energy density by widening the potential window at which these electrodes operate. These surface side reactions can be accelerated if micro-cracks are formed during cycling, an additional contributing factor to battery failure. Subsequently, we propose three methods to improve the surface stability of cathode materials, including selective surface metal segregation, surface coating and electrolyte formulation. Finally, the presentation will give a brief summary of how synchrotron x-ray analytical techniques have assisted the development of battery technologies.

Wednesday, May 10

APS/CNM Workshop 10
Multimodal, *Operando* Imaging Materials, Devices, and Architectures for Neuromorphic Computing

Location: APCF Auditorium

Organizers: Hua Zhou (APS), Yuzi Liu (CNM), Subramanian Sankaranarayanan (CNM), and Youssef Nashed (MCS)

Novel approaches and new concepts to break the fundamental limit of conventional semiconductor devices are urged in order to develop increasingly capable but self-sustaining electronics (e.g., scalable with packing density and foreseeable in energy consumption) in beyond Moore's computing era. New category of analog computing devices emulating neural networks in human brains ("neuromorphic computing") to create a new paradigm of energy efficient infrastructures has caught great attention in the recent decade. A suite of promising materials and devices are on the road for development and implementation, including memristive (either strong correlation or filament formation induced), spin-torques-based, phase-change-based, ferroelectric and tunneling-based, and even battery-inspired devices. However, most use strongly correlated, complex, heterogeneous materials and heterostructures that locally active to drive a dynamical or non-linear action signal. Thus, many open critical questions regarding fundamental material properties, device operational durability and architecture-level understanding remain much less explored, which set outstanding roadblocks for scalable and programmable neuromorphic implementations. Apparently, a full interrogation of the mechanistic picture underlying material transformation and device switching urgently calls for *operando* observation and microscopic characterization.

This workshop will discuss widely what state of art observation platforms and high throughput computational tools available and accessible at national facilities, in particular multiscale, multimodal and *operando* imaging capabilities (combing x-ray, electron and optical microscopies), can help to tackle some fundamental challenges in capturing evolving material states (like defects and ionic motions) in working devices for advancing the deterministic control, visualizing scalable fabrication with reproducibility, and understanding overall performance of architectures by design. The workshop will combine the recent advances in the understanding of neuromorphic computing oriented devices and systems by covering various aspects from applied research to basic science (including endeavors and contributions from the APS and CNM) and hope to bring together a group of experts from different research sectors that include physicists, materials scientists, electronic engineers and neuron scientists.

8:45–9:00	Supratik Guha (Argonne National Laboratory/University of Chicago) *Introductory Remarks*
9:00–9:30	Joshua Yang (University of Massachusetts, Amherst) *Diffusive Memristors for Neuromorphic Computing*
9:30–10:00	Wei Lu (University of Michigan) *Memristive Devices for Neuromorphic Computing*
10:00–10:30	John Paul Strachan (Hewlett Packard Laboratories) *Toward Use of Memristors for Computation*
10:30–11:00	Break
11:00–11:30	Charudatta Phatak (Argonne National Laboratory/Northwestern University) *TEM and X-ray Nanoprobe Studies of Nanoscale Resistive-switching Oxide Heterostructures*
11:30–12:00	Bilge Yildiz (Massachusetts Institute of Technology) *Beyond Electrostatic Effects at Oxide Hetero-interfaces: Electrochemical Phase Change, Strong Electric Fields, and Elastic Strain*
12:00–1:30	Lunch

1:30–2:00	Shriram Ramanathan (Purdue University) *Emergent Intelligence*
2:00–2:30	Junjing Deng (Argonne National Laboratory) *Non-destructive Nanoscale X-ray Ptychographic Imaging of Integrated Circuits*
2:30–3:00	Jerry Ziwen Wang (Stanford University) *Experimental Evidence of Significant Soret Diffusion in Filamentary RRAM Operation*
3:00–3:15	Break
3:15–3:45	Dillon Fong (Argonne National Laboratory) Operando *X-ray Studies of Oxygen Vacancy: Behavior in Complex Oxide Heterostructures*
3:45–4:15	Young-Sang Yu (Lawrence Berkeley National Laboratory) *Advanced X-ray Transmission Microscopy for Three-dimensional Chemical and Morphological Imaging of Single Li_xFePO_4 Particles*
4:15–4:45	David Guzman (Purdue University) *Modeling of Electrochemically Driven Resistance Change Materials*
4:45	Closing Remarks

WK-10

Diffusive Memristors for Neuromorphic Computing

Jianhua Joshua Yang

Department of Electrical and Computer Engineering, University of Massachusetts, Amherst, MA 01003

In the big data and IoT era, the need for faster and more energy efficient computing paradigms as well as high-density nonvolatile memories has become more and more urgent. Emerging devices are critical for fulfilling these computing needs. One of the promising emerging devices is memristor [1]. Numerous perspective applications have been proposed for memristive devices. However, each application emphasizes on different merits of device properties and imposes different challenges on device performance [2]. A practical solution to those challenges is to add another device to each of the memristor. For memory applications, this device is often called "selector", mainly employed to enable large memristor crossbar arrays by mitigating the so-called "sneak path current" issue with its nonlinear current-voltage characteristic. We have obtained over 1E10 nonlinearity in the newly developed diffusive memristors [3], which are essentially volatile threshold switches with tunable switching dynamics for different applications. In neuromorphic computing applications, the accumulation and extrusion of Ca^{2+} in the pre- and postsynaptic compartments play a critical role in initiating plastic changes in biological synapses. To emulate this fundamental synaptic dynamic process in electronic devices, we developed Ag-in-oxide diffusive memristors with a temporal response during and after stimulation similar to that of the synaptic Ca^{2+} dynamics. The diffusive memristor and its dynamics enable a direct emulation of both short- and long-term plasticity of biological synapses and provide a viable solution for the crucial synaptic dynamics in neuromorphic computing [4]. In addition, other applications using diffusive memristors for computing, such as true random number generators and leaky integration and fire neurons will also be discussed in this talk.

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WK-10

Memristive Devices for Neuromorphic Computing

Wei Lu

Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, MI 48109

Memristive devices have attracted significant interest in memory and computing applications. These two-terminal devices exhibit history-dependent, resistive switching behavior and operate on coupled electronic and ionic effects. I will discuss our efforts on the development

and optimization of memristive devices and integrated systems, including techniques of controlling the dynamic ionic migration processes and associated modeling efforts. Detailed TEM studies have been carried out to capture the ionic migration process and verify the switching mechanism. Functional high-density crossbar arrays have been integrated directly on top of CMOS circuits using a back-end-of-line (BEOL) process, enabling hybrid non-volatile memory and reconfigurable circuit applications. Properly tuned devices also exhibit incremental conductance changes that are analogous to the behaviors of biological synapses and are well suited for hardware-based, bio-inspired neuromorphic logic systems. Prototype neuromorphic circuits based on memristor arrays have been shown to be able to perform tasks such as pattern recognition in an unsupervised fashion for intelligent sensing, analysis and other data-intensive applications.

WK-10

Toward Use of Memristors for Computation

John Paul Strachan, Miao Hu, Suhas Kumar, Emmanuelle Merced-Grafals, and R. Stanley Williams
Hewlett Packard Labs, Hewlett Packard Enterprise, Palo Alto, CA 94304

The future acceleration of many computational workloads is expected to depend on novel architectures, circuits, and devices. I describe an effort utilizing the analog nature of memristor crossbar arrays to accelerate vector-matrix multiplication, which underpins many applications in image and signal processing, neural networks, and scientific computations. Significant improvement over CPUs, GPUs, and custom ASICs is anticipated using such systems. I describe our work spanning atomic understanding and engineering of memristors, integration with CMOS circuits, fine programming control over memristors, and a hardware platform for single time-step vector-matrix operations in fabricated memristor arrays.

Additionally, the underlying mechanism for the reversible resistance change in transition metal-oxide systems remains an active area of study, but involves an interaction of electrochemistry, ion motion driven by electric fields and concentration gradients, and interactions with thermal effects. Ultimately, any utilization of this technology depends critically on predictive and microphysically accurate device models, and I will describe our work in this area. While a complete physical understanding is still in development, I will describe some of the insights gained from direct measurements using structurally and chemically-sensitive techniques with nanoscale resolution such as x-ray spectromicroscopy.

WK-10

TEM and X-ray Nanoprobe Studies of Nanoscale Resistive-switching Oxide Heterostructures

Amanda Petford-Long[1,2], Seungbum Hong[1,3], and Charudatta Phatak[1]
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Elucidating the resistive switching behavior of binary oxide nanostructures involves gaining an understanding of how the changes in transport behavior are correlated with local changes to the structure and composition of the oxide. We have explored a number of binary oxides including NiO, CuO and TiO_2 and we will present data that show how correlating different x-ray, electron and scanning probe microscopies will modeling can lead to a fuller understanding of the transport behavior. We will present *in situ* TEM studies of the electroforming and resistive switching behavior of Pt/$NiO_{16\ nm}$/Pt heterostructures, in which the variation in microstructure of adjacent NiO regions, with a width of ~300 nm, lead to local variations in resistive switching behavior. The resistance change could be ascribed to the formation of conducting pathways during *in situ* TEM biasing, in which ordering of oxygen vacancies occurs [1]. We will further present results of experiments carried out at the APS on TiO_2 films, in which a novel photovoltaic effect induced by the incident x-ray beam led to a volatile change in resistance, with a subsequent non-volatile effect induced by the formation of conducting pathways across the irradiated area, observed using conducting AFM, and identified as Ti_4O_7 from cross-section HREM images [2].

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WK-10

Beyond Electrostatic Effects at Oxide Hetero-interfaces: Electrochemical Phase Change, Strong Electric Fields, and Elastic Strain

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Transition metal oxide hetero-interfaces are interesting due to the distinctly different properties that can arise from their interfaces, such as superconductivity, high catalytic activity and magnetism. These interfaces are the source for local heterogeneities in composition, atomic structure and electronic structure. Classically, defect redistribution is quantified at the continuum level by concurrent solution of Poisson's equation for the electrostatic potential and the steady-state equilibrium drift-diffusion equation for each defect. It is possible to inform this level of modeling with first principles calculations of band off-sets, and defect formation and segregation energies at thermodynamically relevant conditions. This approach had numerous successful implementations, including the quantification of charge transport properties at surfaces and grain boundaries.

In this talk, I will discuss three phenomena that also need to be considered in a broader framework of defect structures and distributions at oxide hetero-interfaces.

1. Presence of strong electric fields that can cause polarization of defective systems and affect the defect abundance and structure. We have assessed this effect on neutral oxygen vacancies in simple binary oxides from first principles calculations.
2. Phase change under the effect of local electrostatic potential because of a change in the electrochemical potential of oxygen. We have assessed the ability to trigger phase change electrochemically in two classes of oxides, SrCoOx and VOx, and have quantified the phases and the corresponding distinctly different electronic properties by combining *in operando* x-ray diffraction and x-ray photoelectron and absorption spectroscopy. The results have implications both for oxide hetero-interfaces and for oxide electronic devices that aim to control properties electrically.
3. Elastic strain, that affect the stability and mobility of defects. In this recent work, we have focused on the stability of electronic defects, specifically the electron polarons versus free electrons SrTiO3, as a function of temperature and hydrostatic stress, by combining first principles calculations and quasi harmonic approximation. Our results demonstrate that it is possible to control the type of electronic defect, and so the transport properties, by means of electro-chemo-mechanics.

WK-10

Emergent Intelligence

Shriram Ramanathan

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Cooperation and conflict are essential factors in survival, evolution and adaptation of species. First, I will discuss a few examples from animal colonies discussing specific collective behavioral patterns from field observations by biologists. I will then give examples of how evolutionary forces can be adapted in our quest to mimic features from the natural world in designing artificial brains. I will outline a vision for a new branch of enquiry in advanced materials that display emergent electronic phases that allow us to bridge fact and fiction in the pursuit of artificial life and humanoids.

Collaborators and funding will be acknowledged in the presentation.

WK-10

Non-destructive Nanoscale X-ray Ptychographic Imaging of Integrated Circuits

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Modern integrated circuits (ICs) employ a myriad of materials organized at nanoscale dimensions, and certain critical tolerances must be met for them to function. To understand departures from intended functionality, it is essential to examine ICs as manufactured ideally in a nondestructive way. Ptychography is a scanning version of coherent lensless imaging technique that allows the imaging of extended sample with spatial resolution

better than the focusing optics. Using multi-keV x-rays that provide greater penetration, we show that x-ray ptychography can be used to image circuit details with sub-20-nm resolution through an unprocessed, a few hundred microns thick silicon wafer [1]. By using continuous x-ray scanning [2], massively parallel computation [3], and a new generation of synchrotron light sources, this should enable entire non-etched ICs to be imaged to 10-nm resolution or better.

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WK-10

Experimental Evidence of Significant Soret Diffusion in Filamentary RRAM Operation

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Resistive random access memory (RRAM) is a promising building block for energy efficient and massively parallel neuromorphic computing systems. Understanding the microscopic forces governing atomic motion is the key to fully understanding RRAM device physics. Among the various microscopic forces in filamentary RRAM operation, the significance of Soret diffusion (driven by local temperature gradient, also known as thermophoresis or thermodiffusion) has been relatively unclear due to lack of experimental evidence. This talk focuses on the experimental evidence indicating that Soret diffusion could be important in filamentary RRAM operation. In the first part of the talk, we show evidence of significant Soret diffusion from observation of radial oxygen migration by transmission synchrotron x-ray spectromicroscopy. In the second part of the talk, we show investigation of temperature-dependent switching dynamics of filamentary RRAM, which reveals the significance of Soret diffusion. Our study indicates that Soret diffusion can play an important role in filamentary RRAM operation, and therefore should be taken into consideration in the study of filamentary RRAM devices.

WK-10

Operando X-ray Studies of Oxygen Vacancy: Behavior in Complex Oxide Heterostructures

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Despite the difficulty of tracking oxygen vacancies by x-ray methods, this is one of the few techniques able to monitor their behavior *in situ*. In this presentation, I will discuss recent experiments focused on understanding vacancy behavior at surfaces and interfaces, under applied electric fields, and in electrochemically active environments, often in tandem with electrical transport characterization.

WK-10

Advanced X-ray Transmission Microscopy for Three-dimensional Chemical and Morphological Imaging of Single Li_xFePO_4 Particles

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The demand for tools for the chemical imaging of battery processes with ever increasing chemical and spatial resolution is rising because the processes involved in the reaction occur at length scales that span the atomic to the macro scale. The observation of phase transformations relevant to battery electrodes in single crystals of varying sizes can help identify kinetic limitations to utilization and durability, as well as the existence of non-trivial size effects. Such detailed insight can be employed in the rational design of next generation materials which can achieve the theoretical limits of storage density and life of the materials. Techniques that afford high chemical resolution at the nanoscale are ideally suited for this goal. Soft x-ray ptychographic microscopy combined with x-ray absorption spectroscopy (XAS) is a powerful suite which affords chemical and structural information on large volumes of material at spatial resolutions better than 5 nm [1]. However, to date, this technique has been intrinsically limited to 2-dimensional observations in transmission mode, which causes complications during interpretation, especially in the case of overlapped particles, because the projection images represent an average over the x-ray penetration path within the crystals.

In this study, soft x-ray tomography combined with ptychography, developed at beamline 5.3.2.1 at the Advanced Light Source (Berkeley, CA) is applied to assess the chemical and morphological consequences of electrochemical delithiation of aggregated nano-sized lithium iron phosphate ($LiFePO_4$) plates. Our work provides quantitative analysis of oxidation states in 3-dimensions at the 10 nm scale. After segmentation, statistical analysis of the chemical phase for any given individual particle was achieved, and information was extracted of the particle interior. The ability to visualize the nanoscale chemical state distribution over functional volumes will revolutionize the study of energy storage materials and enable the design of optimized morphologies for the next generation of devices.

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WK-10
Modeling of Electrochemically Driven Resistance Change Materials

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Resistance- and *threshold-switching* electrochemical cells are fascinating devices that can reversibly or irreversibly change their electrical resistance under an applied electric field via a variety of processes induced by electrochemistry [1–3]. These devices are of interest in field of nanoelectronics for emerging memory technologies. Their deceptive simple structures, metal-insulator-metal, hide a variety of coupled, processes that govern their operation, from electrochemical reactions at interfaces, diffusion and aggregation of ionic species, to electron and hole trapping and Joule heating. Despite the significant experimental and theoretical efforts devoted to these devices in recent years the underlying materials processes responsible for their remarkable properties remain unknown.

We developed a new model to capture the effect of external electrostatic potentials in reactive molecular dynamics simulations and applied it to simulate the operation of a resistance switching electrochemical metallization cell that operate via the formation and dissolution of metallic filaments that bridge the two electrodes. The simulations predict the ultrafast switching observed in these devices, with timescales ranging from hundreds of picoseconds to a few nanoseconds for devices consisting of copper as active electrode and amorphous silicon dioxide as dielectric and dimensions corresponding to the scaling limits of this technology. Our results indicate that the formation of stable filaments involves the aggregation of ions into small metallic clusters, followed by a progressive chemical reduction as they become in contact with the cathode. I will present an *ab initio* molecular dynamics study of the structural, electronic, and transport properties of copper-containing germanium-based chalcogenide glasses. These mixed ionic-electronic materials exhibit resistance or threshold switching based on slight changes in chemical composition. Our results show that copper dissolution energies explain the tendency of copper to agglomerate in telluride glasses, consistent with filamentary conduction. In contrast, copper is less prone to clusterize in sulfides and selenides leading to threshold-type of conduction where the nature of transport is mainly attributed to electronic mid-gap states derived from polar chalcogen bonds.

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