APS / CNM 2023 Users Meeting

April 17-21, 2023 and May 1-5, 2023

The 2023 APS/CNM Users Meeting will gather scientists and engineers from diverse fields of research from around the globe to discuss cutting-edge, mission-driven research. The event will feature plenary sessions, workshops, poster sessions, and a vendor expo.

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The Structure of Everyday Life: How the Materials Around us are Structured

Thomas C. Fitzgibbons[1*], Michelle Mejia[1], John Riley[1], Dan Ye[1], Shouren Ge[1], Kaoru Aou[1], Jeff Munro[1], Daniel Miller[1], Keran Lu[1], Lucia Bivona[1]

The Dow Chemical Company, Freeport, TX 77541

Richard Feynman tells a story about beauty and how an artistic friend of his commented that as a scientist Feynman could not see the beauty in the world because he always took things apart and made them mechanical. Feynman mentioned how beauty exists at many levels and as you take things apart you can see the beauty at each level. When viewing the structure of materials a similar corollary can be drawn. As consumers, we often think about the function of a material: is the bed or seat comfortable, does my shampoo and laundry detergent clean effectively, will my garbage bag rip. It is often the underlying structure that exists at the micro and nanoscales that dictates the observed performance. At Dow, our team is interested in understanding the structure of materials in order to accelerate the development of products with improved performance. In this talk, I will walk you through a day in the life to examine the structure and performance of a number of materials that we interact with everyday. Much of the work shown here was done at either the Advanced Photon Source or Dow’s electron microscopy facility.

Making, Measuring, and Modeling Metallic Alloys: Insights from *In-situ* Characterization

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Understanding structure-processing-property-performance relationships of metallic alloys is critical to their manufacture and use in extreme environments. Significant opportunity exists to employ emerging manufacturing technologies like additive manufacturing (AM) and *in-situ* characterization to link processing conditions to metallic alloy microstructural development and microstructural characteristics to properties like never before. Here we highlight examples where synchrotron x-rays have enabled the acquisition of critical, time-resolved information to obtain new insights into metallic alloys during processing or deformation. Specifically, we highlight *in-situ/ex-situ* characterization and modeling of metallic alloys during directional solidification and under AM conditions to inform model predictions and the control of microstructural development during processing. Synchrotron x-ray imaging and diffraction of metastable microstructures during high strain rate deformation also permits the identification of deformation mechanisms to design novel alloying, processing, and microstructural and property design strategies. Studies such as these enable the advanced manufacturing of metallic alloys and evaluations of performance in extreme environments.

Synchrotrons for Solid-state Batteries

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Next generation energy storage systems will need to leverage high energy density anodes, like Li to achieve the required performance metrics (longer vehicle range, long life, production costs, safety). Solid electrolytes (SEs) are promising materials for achieving these metrics by enabling Li metal anodes and high voltage cathodes, but SE cells suffer from poor coulombic efficiencies as well as lifetimes which impede their integration into EVs. In this talk I will detail my I will discuss my journey with APS and synchrotron x-rays to develop *in situ* characterization tools for probing the dynamic processes occurring at the buried solid | solid interfaces in these solid-state batteries. I will discuss several promising solid electrolytes and their underlying processing-structure-function relationships to elicit the mechanisms of failure within these systems. Electrolyte structure anisotropy is identified to be a key factor that initiates failures in solid electrolytes. Finally, I will discuss potential research questions of fundamental interest with regards to solid | solid interfaces that can benefit tremendously from directed efforts of leveraging x-rays post the APS upgrade.

Update on the APS Upgrade Project

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The Advanced Photon Source (APS) is undergoing a comprehensive upgrade that will increase the brightness of the x-ray beams generated by up to 500 times. With enhanced coherence and focusing abilities, the upgraded APS will open the door to new scientific discoveries and will maintain the APS's world-leading position as an x-ray science facility. A year-long pause in operations to enable the removal of the original storage ring and installation of the new state-of-the-art multi-bend achromat lattice begins on April 17. As the project moves into this new phase, Project Director Jim Kerby will provide an update and a look ahead.

Creating a Universe in a Grain of Sand: Nanocrystals, Nanorods and Nanowires Synthesis and Assembly

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Chemical routes now exist to produce nanocrystal materials with a wide range of size, shape, and composition. These materials have characteristic dimensions that are at least 1,000 times smaller than a human hair and exhibit a wide range of unique properties due to their size. For example, semiconductor nanocrystals or quantum dots exhibit size-tunable optical properties that are useful for light-emitting and light-absorbing applications. Semiconductor nanowires have attributes of polymers like mechanical flexibility combined with the useful electronic and optical properties of semiconductors in one material. This presentation will highlight some of our recent work in the synthesis and self-assembly of silicon, germanium, HgTe and lead halide perovskite nanomaterials, into superlattices and films, and their use in applications ranging from biological cell imaging to paper solar cells to infrared photodetectors.

Building with Artificial Atoms: Structural and Functional Studies of Multifunctional Nanomaterials Created by Multiscale Nanocrystal Self-assembly

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The synthesis of monodisperse colloidal nanocrystals (NCs) with controlled composition, size, and shape provides ideal building blocks for assembling new thin films and devices. These monodisperse colloidal NCs act as "artificial atoms" with tunable electronic, optical, and magnetic properties that allow the development of a new periodic table for design at the mesoscale. In this talk, I will briefly outline the current state of the art in synthesis, purification, and integration of single-phase NCs and core-shell (heterostructures) NCs emphasizing the design of semiconductor building blocks with tunable shapes (spheres, roads, cubes, discs, octahedra, etc. I will then share how these tailored NCs can be directed to assemble into single-component, binary, ternary NC superlattices providing a scalable route to producing multifunctional thin films. The modular assembly of these NCs allows the desirable features of the underlying quantum phenomena to be enhanced even as the interactions between the NCs allow new delocalized properties to emerge.

The discussion will highlight the power of combining advanced electron microscopy, tomography, and crystallography with *in-situ* and *ex-situ* synchrotron-based scattering (SAXS, WAXS) and absorption (EXAFS), especially in the interrogation of extended NC-based superstructures. Synergies in electronic, optical coupling between NCs will be emphasized as we push toward realizing artificial solids with new 3D structures that reach from the nanoscale to the micron scale, where additional photonic resonances can be identified and harnessed. I will share recent developments in the colloidal generation and characterization of 3D "superparticles" comprised of a selected combination of monodisperse NCs. I will present specific case studies in thin-film transistors, solution-processable films, and optical devices and demonstrations of tunable microcavity lasing in strongly coupled NC Superparticles.

In the final section of the talk, I will discuss multiscale hetero-integration in service of catalysis. I will present our progress in co-assembling NCs for targeted applications in heterogeneous catalysis and electrocatalysis, focusing on size and shape-selective chemical activity for the oxygen reduction reaction (ORR) and biomass upgrading hydrodeoxygenation (HDO). Recent examples will be shared, highlighting the use of magnetic oxide and intermetallic heterostructured NC catalysts with the potential for inductively enhanced catalytic activity.

Accelerating *In Situ* Mesoscale Materials Characterization Using Machine Learning

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Developing advanced materials with tailored properties requires a deep understanding of the relationship between materials structure and properties at the mesoscale. However, slow data acquisition and analysis are major constraints for impactful *in situ* mesoscale materials characterization experiments. In this talk, we will present a novel approach to address these challenges using advanced data analysis frameworks that combine machine learning techniques, micro-mechanics simulations, and adaptive model-independent optimization methods to enable real-time feedback during microstructure evolution studies. We will present three case studies on the application of machine learning methods for faster data reconstruction for electron backscatter diffraction microscopy, Bragg coherent diffractive imaging, and high-energy x-ray diffraction microscopy. Finally, we will discuss the challenges and future opportunities in employing machine learning methods for materials characterization.

Design of Functional Multicomponent Nanoporous Metal Oxides and their Heterostructures Using Polymer Templates

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Robust and efficient process for synthesis of various composition inorganic coatings with controlled nanoporosity and structure is highly desirable for design of efficient catalytic, purification, and detection systems. Recently, infiltration of a nanoporous polymer template with inorganic precursors using sequential infiltration synthesis with inorganic vapor precursors followed by oxidative annealing was proposed as a new and efficient approach to create porous inorganic structures with tunable porosity and composition. The major limitations of the original water-based thermal sequential infiltration synthesis, though, are the thickness of the patterned structure being limited by vapor penetration depth of the precursors into the polymer template and the resulting material selection being restricted by the availability of high vapor pressure precursors. Here, we propose a swelling-based modification to the polymer infiltration process that allows to overcome these limitations. We summarize the basics of the multi-step infiltration approach, the structure and properties of the resulting materials, and their functional potential for practical applications. We report ultra-high accessibility of the pores when porous films are prepared via the polymer swelling-based infiltration synthesis (SBI). Using a quartz crystal microbalance (QCM) technique, we demonstrate increased solvent absorbing capabilities of highly porous ceramic films as a result of high interconnectivity of the pores in such structures. Our results show that the approach can be extended toward preparing conformal coatings, freestanding membranes, and powders consisting of metal or metal oxide nanoparticles embedded in a porous oxide matrix.

The authors acknowledge the support of this work by the National Science Foundation, Award No. 2045662. The work at the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, and Division of Chemical Sciences, Geosciences, and Biosciences under Contract No. DE-AC0206CH-11357.

Electronically Integrated Autonomous Microscopic Robots

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What would we be able to do if we could build electronically integrated machines the at a scale of 100 microns? At this scale, semiconductor devices are small enough that we could put the computational power of the spaceship Voyager onto a machine that could be injected into the body. Such robots could have on board detectors, power sources, and processors that enable them to sense, interact, and control their local environment. In this talk I will describe several cutting-edge technologies we are developing to achieve this vision.

CNM WK#1: Nanomaterials Interfaces: from Fundamentals to Applications

Organizers: Elena Rozhkova and Richard Schaller

The directed evolution of the properties of a new material, either at the level of a single nanostructure or integrated into a hybrid or device, is inevitably associated with the formation of interfaces. As an integral part of virtually any material design, interface development covers a wide range of fundamental research and applied areas, blending approaches from physics, chemistry, materials, and life sciences. Thus, the properties of the interface determine the transfer of energy, charge, and spin through nanostructured materials. The fabrication of batteries and fuel cells involves the detailed interfacing of several materials at the electrodes to achieve high performance. Semiconductor-semiconductor or semiconductor-metal interfaces also prescribe charge transfer processes for photovoltaic or photocatalytic response. Further, the nanomaterial - biological entity interface requires educated approaches to combine them into functional hybrids and optimize surface properties for biolectronic, sensors and biomedical applications.

The nanomaterial interfaces engineering requires advanced characterization tools, synthetic and fabrication approaches, and computational methods. The purpose of this workshop is to present major trends in interface research and discuss the tools, expertise, and approaches that the Center for Nanoscale Materials can bring to the wider scientific community.

This workshop will cover but not be limited to the following areas:

- Modeling of interfaces toward applications
- Fundamental aspects of nanomaterial interfaces
- Synthesis of novel nanomaterials with optimized interfaces (e.g., defects, doping, band gap engineering etc.)
- Characterization of nanomaterial interfaces
- Interfaces in nanomaterial-design for application in (electro/photo) catalysts, batteries, fuel/solar cells, (opto)electronic devices, (bio)sensors, and biomaterials.

Colloidal Nanocrystals to Advance Catalysis and Energy Technologies

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Affordable clean energy and climate action are two of the sustainable development goals set by the United Nations to be achieved by 2030. The vast majority of energy technologies relies on nanomaterials and their progress is strongly connected to the ability of material chemists to tune their property and function-dictating features (i.e. size, composition, composition, morphology, interfaces).

In this talk, I will present our recent group efforts towards the synthesis via colloidal chemistry of atomically defined nanocrystals (NCs) with properties of interest for catalysis and energy conversion.

The first part will focus on our studies on the synthesis of Cu-based nanostructures which serve as ideal platforms to advance our current knowledge towards improved selectivity in the electrochemical CO2 reduction reaction. I will then share our results evidencing that these NCs can sustain their catalytic activity and selectivity at technologically relevant conditions, therefore might also offer practical solutions.

The second part will be dedicated to our colloidal atomic layer deposition (c-ALD) method to grow tunable oxide shells around different inorganic NC cores. In addition to preserve their colloidal stability, these oxide shells confer the NC with improved stability and enable further functionalization and post-processing. I will discuss the formation mechanism of the shell by sharing our insight into the surface chemistry. I will then present how we manipulated the growth process in order to incorporate an assortment of photoactive ligands as integral components of the metal oxide shell, which creates organic/inorganic hybrid structures with potential applications as photocatalysts and sensitizers for incoherent photon conversion.

Light-induced Interfacial Interactions in Mixed Dimensional Van der Waals Heterostructures

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Mixed dimensional heterostructures incorporating atomically thin transition metal dichalcogenides (TMDs) and non-Van der Waals nanomaterials provide interesting physics at low dimensions and beyond that of pristine TMDs. Of particular interest to us are light stimulated interfacial phenomena such as energy transfer and charge carrier transfer that help enhance light harvesting and/or charge carrier generation in the TMDs. Using concepts of self-assembly, we discuss mixed dimensional heterostructures with tunable interfacial interactions through bandgap engineering, morphology engineering, and external factors control, while utilizing nanomaterials like colloidal quantum dots, nanowires and light harvesting proteins.

Part of the research presented here used resources of the Center for Functional Nanomaterials (CFN), which is a U.S. Department of Energy Office of Science User Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

Spectroscopic Measurements of Heat Transfer at Organic-inorganic Nanoscale Interfaces

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Transport of thermal energy at nanoscale interfaces imposes practical limitations on optoelectronic devices such as LEDs or lasers. Direct measurements of interfacial thermal conductance in semiconductor nanoparticle systems are not, however, straightforward. This presentation will discuss ultrafast spectroscopic measurements to vibrationally excite organic ligand coatings on semiconductor nanoparticles and probe heat transfer processes into the particle with precision as good as 0.1 K. Thermal energy transfer is observed in the quasi-equilibrium regime, in which phonon occupation has a well-defined temperature, and the non-equilibrium regime, in which high-energy phonons are populated on a much slower time-scale. These infrared pump, electronic probe measurements may be used to extract through-bond thermal conductance from the ligand coating to the inorganic core and the slower dissipation of heat to the surroundings, such as solvent. Results comparing dependence on size and shape, fluence, temperature, and ligand coverage will be presented.

This work was performed at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, and supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.

Driving Redox Enzyme Catalysis with Photoexcited Nanocrystals

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The synthetic tunability of electronic structure and surface chemistry of semiconductor nanocrystals make them attractive light absorbers for light-driven chemistry. A variety of architectures have been constructed where nanocrystals are coupled with multielectron redox catalysts to drive reactions like H_2 generation, CO_2 reduction, N_2 reduction, and water oxidation with light. In these systems, light absorption in nanocrystals is followed by charge transfer to catalysts, which then use them for redox transformations, and/or to sacrificial carrier scavengers. Interfacial charge transfer between the nanocrystal and the catalyst and its competitiveness with other relaxation pathways in nanocrystals are of paramount importance to the overall photochemical reactivity. In this talk, I will focus on our efforts to elucidate both the kinetics of charge transfer and the kinetics and mechanisms of the competing photophysical pathways in nanocrystal-based systems for light-driven multielectron chemistry. This work entails transient absorption spectroscopy measurements and extensive kinetic modeling to extract rate constants of relevant processes in these heterogeneous systems.

Interfaces in Organic Photovoltaics

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Organic solar cells (OSCs) feature several advantages for application in flexible and portable devices such as low cost, light weight, and large area printable fabrication. The power conversion efficiency of single junction OSCs has surpassed 19%, largely due to development of new materials for the photoactive layer (PAL) and the charge transport layers (CTLs). Here we will explore energy level alignment at PAL donor:acceptor heterojunctions and PAL/CIL/electrode interfaces relevant to state-of-the-art OSCs. We utilize the Langmuir-Schäfer technique to map the energy level alignment at well-defined donor-acceptor interfaces, thus avoiding the problem of intermixing. By using UPS, AFM and NEXAFS we track the evolution of the energy landscape and its correlation to molecular orientation monolayer-by-monolayer. We demonstrate significant and abrupt vacuum level shifts at the donor:acceptor interfaces, in contrast to the vacuum level alignment assumption commonly used in literature. We further show that the vacuum level shifts reshuffle the energy level alignment inferred from neat materials, resulting in reduced interfacial energetic offsets and increased charge transfer state energies in the corresponding OSC devices. These findings rationalize the co-existence of efficient charge separation and small voltage losses in non-fullerene OSCs.[1] We further discuss energy level alignment at metal/organic semiconductor contacts and how CTLs can tune both work function and the electrostatic interaction between the organic semiconductors of the PAL and the metal electrodes.[2]

[1] "Mapping the energy level alignment at donor/acceptor interfaces in non-fullerene organic solar cells", Xiane Li, Qilun Zhang, Jianwei Yu, Ye Xu, Rui Zhang, Chuanfei Wang, Huotian Zhang, Simone Fabiano, Xianjie Liu, Jianhui Hou, Feng Gao, and Mats Fahlman; *Nature Communications*, 13 (2022) 2046.

[2] "Interfaces in organic electronics", Mats Fahlman, Simone Fabiano, Viktor Gueskine, Daniel Simon, Magnus Berggren, and Xavier Crispin, *Nature Reviews Materials*, 4 (2020) 627.

Hybrids of DNA and Single Walled Carbon Nanotubes (SWCNT)

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We will describe the DNA/SWCNT system. DNA forms a strong hybrid with SWCNTs, rendering them dispersible in aqueous media, thus enabling a number of applications including SWCNT sorting and development of biosensors. In this talk, we will describe what we know about the physical properties and structure of these hybrids. We will also describe their use in biosensing applications, including recently developed analyte-agnostic trainable nanosensor arrays for diagnostic applications.

Chirality-complexity Relations for Nanostructures

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Chiral nanostructures are a large and rapidly evolving class of multifunctional materials. Besides fascinating optical, catalytic, and biological properties, the studies of chiral nanostructures revealed something more. Unlike other geometric properties, mirror asymmetry is invariant to scales. Analysis of the hierarchically organized micro- and macrostructures obtained by the self-assembly of chiral nanoparticles demonstrated the mechanism of the emergence of *effective complexity* in such systems. These findings became possible by applying graph theory (GT) for the calculation of their complexity measures by describing the constituent NPs as nodes and the interfaces between them as edges. Taking an example of hierarchically organized particles with twisted spikes from polydispersed Au-cysteine nanoplatelets [1], we found that the:

(a) formation of complex structures does not require monodispersity;
(b) complexity of synthetic particles can be higher than biological prototypes; and
(c) complexity emerges from competing chirality-dependent assembly restrictions.

The GT description of chiral hedgehog nanoparticles can be expanded to include other nanoscale structures, such as complex porous particles and open superlattices [2], creating analogs of chemical formulas for particle systems.

The analysis of chirality-complexity relations leads to the design of chiral nanoparticles with hierarchical asymmetry and self-assembled particle systems for enantioselective catalysis [3,4], immune modulation [5], and machine vision [6,7].

[1] W. Jiang, et al., Emergence of Complexity in Hierarchically Organized Chiral Particles, *Science*, **2020**, 368, 6491, 642-648.
[2] S. Zhou, et al, Chiral assemblies of pinwheel superlattices on substrates, *Nature,* **2022,** 612, 259-265.
[3] R. Gao, et al., Site-selective proteolytic cleavage of plant viruses by photoactive chiral nanoparticles, *Nature Catalysis*, **2022**, 5, 694-707.
[4] S. Li, et al., Single- and Multi-Component Chiral Supraparticles As Modular Enantioselective Catalysts, *Nature Comm*, **2019**, 10, 4826.
[5] L. Xu, et al., Enantiomer-Dependent Immunological Response to Chiral Nanoparticles, *Nature*, **2022**, 601, 366-373.
[6] J. Cai, et al., Polarization-Sensitive Optoionic Membranes from Chiral Plasmonic Nanoparticles, *Nature Nanotechnology*, **2022**, 17, 408-416.
[7] P. Kumar, et al. Photonically Active Bowtie Nanoassemblies with Chirality Continuum, *Nature,* **2023**, 615, 418.

Structure and Dynamics at Metal Electrode/Electrolyte Interface Probed by *In Situ* Electrochemical Surface Enhanced/Selective Vibrational Spectroscopic Methods

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Structure and dynamics of electric double layer (EDL), the sub-nanometer region at the electrode/electrolyte interface, are essential to the function and performance of many energy conversion and storage devices, ranging from electrolyzers, photoelectrochemical cells, fuel cells to batteries. *In situ* probe of the EDL structure and dynamics at the molecular level requires advanced molecular spectroscopic tools with interfacial sensitivity and/or selectivity. In this talk, I will discuss three recent studies in developing and applying vibrational sum frequency generation (VSFG) spectroscopy and surface enhanced Raman spectroscopy (SERS) as powerful in situ interface specific/sensitive vibrational spectroscopic tools. 1) Using combined VSFG and DFT calculation, we determine the binding structure of a molecular CO2 reduction catalyst on metal electrodes and interfacial electric field profile in the EDL, revealing surprisingly large electrode induction effects on molecular catalyst. 2) Using combined SERS and MD simulation, we obtain an atomistic view of the structure of solvent and ion molecules at the EDL, revealing an unconventional interfacial water structure change at high negative electrode polarizations in water-in-salt electrolytes. 3) Using time-resolved VSFG, we directly measure hot electron transfer induced vibrational dynamics of adsorbates on metal electrodes, suggesting the possibility of plasmon (or light)-enhanced electrochemistry.

Ultrafast Probes of Interfacial Charge and Lattice Dynamics

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I will describe recent ultrafast electron scattering and THz emission studies probing coupled charge and lattice dynamics in two-dimensional heterostructures. Our studies provide direct information about the time-scales and mechanisms for charge transfer, phonon, and energy transport across 2D atomic junctions.

Biologically Inspired Strategies for Interfacial Control in Nanomaterials

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Sessile marine organisms are very effective at adhering to wet substrates in harsh, turbulent environments. The proteins employed by mussels, for example, have very specialized compositions that make them well-suited to the challenges of achieving permanent adhesion in the wet marine environment. Mussel adhesive proteins (MAPs) are known to contain high levels of 3,4-dihydroxy-L-alanine (DOPA), a catecholic amino acid that is believed to confer cohesive and adhesive properties to these proteins. In this talk I will summarize the roles of DOPA in wet biological adhesion and introduce some of our efforts to exploit synthetic catechol containing molecules and polymers for control of interfacial properties in biomimetic coatings and nanomaterials. Synthetic mimics of MAPs take the form of linear or branched polymers with catecholic endgroups or side chains, where the catechols serve the role of a surface anchor for attachment to surfaces. These polymer coatings are able to confer a variety of functional properties to materials. For example, with appropriate design one can either encourage or discourage interfacial interactions between dissimilar materials, or between materials and biomolecules.

The Chiral-induced Spin Selectivity (CISS) Effect: From Electron Transfer in Biology to Spintronics

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Spin based properties, applications, and devices are commonly related to magnetic effects and to magnetic materials. However, we established that chiral organic molecules can act as spin filters for photoelectrons transmission, in electron transfer, and in electron transport. The effect, termed Chiral Induced Spin Selectivity (CISS) [1], has interesting implications for the production of new types of spintronics devices [2] and on the importance of chiral molecules in biological systems [3]. The basic effect, and its applications and implications, will be presented.

[1] T. K. Das, F. Tassinari, R. Naaman, J. Fransson, The Temperature-Dependent Chiral-Induced Spin Selectivity Effect: Experiments and Theory. *J. Phys. Chem. C*, **126**, 3257−3264 (2022).
[2] S.-H. Yang, R. Naaman, Y. Paltiel, S. Parkin, Chiral spintronics, *Nat. Rev. Phys*. **3**, 328–343 (2021).
[3] R. Naaman, Y. Paltiel, D. H. Waldeck, Chiral Induced Spin Selectivity and Its Implications for Biological Functions, *Annu. Rev. Biophys*. **51**, 99-114 (2022).

Non-genetic Biological Modulation: Harnessing the Power of Semiconductors at All Length Scales

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Semiconductors have emerged as powerful tools in electronic and photonic biointerface studies, enabling the development of multifunctional devices such as sensors, modulators, and switches. Our research aims to provide a non-genetic solution for biological modulation at all length scales. By leveraging the interaction of light with semiconductor materials and devices, we have developed a series of biological modulation methods that enable multiplexed and patterned stimulation with high flexibility and spatial resolution, all without the need for excessive wiring. Our studies have shown how the photothermal, photofaradic, and photocapacitive effects of nanostructured semiconductors can be identified, quantified, and utilized to modulate neural, cardiac and microbial activities at semiconductor-based biointerfaces. Unlike current metal electrode-based devices, these materials-based methods are non-genetic and free-standing, overcoming many limitations in current approaches.

In this presentation, I will discuss recent research findings from our laboratory, including a novel nanoporous/non-porous heterojunction that improves optical modulation biointerfaces. This heterojunction enables non-genetic pulse stimulation of tissues in vivo with light intensity similar to that used in optogenetics. Additionally, we will present preliminary results on the use of electrically or photoelectrochemically produced subcellular components, including extracellular vesicles and intracellular liquid condensates, for regenerative medicine in excitable tissues. In my concluding remarks, I will unveil our future research directions that have the potential to revolutionize the field of biological modulation at all length scales.

APS WK#2: Bright Perspectives of Inelastic X-ray Scattering in the Post-APS-U Era

Organizers: Jiyong Zhao, Ayman Said, Ahmet Alatas, Jungho Kim, Michael Hu, and Ercan Alp

The Advanced Photon Source is home to various state-of-the-art high-resolution inelastic x-ray scattering (IXS) methods. Among them, momentum-resolved meV inelastic x-ray scattering, resonant inelastic x-ray scattering, and nuclear resonant inelastic x-ray scattering methods all have dedicated beamline at APS. These spectroscopy techniques are powerful in providing unique information on atomic dynamics and electronic excitations in condensed matter under ambient and extreme thermodynamic conditions. These methods are growing and have gained popularity in the last decade and have many reasons to look forward to the realization of the APS Upgrade project. The timing of the workshop coincides with the start of the APS upgrade's shutdown which will help users be informed about the new APS ring and stay engaged.

The workshop will be run in three half-day sessions, focusing on resonant inelastic x-ray scattering (RIXS) at 27-ID, momentum-resolved high energy resolution inelastic x-ray scattering (HERIX) at 30-ID and nuclear resonant scattering (NRS) at both 3-ID and 30-ID, respectively. The status, future development, and user applications at the post-APS-U period will be presented and discussed.

APS-U and Sector 30 Beamline Update

Ahmet Alatas[1]

[1]Advanced Photon Source, Argonne National Laboratory, Lemont, IL 60439

Inelastic x-ray scattering is a unique technique that has increasing impact in addressing lattice dynamics related issues in wide range of scientific areas including condensed matter physics, geophysics and biology.

In this talk, an overview of the high-energy resolution momentum resolved IXS program at sector 30 will be presented.[1,2] New APS ring and future developments under APS-U enhancement project will be discussed.

[1] Said A.H. *et.al.*, J. Synch. Rad. **27**, 827, (2020)
[2] Toellner T.S. *et.al.*, J. Synch. Rad. **18**, 605, (2011)

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High-pressure Studies of Kagome Magnets

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Kagome lattice system has attracted great research interest as a platform for frustration-driven exotic spin liquid phases, lattice-driven massive Dirac fermions and dispersionless flatbands. In flat bands the kinetic energy of electrons is quenched while the Coulomb repulsions prevail, leading to emergence of exotic quantum phases such as ferromagnetism, fractional quantum Hall effect, and high T_C superconductivity. Materials with Kagome lattice including of 3*d* transition elements allows introduction of magnetism, which provides a versatile test ground for correlated topological phase hosting symmetry protected electronic excitations and magnetic ground state. We have applied external pressure to tune the binary Dirac-Kagome metals, Fe_3Sn_2 and FeSn and investigate the interplay of strong interacting frustrated magnetism, crystal structure, and lattice dynamics. In this talk, I will discuss our recent experimental results from x-ray diffraction, time-domain synchrotron Mössbauer spectroscopy, and nuclear resonant inelastic x-ray scattering in ^{57}Fe and ^{119}Sn.

Towards Control of Quantum States in High-Z Materials via Electric Currents and Magneto-synthesis

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High-Z transition metal materials host a unique hierarchy of energy scales defined by comparable spin-orbit and Coulomb interactions (Z = atomic number; spin-orbit interaction ~ Z^2). This energy setting generates a delicate interplay between the fundamental interactions and leaves these materials precariously balanced on the border between distinct ground states, and extremely susceptible to small, external stimuli.[1,2] Here I report two new approaches we have developed in recent years to control quantum states/materials via (1) application of small electric currents, as a new external stimulus,[1,3,4] and (2) magneto-synthesis or field-editing crystal structures during the formation of single crystals at high temperatures.[1,5] Both are surprisingly effective in controlling the lattice, thus quantum states via the strong spin-orbit interaction and magnetoelastic coupling in these materials.[1] Representative results obtained using the two approaches will be presented and discussed.

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APS-U Beamline Upgrade

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The post APS-U operation of the RIXS program at 27ID will enormously benefit from the conjunction of a far more brilliant source and ultra-high energy resolution quartz-based analyzer optics. In order to deliver maximum flux to the sample with high data throughput and operational efficiency at <10meV energy resolution, significant upgrades are also required of nearly all other beamline components. Different designs and strategies will be discussed in the context of present and future GUP science requirements.

Antiferromagnetic Excitonic Insulator State in $Sr_3Ir_2O_7$

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Excitonic insulators are usually considered to form via the condensation of a soft charge mode of bound electron-hole pairs. This, however, presumes that the soft exciton is of spin-singlet character. Early theoretical considerations have also predicted a very distinct scenario, in which the condensation of magnetic excitons results in an antiferromagnetic excitonic insulator state. Here we report resonant inelastic x-ray scattering (RIXS) measurements of $Sr_3Ir_2O_7$. By isolating the longitudinal component of the spectra, we identify a magnetic mode that is well-defined at the magnetic and structural Brillouin zone centers, but which merges with the electronic continuum in between these high symmetry points and which decays upon heating concurrent with a decrease in the material's resistivity. We show that a bilayer Hubbard model, in which electron-hole pairs are bound by exchange interactions, consistently explains all the electronic and magnetic properties of $Sr_3Ir_2O_7$ indicating that this material is a realization of the long-predicted antiferromagnetic excitonic insulator phase.[1] Time permitting, I will also discuss our discovery of emergent spinons in a two-dimensional timer lattice.[2]

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Strong Anharmonicity and Electron-phonon Coupling Beyond the Phonon Quasiparticle Picture: How IXS Informs our Understanding of Complex Atomic Dynamics in Materials

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Strong anharmonicity or disorder can disrupt the conventional phonon quasiparticle picture while large vibrational amplitudes renormalize the electronic structure and electron-phonon interactions. Our studies with IXS, together with simulations and complementary neutron experiments, reveal such effects to be prominent in numerous materials of importance for energy applications. A deeper understanding of unusual atomic motions in solids exhibiting these behaviors is therefore needed to refine microscopic theories of transport and thermodynamics and enable the design of improved materials. This presentation will illustrate the need for IXS measurements to rationalize atomic dynamics in materials ranging from superionic conductors for solid-state batteries, thermoelectrics for cooling or waste-heat harvesting, and to understand metal-insulator phase transitions or electron-phonon coupling in halide perovskites. Our approach combines IXS with neutron scattering and diffuse x-ray/neutron scattering to probe a wide range of spatiotemporal correlations. We integrate these experiments with our first-principles and machine-learning based simulations to enable the quantitative rationalization of large datasets, and identify key atomistic mechanisms relevant to material behaviors.

NRIXS and NFS Studies of Phonon and Spin Thermodynamics

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Nuclear resonant inelastic nuclear x-ray scattering (NRIXS) provides phonon spectra, and nuclear forward scattering (NFS) measures the magnetism of ^{57}Fe. With analysis, these NRIXS and NFS spectra give entropies of vibration and magnetism. Entropy, S, is fundamental to many thermophysical properties of materials, and a thermodynamic Maxwell relation shows that the change in entropy with pressure, $\partial S/\partial P$, is equal to $-\partial V/\partial T$. This $\partial V/\partial T$ (times $1/V$) is the volume coefficient of thermal expansion. From NRIXS and NFS measurements and this Maxwell relationship, we found the thermodynamic origin of the Invar effect, where an Fe-Ni alloy has very low thermal expansion near room temperature.

As a preliminary with x-ray diffraction measurements at pressure and temperature, we found that $Fe_{64}Ni_{36}$ Invar has zero thermal expansion at pressures from 0 to 3 GPa near 300 K. The pressure dependences of phonon entropy and magnetic entropy were obtained from NRIXS and NFS measurements on isotopic $^{57}Fe_{64}Ni_{36}$ in a diamond anvil cell at 300 K. The contributions to $\partial V/\partial T$ from phonons and spins were found to have opposite signs, and both increase by more than a factor of two in the region of Invar behavior. Remarkably, there is a precise cancellation of the pressure dependences of entropies from phonons and spins during Invar behavior. (At pressures above 3 GPa this cancellation is lost, but the analysis still predicts accurately the thermal expansion.) The phonon counterbalance of the thermal expansion from magnetism causes the Invar effect in $Fe_{64}Ni_{36}$. For understanding the Invar effect, this role for phonons is new.

Our theory collaborators showed that spin-phonon interactions aid the precision of this cancellation of spin and phonon contributions to thermal expansion. A magnetic Grüneisen parameter may be helpful for identifying spin-phonon interactions in other experimental measurements with NRIXS and NFS.

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RIXS Interferometry on Cluster Mott Insulators and Bond-directional Excitations in Kitaev Materials

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The Kitaev quantum spin liquid is based on bond-directional exchange. It is a topical example for novel types of quantum magnets that may emerge from exotic exchange couplings. In cluster Mott insulators, electrons are localized on a cluster such as a dimer but occupy quasimolecular orbitals delocalized over the cluster. This provides a promising route to unconventional magnetic moments with yet to be explored interactions. Hard x-ray RIXS interferometry studies the RIXS intensity over a broad range of transferred momentum **q** and thereby measures the dynamical structure factor S(**q**,ω) [1-3]. In cluster Mott insulators, it reveals the symmetry and character of excited states in the same way as elastic scattering does for the ground state, offering a powerful tool to study the electronic structure. RIXS data of, e.g., the spin-liquid candidate $Ba_3InIr_2O_9$ [2] with 3 holes per dimer demonstrate the spin-orbit-entangled quasimolecular $j_{dim} = 3/2$ character of the magnetic moments. In $Ba_3Ti_{3-x}Ir_xO_9$, RIXS reveals an unconventional realization of strong disorder that affects the character of the local moments [3].

The same approach can be applied to Kitaev materials in which Kitaev exchange restricts spin-spin correlations to nearest neighbors, giving rise to a dimer-like dynamical structure factor. RIXS on the honeycomb iridates Na_2IrO_3 and α-Li_2IrO_3 found distinctive fingerprints of Kitaev physics, in particular a continuum-like magnetic excitation that persists up to 300 K and shows dynamical spin-spin correlations that are restricted to nearest neighbors, even in the magnetically ordered state [4]. Furthermore, bond-directional exchange implies the existence of bond-directional excitations. Making use of polarization selection rules, RIXS demonstrates the bond-directional character of magnetic excitations in Na_2IrO_3 [5], which requires to determine both the bond direction and the spin operator creating the excitation. Altogether, RIXS provides a comprehensive picture of these unusual magnetic excitations and uncovers the properties of these ‘proximate Kitaev spin liquids.’

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Sn Nuclear Resonant Scattering

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In 2014, Sn-119 nuclear resonant scattering (NRS) program at Advanced Photon Source moved from Sector 3 to Sector 30 for the much better flux there, providing enhanced performance for Sn NRS studies. It shares the same undulators and high-resolution monochromator with the high energy-resolution inelastic x-ray scattering (HERIX) program already at Sector 30. Since 2015, general user proposals (GUPs) have been accepted and experiments conducted with continuing and guaranteed beamtime allocation each APS run cycle. Sn NRS program at 30-ID will continue when the new APS turns the light on in a year’s time. Brief overview of the instrumentation and research done will be presented, as well as some perspectives for development in the new APS-U era.

Constraints on the Temperature of Earth's Core

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The boundary layer separating the iron-dominant liquid outer core from the silicate-rich mantle is a region of great complexity, where extreme contrasts in material properties promote the persistence of multi-scale structural heterogeneities, as evidenced through seismic observations. The thermochemical variations at Earth's mantle base play an important role in the evolutionary history of the Earth through regulation of heat flow that influences the dynamics of both the mantle and the core. Despite the significance of this region for Earth's evolution, many open questions remain regarding its thermal state, as well as the characteristics, origins, and dynamic interactions of the observed heterogeneities, such as large thermochemical piles, regions of ultralow seismic velocities, and subducted former oceanic material [e.g., 1]. As individual observational studies of such features and experimental investigations into candidate compositions continue to develop, a synthesis of results from seismology, geodynamic modeling, and mineral physics provides quantitative and systematic avenues for revealing new insights into this complex region. The temperature of Earth's core is a major controlling factor in determining the nature of this boundary, which will be the focus of my talk.

We highlight new developments in mineral physics pairing independent *in-situ* techniques utilizing highly coveted qualities of synchrotron generated x-radiation to study melting of iron-rich phases at high-pressures: x-ray diffraction, sensitive to the loss of long-range crystalline order due to melting, and time-domain Mössbauer spectroscopy, sensitive exclusively to the dynamics of solid-bound iron nuclei. Emphasizing different time and length scales of the involved spatio-temporal atomic arrangements, a recent application of this approach to an iron-nickel-silicon alloy offers a comprehensive understanding of phase relations, melting, and places constraints on the temperature of Earth's core-mantle boundary [2]. The discussion in this talk focuses on the core-mantle boundary region, with implications for plume roots beneath Hawaii [3,4].

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Fractionalization of Magnons in Square-lattice Iridates

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Spinons are fractional spin excitations that are of great interest in condensed matter physics due to their connection to superconductivity and topological orders. While their existence in two dimensions remains controversial, an anomalous feature that is ubiquitous in the excitation spectrum of square-lattice cuprates has been interpreted as a spinon continuum. The pseudospin-1/2 Heisenberg antiferromagnet realized in square-lattice iridates can provide a fresh insight into this long-standing issue, as they can be studied using hard x-ray resonant inelastic x-rays scattering (RIXS) over a wide momentum region. In this talk, I will talk about our recent results on square-lattice iridates $Sr_2IrO_4$and $Sr_5Ir_3O_{11}$, the latter of which is a superlattice of Sr_2IrO_4 and $Sr_3Ir_2O_7$. By measuring the spectra in different scattering geometries, we are able to resolve transverse and longitudinal channels, and thereby separate the single-magnon component and the continuum. Our result shows that the $(\pi,0)$ spectrum of Sr_2IrO_4 is fully isotropic, implying complete breakdown of magnons. This result provides strong evidence for the existence of spinons in the square-lattice iridates. Surprisingly, such behavior is found in the entire region along the zone boundary in $Sr_5Ir_3O_{11}$. I will discuss the possible origin of the observation.

Origin of chirality in transition-metal dichalcogenides

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1T-TiSe2, an archetypal charge density wave (CDW) system with a 2×2×2 unit cell below T_C=200K, is proposed to exhibit chirality at T*=180K by various experiments such as photogalvanic effect, transport and specific heat measurements, but the mechanism how chiral symmetry is broken remains poorly understood. In this talk, we will discuss our measurements using Raman spectroscopy, x-ray diffraction and inelastic x-ray scattering (IXS). We show that chiral symmetry in the lattice sector is already broken at the T_C and therefore that a second order transition at T* is absent. Our IXS data show no anomaly of phonons at the zone center of the 2×2×2 unit. Instead, we observe splitting of Eg phonon modes measured by Raman spectroscopy, and a forbidden reflection by x-ray diffraction, which indicate breaking of the chiral symmetry. Our results show that chirality in the CDW phase arises from mutually incompatible symmetryproperties of charge density modulations and atomic displacements, transforming as a continuous scalar field and a vector field on a discrete lattice, respectively.

RIXS Investigation of Rhenium Double Perovskite Materials

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RIXS has been instrumental in elucidating the physics of magnetic materials with strong spin-orbit coupling. Iridates remain the best known and most successful examples, while its success has not been reprised in other 5d transition compounds to date, mostly due to the limited energy resolution. This remains a promising path forward in the hard x-ray RIXS community. In this talk, we will summarize our recent efforts to study rhenium double perovskite compounds with RIXS, focusing on two examples. The first is the epitaxial thin-film sample of Sr_2CrReO_6, which has an extremely high ferrimagnetic ordering temperature of around 600K. We found a clear difference between the RIXS spectra obtained at the L2 and L3 absorption edges, which indicates the importance of spin-orbit coupling even in this metallic system. The second example is a d1 system, Ba_2MgReO_6, in which the magnetic moment is expected to vanish since spin and orbital components cancel each other exactly. We will discuss our RIXS results in the context of the multipolar physics predicted in this and other related materials.

Application of Nuclear Resonance Vibrational Spectroscopy to Elucidate the Electronic Structures of Iron-NO Complexes with Relevance to NO Sensing and Detoxification in Biology

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Nuclear resonance vibrational spectroscopy (NRVS) measures the inelastic scattering of light in resonance with the nuclear transition of iron-57 at 14.4125 keV. In this sense, NRVS could be considered the nuclear scattering variant of resonance Raman spectroscopy. However, the selection rule for NRVS is very different: the intensity of a normal mode in NRVS scales with the amount of iron motion (the iron displacement) of this vibration. Hence, NRVS is ideal for the investigation of low-energy iron–ligand stretching and bending vibrations, which are, in many cases, weak in IR and Raman spectroscopy, and, hence, difficult to identify with these methods. However, these modes are commonly very intense in NRVS. Because of this, NRVS is now frequently applied to iron complexes and corresponding proteins, in particular, iron porphyrins.

In addition to the valuable information available from NRVS spectroscopy, the simple relation between the NRVS intensity and the iron displacement makes this method particularly interesting for Normal Coordinate Analysis (NCA) simulations. Traditionally, NCA has been limited to simulate vibrational energies of molecules and corresponding isotope shifts because the IR and Raman intensities of a normal mode cannot be directly calculated from the NCA force field. In contrast to this, *NRVS intensities can actually be directly calculated for a given normal mode, and, in this way, complete NRVS spectra can be obtained from NCA results in a straightforward way*. This offers a whole new dimension for the assignments of molecular vibrations and the application of NCA for this purpose.[1]

In this presentation, several applications of NRVS to elucidate the geometric and electronic structures of heme and non-heme iron-NO complexes are discussed,[2]-[4] and methods for the analysis of these data are introduced.

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Monolayer-like Lattice Dynamics in Bulk WSe2

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Understanding the microscopic lattice dynamics is essential for regulating the thermal properties in two-dimensional layered materials. In transition metal dichalcogenides, the layered structures result in different but closely related phonon dispersions between monolayer and bulk. Here, by combining inelastic x-ray scattering and first-principles calculations, the lattice dynamics of tungsten diselenide (WSe2) was investigated comprehensively, and a monolayer-like lattice dynamics in the bulk WSe2 was revealed. We performed the first measurements of the temperature-dependent phonon dispersions and the mode Grüneisen parameters of bulk WSe2, which are found to be in better agreement with the calculations on the monolayer system than those of the bulk. This observation indicates that lattice dynamics in bulk WSe2 hold the characterization of monolayers. The result provides valuable insights into the thermal properties of WSe2-based devices.

Topological Magnon-phonon Interaction, High-throughput Phonon Dispersion Calculation, and Open Questions of Phonon Sciences for APS-U

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Non-resonant, meV-scale inelastic x-ray scattering (IXS) offers an extremely powerful tool to investigate the elementary lattice collective excitations in energy-momentum space. In this Users' Meeting, we introduce two of our recent works that could be used to support IXS for other elementary excitations and beamtime planning in complex materials design space. One, we show that by applying external magnetic field to an IXS setup, it can be used to probe the nontrivial topological nodal structures and magnon-phonon interactions. Two, we show that machine learning can be used to predict full phonon bandstructures in nearly arbitrarily complex solids such as alloys [1]. We envision a few scenarios that the upgraded APS+U can be used for studying samples and phenomena that have not been accessible with the current setup.

[1] https://arxiv.org/abs/2301.02197

Phonon Dispersion, Lifetimes, and Thermal Transport in Nuclear Fuel Materials

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The extraction of useful energy from nuclear fuel requires materials that can withstand extreme conditions of high temperatures and radiation levels. Controlling the transport of heat under these conditions is essential for reactor efficiency and safety. To better understand the mechanisms controlling phonon thermal transport it is critical to measure the phonon dispersion curves, including the linewidths. From these measurements it is possible to calculate phonon group velocities, lifetimes, and mode specific heat capacities, all of which can be used to benchmark thermal transport calculations. In this talk, I will present inelastic x-ray scattering measurements of phonon dispersion curves and lifetimes in both oxide and metallic nuclear fuel materials. In a metallic fuel material, UZr_2, we show that proton-irradiation-induced defects and an associated nanostructure decrease the phonon lifetimes, thereby suppressing thermal transport. Additionally, a texture in the observed nanostructure further explains why the decrease in phonon lifetimes occurs preferentially in the crystallographic basal plane, rather than along the c-axis. These and other insights obtained from IXS measurements should help in the design of safe and efficient of nuclear reactors.

Spin-phonon Coupling Driven Charge Density Wave in a Kagome Magnet

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The intertwining between spin, charge, and lattice degrees of freedom can give rise to unusual macroscopic quantum states, including high-temperature superconductivity and quantum anomalous Hall effects. Recently, a charge density wave (CDW) is observed in the kagome antiferromagnet FeGe, indicative of possible intertwining physics. An outstanding question is that whether magnetic correlation is fundamental for the spontaneous spatial symmetry breaking order. Here, utilizing elastic and high-resolution inelastic x-ray scattering, we discover a charge dimerization superlattice that coexists with the 2×2×1 CDW in the kagome sublattice. Most interestingly, between the magnetic and CDW transition temperature, the phonon dynamical structure factor shows a giant phonon-energy hardening and a substantial phonon linewidth broadening near the charge-dimerization wavevectors, both signaling the spin-phonon coupling. By first principles calculations, we show that both the static and dynamic spin excitations intertwine with the phonon to drive the spatial symmetry breaking.

Study of the Dynamics of Glasses Using Nuclear Resonance Time Domain Interferometry with Annular Slits

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A new x-ray spectroscopic method, Nuclear Resonance Time Domain Interferometry (NR-TDI), was developed to measure nanosecond time scale dynamics of liquids and glasses at the atomic and molecular length scales. The NR-TDI technique can be used to measure the diffusional dynamics of liquids and glasses at various temperatures, pressures, or compositions. The time-dependent scattering intensity from Mössbauer resonant iron foils and a non-resonant liquid sample is directly related to the average diffusion relaxation time. A set of annular slits were fabricated to capture the entire x-ray diffraction ring thereby increasing the count rate by two orders of magnitude for glycerol at $q = 14\text{nm}^{-1}$. Relaxation times determined using the Kohlrausch–Williams–Watts (KWW) stretched exponential model gives insight into the dynamics of the electron density fluctuations in glycerol. The Vogel–Fulcher–Tammann (VFT) equation was used to determine the glass transition (T_G = 185 K) of glycerol, and the Arrhenius equation was used to find its activation energy (E_a= 63 kJ mol−1). The significant increase in count rate using an annular slit makes it possible to do material science experiments on various liquid systems like glycerol, liquid crystals, proteins, colloids, and biomolecules.

Characterization of Natural Amphibole Crystals through a Combination of Microanalytical Techniques including Single-crystal Synchrotron Mössbauer Spectroscopy

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Amphibole is an important fractionating mineral phase in subduction zone magmatism, capable of recording melt compositions during its crystallization and driving melt silica-enrichment during magma differentiation. Using amphibole chemistry as a tool to study arc magmas requires high spatial-resolution and high precision documentation of amphibole chemistry at the sub-crystal scale. We developed a workflow combing several microanalytical techniques on the same analysis area of individual crystals, allowing for multi-faceted data sets for the same analytical spot. These analytical techniques include electron microprobe analysis (EMPA) for major and minor element concentrations, secondary-ion mass spectrometry (SIMS) to measure water content and hydrogen isotope compositions, as well as single-crystal synchrotron-based Mössbauer spectroscopy (SMS) in combination with x-ray diffraction (XRD) to determine Fe^{3+}/Fe^{T} ratios. In particular, SMS provides the necessary high spatial-resolution and precision to avoid analyzing Fe-bearing mineral inclusions common in natural amphiboles and allows resolving small intra-crystal compositional differences in individual amphiboles (i.e., zonation; [1]).

We apply this workflow to a set of volcanic amphiboles, which crystallized from magmas recording a wide range of magmatic oxygen fugacity (ΔNNO = -1.0 to + 2.0, log units relative to the Ni-NiO buffer). Combining H_2O content and H isotopes in amphibole can distinguish between amphiboles that have experienced post-crystallization Fe oxidation versus those recording magmatic Fe^{3+}/Fe^{T} ratios. We observe that amphiboles recording magmatic conditions and amphiboles that have been affected by post-crystallization modifications both exist in a single hand sample. Present results show that magmatic amphibole Fe^{3+}/Fe^{T} ratios do increase with increasing oxygen fugacity of the magma from which they crystallized indicating that primary amphibole Fe^{3+}/Fe^{T} values may be useful monitors of magmatic oxygen fugacity.

[1] Ratschbacher, B. C., Jackson, J. M., Toellner, T. S., Bucholz, C. E., Sturhahn, W., & Solomatova, N. V. (2023). Fe^{3+}/Fe^{T} ratios of amphiboles determined by high spatial resolution single-crystal synchrotron Mössbauer spectroscopy. American Mineralogist, 108(1), 70-86.

Straight Out of the Asteroid Belt to Sector 3 at the Advanced Photon Source: Iron Valence State and Mineralogy in Particles from Asteroid Ryugu

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Iron is a major element in rocky material from the solar system that can occur under multiple valence state. As such it can be used to trace geological processes that occurred on asteroid Ryugu, including thermal metamorphism and aqueous alteration. Observations of the mineralogy of carbonaceous chondrites have revealed the presence of mineral assemblages that are barely in thermodynamic equilibrium. Even at the micron-scale, iron is often present under multiple valence state (most frequently 0, +2, or +3) in a wide range of minerals (primary or secondary in nature), including silicates, oxy-hydroxide, sulfides, sulfates, clay minerals and carbonates. Such heterogeneous assemblages are the results of post-accretion processes that often triggered a partial textural and chemical equilibration, associated to a modification of primary Fe-bearing minerals and their valence state. It is therefore tricky to disentangle the different processes recorded by the iron mineralogy of chondritic materials. Furthermore, since most Fe-bearing phases are redox-sensitive, exposure to terrestrial atmosphere may also induce iron oxidation and additional, late modifications of the iron mineralogy. In this context, Hayabusa2 sampled Ryugu, an asteroid that did not suffer extensive thermal metamorphism, and returned rocks to Earth with minimal air exposure. It offers a unique opportunity to study the redox state of carbonaceous asteroids and evaluate the overall redox state of the most oxidized primitive rocks of the solar system.

Here, we determine the mineralogy and the redox state of Fe-bearing minerals from ten Ryugu samples prior to and after exposure to air. We use Synchrotron Mössbauer Spectroscopy (SMS) technique that enables to probe the bonding environment of iron at the microscopic scale. These measurements are combined with co-aligned x-ray diffraction, permitting to assess locally the mineralogy and valence state of iron in Ryugu particles. We also apply conventional Mössbauer spectroscopy on a couple of large (mm-size) Hayabusa returned samples.

We will present the bulk proportions of iron-bearing minerals and the Fe redox state (Fe^{3+}/Fe_{tot}) at the grain scale. We will then provide the first estimate of the redox state of Ryugu as compared to the large array of bulk redox data collected over several decades on meteorites. We will also describe the redox states of iron-bearing clay minerals before any air contamination. The first clues on the ageing of these minerals after exposure to air will be discussed based on data collected on the same sample before and after exposure to air. We will compare in greater details Ryugu samples to a series of well-known chondritic meteorites including Orgueil and Murchison. We will show, more specifically, that most of the iron is accommodated in magnetite and sulfides (pyrrhotite and pentlandite). Clay minerals also contain a fraction of the total iron. Overall, the investigated Ryugu samples appears to be (or are) more reduced than the Orgueil, both considering the bulk composition and the clay minerals fraction.

Exploration of Spins and Phonons in Single-molecule Magnets and Molecular Switches Using ^{161}Dy and ^{57}Fe as Nuclear Probes

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With the contemporary evolution of spintronics, molecular electronics and quantum computing, single-molecule magnets (SMMs) arouse an immense amount of interest. Lanthanide-based compounds and especially Dy-containing ones are among the best high-performance SMMs, characterized by long relaxation times of the magnetization reversal and high blocking temperatures. As a novel method for the characterization of these molecular materials, synchrotron-based ^{161}Dy Mössbauer spectroscopy in the time domain, delivers complementary information to conventionally applied magnetization measurement techniques [1]. Investigations of the vibrational properties of Dy containing SMMs are now possible via ^{161}Dy Nuclear Resonance Vibrational spectroscopy (NRVS) [2]. Simulations using density functional theory (DFT) have been used to assign observed bands to specific molecular modes. In this contribution we will also present first results on the detection of transient vibrational modes in optically excited iron containing molecular switches by means of optical pump ^{57}Fe-NRVS probe experiments [3].

[1] L. Scherthan, S. F. M. Schmidt, H. Auerbach, T. Hochdörffer, J. A. Wolny, W. Bi, J. Zhao, M. Y. Hu, T. Toellner, E. E. Alp, D. E. Brown, C. E. Anson, A. K. Powell, V. Schünemann, Angew. Chemie Int. Ed. 58, 3444 (2019).
[2] L. Scherthan, R.F. Pfleger, H. Auerbach, T. Hochdörffer, J. A. Wolny, W. Bi, J. Zhao, M. Y. Hu, E. E. Alp, C. E. Anson, R. Diller, A. K. Powell, V. Schünemann, Angew. Chem. Int. Ed., 59, 8818 (2020).
[3] S. Sadashivaiah, J.A. Wolny, L. Scherthan, K. Jenni, A. Omlor, C.S. Müller, I. Sergueev, M. Herlitschke, O. Leupold, H.-C. Wille, R. Röhlsberger, V. Schünemann J. Phys. Chem. Lett. 12, 3240 (2021).

Developments in Uniaxial Strain Tuning for Inelastic X-Ray Scattering Measurements

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Uniaxial strain tuning is a powerful tool to probe the relationship between structural and electronic properties in materials. In this talk we will discuss the integration of strain tuning into inelastic x-ray scattering measurements and how the APS upgrade will support the development of this method. The rare earth tritellurides (RTe_3) crystal family will be used as a model system to explore this technique. RTe_3 (R=La-Nd, Sm, Gd-Tm, Y) is a layered material that displays in-plane, unidirectional charge density wave (CDW) order on a nominally square lattice. Transport measurements and recent x-ray diffraction measurements performed at the APS reveal the ability of anisotropic strains to rotate the primary CDW wavevector in the material. Little is known however about the character of this strain induced state. Inelastic x-ray spectroscopy measurements allow us to investigate the lattice dynamical properties of the rotated CDW phase transition in RTe_3. We will discuss the technical challenges of *in-situ* strain tuning for phonon spectroscopy measurements as well as preliminary data of the evolution of the soft mode associated with the CDW phase when the system is strained. This study of the reorientation of the CDW state will expand our understanding of the ability of uniaxial strain to restore the rotational symmetry of the system establishing RTe_3 as a model material to investigate nematic order arising from CDW fluctuations. Ultimately these strain-based phonon spectroscopy measurements may provide additional insight into the nature of the CDW phase in RTe_3 and more broadly into the origin and behavior of CDW states in 2D materials.

Mössbauer Microbeam Spectroscopy after the APS Upgrade

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Performing Mössbauer microbeam spectroscopy (MMS) at the Advanced Photon Source (APS) has historically involved the measurement of time spectra of the nuclear decay via nuclear forward scattering. This exploits the pulsed x-ray time structure that is native to synchrotron sources like the APS but requires adequate dark time between pulses on the scale of a nuclear lifetime or longer. After the APS Upgrade, the available dark time between pulses will be reduced significantly making it much less suitable for Fe-57 MMS given the Fe-57 nuclear lifetime of 141ns. To maintain the capability to perform MMS on Fe-containing samples after the APS Upgrade a new measurement approach is needed.

Various measurement modalities have been investigated and a method that involves measuring Mössbauer absorption spectra in the energy domain demonstrates excellent stability and does not rely on the specific timing mode of the storage ring. This approach uses an optically-active medium between orthogonal polarization filters to generate a source of gamma-rays with a well-known, very stable spectral distribution composed of multiple, well-separated, neV-bandwidth lines. Placing the optically-active medium on a velocity transducer allows one to use the Doppler effect to sweep the beam energy to create a tunable source of gamma-rays to perform Mössbauer absorption spectroscopy. Combining this novel gamma-ray source with the low emittance of the upgraded storage ring and a new Kirkpatrick-Baez mirror system will allow the beam to be focussed to a 1um spot size (compared to 20um currently) for measuring microscopically-small regions of Fe-containing samples.

A test setup was implemented to demonstrate the approach and assess possible performance enhancements to be implemented in a future spectrometer. The method and preliminary results will be presented along with what to expect after the APS Upgrade.

APSU and 3ID Beamline Upgrades: New Opportunities and Challenges

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As the APS storage ring will experience a one-year upgrade period starting from April 2023, Nuclear Resonant Scattering (NRS) programs at 3ID and 30ID will undergo major changes to take advantage of the upgraded light source properties, such as smaller beam and higher flux. Meanwhile, efforts are being done to address the upcoming challenges of the future APS storage ring on NRS techniques, including issues like unfavored bunch timing structures. Details will be discussed in the presentation.

Joint WK#3: Toward Synchrotron-based Autonomous Scattering Studies of Synthesis and Processing

Organizers: John Mitchell, Maria Chan, and Uta Ruett

In situ scattering x-ray experiments offer powerful approaches to follow reaction pathways and their underlying kinetics in great detail, providing a critical the pathway to closed-loop studies of syntheses. For example, the progression from nucleates through intermediates and to final products can be characterized under realistic conditions without interrupting the reaction. Synthesis is a multidimensional problem involving various parameters, such as temperature, pressure, pH, morphology and structure of the precursor material, solvents, etc. The upgrade of the APS with its enhanced flux, high-energy x-rays offers an unprecedented opportunity to navigate this multidimensional space with the speed and fidelity needed for studies of material synthesis. Leveraging advanced multimodal characterization techniques and sophisticated robotic systems for automated measurements, APS users will be empowered be able to combine high-performance computing and the latest developments in ML/AI for fast data analysis, modelling, and prediction to accelerate materials discovery, and to more completely and efficiently understand synthesis and processing. APS-U will also usher in a new age of autonomous discovery applied to synthesis. While huge progress was made in the field of lab-based autonomous synthesis experiments in recent years, the expansion of autonomy to the high-end characterization tools available at synchrotrons is still very much in its infancy.

This workshop will discuss the opportunities and challenges for a new era of highly automated and autonomous experiments guided by AI to accelerate the materials discovery at the synchrotron. We will bring together experts in the field to encourage collaborations to become ready for revolutionary experiments at the upgraded APS. The scope will span from instrumental design and high-speed sparse data collection to high-throughput data analysis and simulation for adaptive decisions using AI.

Artificial Intelligence-enabled Optimal Materials Discovery

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A priori and reliable simulations coupled with emerging Artificial Intelligence (AI) approaches can enable timely and cost-efficient design and discovery of materials for energy. Fundamental understanding of the accurate and reliable prediction of properties (redox potentials, solvation, diffusion, adsorption, reactivity, and stability) are critical for down-selecting optimal materials or material combinations from large chemical/materials space. In this presentation, first, I will describe some of our recent efforts in active learning coupled with large scale first principles simulations to down select/optimize desired molecules for non-aqueous flow battery innovation. This molecular optimization concept can be utilized for autonomous design of experiments. Second, I will describe some of our quantum chemistry-informed molecular property predictions of redoxmers and liquid organic hydrogen carriers from billions of chemical spaces. Third, in addition to molecules, I will present a data driven approach to study longer time scale diffusion of ions in layered solid materials for multivalent battery concepts. Finally, I will briefly describe a data-driven and deep learning approach for heterogeneous catalytic property prediction relevant to Biomass conversion processes.

Autonomation for Scientific Discovery: Beamline Experiments of the Future, What They Might Look Like, and How to Get There

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This talk will explore whether and how autonomation can accelerate scientific discovery. By autonomation, we mean computer controlled measurements where an adaptive decision policy is carried out also by the computer without a human in the loop. Subsequent measurements are run based on the results of prior experiments and the overall goals of the experiment. This raises the possibility of enormously accelerated experimental campaigns that can make the best use of available resources (not least, beamtime). It is clear that such strategies can work when carrying out optimizations over high dimensional input parameter spaces, and when experiments are reversible or under continuous flow conditions. However, an interesting question remains about how such experiments can result in novel experimental discoveries, and exactly how the experiments will interact with scientists and vice versa. I will explore some of these questions in the context of experiments at synchrotron facilities.

Autonomous Thin-film Synthesis and Characterization System

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Here, we highlight our recent *autonomous* materials exploration that combines machine learning and robotics. We show the synthesis and resistance minimization of TiO_2 thin films as proof of concept. The system fully automates sample transfer, thin film deposition, and growth condition optimization—all addressing the physical aspects of fabrication [1]. Combining Bayesian optimization with robotics illustrates how the required speed and volume of a future big-data collection in materials science will be achieved and demonstrate the potential of this approach. We briefly discuss the outlook and significance of these results and discuss a new materials research style to accelerate materials science.

[1] Shimizu, Hitosugi *et al.*, APL Mater. 8 (2020) 111110.

Autonomous, Physics-informed Experiments for Materials Discovery

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The last few decades have seen significant advancements in materials research tools, allowing scientists to rapidly synthesis and characterize large numbers of samples - a major step toward high-throughput materials discovery. Autonomous research systems take the next step, placing synthesis and characterization under control of machine learning. For such systems, machine learning controls experiment design, execution, and analysis, thus accelerating knowledge capture while also reducing the burden on experts. Furthermore, physical knowledge can be built into the machine learning, reducing the expertise needed by users, with the promise of eventually democratizing science. In this talk I will discuss autonomous systems being developed at NIST with a particular focus on autonomous control over user facility measurement systems for materials characterization, exploration and discovery.

ARES™ Autonomous Experimentation

Benji Maruyama[1]

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The current materials research process is slow and expensive, taking decades from invention to commercialization. The Air Force Research Laboratory pioneered ARES™, the first autonomous research system for materials development. A rapidly growing number of researchers are now exploiting advances in artificial intelligence (AI), autonomy & robotics, along with modeling and simulation to create research robots capable of doing iterative experimentation orders of magnitude faster than today. We will discuss concepts and advances in autonomous experimentation in general, and associated hardware, software and autonomous methods.

For Carbon Nanotubes (CNTs), we show progress in autonomous and data science methods to understand and control the fundamental mechanisms that drive CNT synthesis via CVD. We will explore the importance of the oxidizing or reducing nature of the CVD environment on nucleation and growth.

In the future, we expect autonomous research to revolutionize the research process, and propose a “Moore’s Law for the Speed of Research,” where the rate of advancement increases exponentially, and the cost of research drops exponentially. We also consider a renaissance in “Citizen Science” where access to online research robots makes science widely available.

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Human/AI-interfaces for the Next Generation of Autonomous Beamline Experiments

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As new and upgraded sources are established alongside advances in detector technology, the data generation rates at x-ray light sources beamlines are skyrocketing. Despite these increased capacity to measure data, user throughput has not seen nearly as dramatic an increase. This is in part due to the issue that data collected in fractions of a second to minutes may take weeks to months to process and understand. Such a dramatic mismatch in measurement-to-analysis times can, in part, be attributed to a lagging effort towards modernizing data analysis methods. The lack of available real-time feedback during an experiment can force beamline users into 'flying blind' at the beamline, leading to missed opportunities and mistakes. New streaming analysis methods, particularly those employing Artificial Intelligence (AI), have demonstrated the ability to expedite data analysis to the speed and scale required for the light source community. Beyond the ability to accelerate researchers real-time understanding of their ongoing experiment at the beamline, these methods offer the potential to run fully automated experiments that are driven by directed scientific inquiry. For example, searching for a boundary in a phase-map or tuning synthesis conditions to maximize product. Brining these methods to bear at large-scale user facilities has the potential to increase user access and overall scientific output. However, this level of automation does not need to be limited to a single measurement. Increasingly, the use of multimodal characterization is required to fully understand the structure and function of complex materials. The inherent information content from one measurement can be used to inform and drive others, such as using relatively fast powder diffraction measurements to drive slower, but equally critical spectroscopic studies.

Ultimately, the ability to utilize AI-driven analysis or beamline control does have the potential to dramatically change the face of science at light sources, but only if we can implement it in an accessible, maintainable, and extendable way. While the potential of future self-driving beamlines is possible, the precious nature of beamtime suggests human researchers will be part of any future access models. As such, it is critical that these methods be developed with human-in-the-loop design – particularly with consideration for a wide swath of researchers that may have limited experience with AI-methods. In this contribution, I will discuss the challenges and ongoing developments we have been pushing in this area.

Machine Learning-guided Experimental Materials Discovery

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Rapidly emerging fields of Artificial Intelligence (AI) and Machine Learning (ML) unplugged an exciting new direction and have become dominant problem-solving approaches for material discoveries. Usually, the discovery of new material or the probability of finding desired alloy systems expands in higher dimensional space, however, the challenge lies in the complex compositional space, which is very expensive, complex, and time-consuming. In general, understanding physio-chemical theories of vast spaces is fundamental to designing a material with targeted properties. Even though these physio-chemical theories are developed over decades of knowledge, they sometimes overlooked the subtlety that experimental observation can capture. Therefore, data-driven machine learning approaches are promising to guide this search space. However, the limitation is the availability of the quality and quantity of the training datasets. In addition, as we look towards more and more practical applications, the perils of computational material databases become prominent, therefore, there is a rapid blooming of high-throughput (HiTp) experimentation research of parallel synthesis and characterization in higher dimensional space by thin-film deposition also known as combinatorial libraries, and high-throughput bulk materials synthesis that can create large datasets to verify the feasibility of hypotheses and rapidly validate any computational models. In this talk, I will show different strategies to discover new materials with sparse data and take advantage of existing domain science and data-informed machine learning to assist high-throughput experimentations. These strategies could be easily adaptable to efficiently explore material design and discovery where data is sparse and domain knowledge is insufficient.

Using Artificial Intelligence to Discover Novel Catalysts and Accelerate the Change to Sustainable Feedstocks within the Chemicals Industry

Christopher Tassone[1], Anthony Fong[1], Lenson Pellouchoud[1], Malcolm Davidson[2], Richard Walroth[1], Carena Church[2], Ekaterina Tcareva[1], Liheng Wu[1], Kyle Peterson[2], Bryce Meredig[2], and Sathya Chitturi[1]

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Ambitious societal goals to address sustainability are being made across the globe. Recent improvements in energy systems provides a path forward to decarbonizing many sectors of our economy. However, there still remaining substantial challenges to decarbonize manufacturing. How we make chemicals, materials and products will need to fundamentally change such that we are using net carbon neutral, or preferably net negative, feedstocks as inputs to processes which can be driven using decarbonized energy. This will require a complete re-optimization of the integrated value chain or reaction networks that is the chemicals industry. Additionally, these changes need to occur on the fastest timescale ever before in history if we are to meet current federal targets of a net zero economy by 2050. In order to accomplish this we need to translate foundational basic scientific discoveries to industry orders of magnitude faster, and with a much broader scope than we have previously been able to.

In this talk, I will discuss how we can accelerate the discovery of new catalysts which function on new feedstock sources, at lower energy and carbon intensity, but which can utilize the infrastructure already present in the petrochemical and agrochemical industrial complex. Colloidal nanoparticles embedded in mesoporous hosts, provide ideal systems to control the physico-chemical properties of a catalyst in order to realize high selectivity and activity, while also understanding reactivity patterns and chemical mechanisms across an enormous range of chemical reactions. Developing this understanding requires the synthesis of well controlled materials where the structure of the nanoparticle needs to be controlled with near atomic precision. I will discuss how we take advantage of high throughput synchrotron x-ray scattering experiments to develop a fully automated closed-loop platform for the synthesis of nanostructured catalysts. We are able to demonstrate that in as few as 30 unsupervised experiments our AI is able to determine how to synthesize a class of nanocrystals of varied sizes, inform researchers about what syntheses are improbable, and provide a model which can be queried to perform virtual syntheses without running subsequent experiments. These developments provide a roadmap as to how to build AI driven R&D to both predict catalytic targets as well as how to make them.

Autonomous Platform (Polybot) for Polymer Thin-film Processing

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Modern materials processing and technologies often occur far from equilibrium. For instance, the processing of complex materials such as polymer solutions/melts and nanocomposites generally occurs under strong deformations and rapid flows, conditions under which equilibrium thermodynamics does not apply. As a result, the ability to control the molecules packing during formulation and processing has been one of the long-standing challenges in materials science. In the current paradigm, newly designed materials that promise improved functionalities must first be subjected to a years-long processing effort to meet the performance targets. One of the major hurdles in meeting these performance goals is the high dimensionality of the searching space associated with the formulation and processing variables. I will introduce a new experimental paradigm we recently developed that combines the strengths of rapid and robust experiment acquisition from robotic technologies (i.e., high-throughput processing and characterization) and fast analysis of complex datasets using machine learning (ML) for autonomously processing polymer thin films towards desired solid-state properties. Utilizing this autonomous platform (PolyBot, https://www.anl.gov/cnm/polybot), we were able to identify the processing path much more efficiently and extract the high-dimensional formulation-processing-property relationships for revealing the general design principles. This new experimental framework is amenable to continuous improvement, such that sophistication can be added over years to continually redefine the cutting-edge of autonomously controlled conjugated polymer assembly.

Self-driving Laboratory for Inorganic Solid-state Synthesis

Yan Zeng[1]

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Self-driving autonomous laboratories are paving the future for chemical and materials research. By integrating computational design, automated instrumentation, robotics, and AI/ML, autonomous laboratories drive more rapid and closed-loop execution of experimentation, data interpretation, and decision making, which will eventually accelerate chemical and materials discovery. We have built a self-driving lab focusing on solid-state bulk materials synthesis, where the challenges lie in many aspects but particularly solid-phase (powder) handling and phase identification on the products when there are multiple phases. I will talk about 1) instrument integration for modular-based solid-state synthesis, 2) design in-house made tools and devices to tackle the challenges in powder handling, and 3) using AI/ML for the acquisition and interpretation of XRD data.

APS WK#4: Materials Discovery with Grazing-incidence X-ray Photon Correlation Spectroscopy: Opportunities and Challenges

Organizers: Joseph Strzalka, Zhang Jiang, and Jin Wang

X-ray Photon Correlation Spectroscopy (XPCS) has become established in the 21st century as a critical tool for investigating dynamics in bulk systems. In this time, pioneering work has applied XPCS to surfaces and interfaces in a grazing incidence (GI) geometry. Now, with the advent of next generation synchrotron sources like the APS-U, GI-XPCS is poised to break through from unusual experiment to more routine application. Facilities like the new APS-U beamline 9ID promise to make GI-XPCS as accessible as GISAXS/GIWAXS. This will bring new and impactful insights into the dynamics of thin film materials in such vital areas as renewable energy, advanced microelectronics and the manufacturing techniques needed to bring these materials from lab to fab. In particular, the brilliance of new sources like APS-U will enable operando studies of devices and deposition processes, revealing the evolution of dynamics under a range of conditions. Scientific progress will require concomitant progress in the development of GI-XPCS to address challenges in the collection and processing of experimental data, as well as in the interpretation of results. This workshop is an opportunity to chart the course ahead, identify areas most in need of development, and steer the field along the most promising avenues of research.

GI-XPCS on Thin Films

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XPCS (X-ray Photon Correlation Spectroscopy) is a powerful technique to characterize dynamics on the nanoscale. While dynamics are still mostly examined in bulk, they are also highly interesting in confined systems such as thin films. When working with thin films the grazing incidence geometry is a standard measurement configuration. However, in that measurement configuration we do not merely need to take into account scattering processes but also reflections at the interfaces as well as refraction effects.

Therefore the observed speckle pattern needs to also be carefully interpreted. We show in this presentation under which conditions the grazing incidence geometry results in multiple signal detection within one pixel and from which origin the contributions arise.

Structure and Dynamics of Block Copolymer and Brush Polymeric Thin Films

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Polymeric thin films have numerous applications as functional materials ranging from protective nanocomposite barrier coatings and lubricating slip surfaces to membranes for separations and energy storage hybrid and dielectric materials for electronics. Most often these films do not have the required properties as prepared, rather they require careful subsequent processing pathways to obtain desired structures that have the functional properties. Processing methods can include approaches that provide controlled mobility for self-organization to the polymer chains in useful structures. Thus, it is important to understand how the structure and dynamics of polymer chains with diverse architectures evolve into self-assembled structures. For an important class of self-assembling block copolymer (BCP) films, we have developed a dynamic thermal processing method known as “Cold Zone Annealing (CZA).” Unlike traditionally static oven thermal annealing above the glass temperature of the block component, in CZA, the cast mostly disordered BCP film is passed over a sharp temperature spike that induces localized order in a gradient thermal field. Various modes of CZA were developed that include CZA-SS (Soft Shear), CZA-R (Radial), CZA-AS (Asymmetric gradient). Using grazing incidence x-ray scattering, it is possible to examine the structure evolution in the heating and cooling region of the narrow spike *in-situ* in real-time CZA, and potentially characterize the dynamics of the polymer surface fluctuation with x-ray photon correlation spectroscopy (XPCS). The surface fluctuations in the BCP films are expected to be analogous to the dynamics of polymer brushes that have been extensively studied by XPCS and will be discussed. The use of block selective plasticizer such as ionic-liquid vastly enhances the dynamics and ordering kinetics of the BCP chains for enabling long-range ordering with orientation control.

Coherent X-ray Scattering as a New Tool for Study of Surface Growth and Patterning Dynamics

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In collaboration with colleagues from University of Vermont, Naval Research Laboratory, NSLS-II and APS, we have been developing coherent x-ray scattering in a surface-sensitive geometry as a new tool to examine nanoscale dynamics of surface growth and patterning processes. We've found that surface-sensitive X-ray Photon Correlation Spectroscopy (XPCS) enables new insights into the imperfect surface patterning and epitaxial crystalline/polycrystalline film growth processes found in many technological applications. Traditional "low-coherence" diffraction techniques used to investigate surface evolution incoherently average over the surface. This results in the loss of information unless the growth or patterning process is highly perfect in phase across the illuminated surface, which is relatively uncommon within the broad spectrum of technologically and scientifically interesting materials. In contrast, XPCS works by examining the evolution of the coherent x-ray scattering speckle pattern, which is a fingerprint of the actual surface microstructure. We have shown how the technique can be used to investigate surface step flow during epitaxial growth of polycrystalline C60 films and to reveal intra- and inter-cycle correlations during the plasma-enhanced atomic layer deposition of InN films. In addition, our surface-sensitive XPCS studies of ion beam nanopatterning have been able to examine structural correlations as a function of length scale and to measure the flow velocity of surface features across the surface, driven by the ion beam. These provide tests of theory not previously easily accessible.

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Light-induced Structural Dynamics in 2D Halide Perovskites

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Two-dimensional halide perovskites (2D-HaP) are a sub-class of 3D perovskites, which have emerged as a new class of solution-processed organic-inorganic (hybrid) low-dimensional semiconductors. They imbibe their properties from four exciting classes of novel materials - quantum wells, atomically thin 2D materials, organic semiconductors, and 3D halide perovskites. There is growing consensus that their physical properties are dictated by the interaction between the organic cation and the inorganic framework, which presents a unique opportunity to tailor their behaviors. In this talk I will describe our work over the year on 2D-HaPs on understanding and tailoring light-induced structural behaviors, novel photo-physical behaviors, and charge transport for high-efficiency optoelectronic device, with technologically relevant durability.

Past and Future Problems and Opportunities with XPCS at Grazing Incidence

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XPCS at grazing incidence geometry has become increasingly popular in recent years. In this talk, I will attempt to review some of the early developments in this field, which were mainly focused on studying the surface fluctuations of thin liquid films. I will also discuss more recent and diverse applications of the technique and possible new scientific opportunities. The DWBA has not usually been necessary to analyze these experiments, and I will discuss the reasons for this.

APS-U Feature Beamline 9-ID: The Expanded Program in Nanoscale Structure, Kinetics – and Dynamics – at Surfaces and Interfaces

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The migration of the Grazing-Incidence X-ray Scattering (GIXS) instrument from APS Beamline 8-ID-E to its new home at APS-U Feature Beamline 9-ID CSSI will transform the program in nanoscale structure and kinetics by enabling the study of dynamics via Grazing-Incidence X-Ray Photon Correlation Spectroscopy (GIXPCS). Features of the new beamline supporting this transformation include:

- Tunability between 6 and 25 keV
- In-vacuum Eiger 16M detector for dynamics timescales 0.002-1000 s
- Large vacuum flight path with sample-detector distance variable between 3 and 20 m
- Transfocators to focus the beam to sizes 29 µm x 16 µm or 3 µm x 1.2 µm
- Motion system for a second in-air WAXS detector 0.2-0.5 m from the sample with potential for simultaneous GISAXS/GIWAXS/XPCS
- Automated workflows for real-time high-performance computer processing of XPCS and GISAXS/GIWAXS data.
- Robust and versatile diffractometer to support vacuum/environmental/processing platforms

Bringing together the capabilities for structural and dynamic investigations in one instrument will lead to new synergies accelerating progress in materials for energy applications and foster new collaborations and growth within our user community.

Development of APS-U Feature Beamline 9-ID CSSI has been a team effort and we gratefully acknowledge essential contributions from Dana Capatina, Atlaf Khan, Jayson Anton, Deming Shu, Raymond Ziegler, Xianbo Shi, Luca Rebuffi, Jonathan Knopp, Sunil Chitra, Miaoqi Chu, Ashish Tripathi, Peco Myint and Suresh Narayanan. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science user facility at Argonne National Laboratory and is based on research supported by the U.S. DOE Office of Science-Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Understanding Dynamics, Strain, and Reversibility of an Organic Mixed Ionic-electronic Conductor Using *Operando* GIXPCS

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Organic mixed ionic-electronic conductors (OMIECs) show promise in an increasing number of fields, including energy storage, neuromorphics, and bioelectronics. The ability to simultaneously transport and conduct ionic and electronic charges represents an important area of materials research; however, the fundamental mechanisms governing carrier transport in these soft materials is not well understood. In particularly, the dynamic aspect of electronic and ionic carriers is not well understood under relevant operating conditions. Here we present work understanding the reversible, irreversible, and dynamic aspects of device operation under adiabatic and non-adiabatic conditions with *operando* grazing incidence XPCS (GIXPCS). Combined with complementary *operando* GIWAXS, electrochemical quartz crystal microbalance, and spectrochemical characterization, the GIXPCS results suggest an unexpected interaction between polaron and bipolaron charge carriers and a long timescale equilibration process that extends ~100x the observed electrochemical transients. The work highlights the need for advanced *operando* coherent x-ray techniques and the critical role of dynamics in OMIECs.

Some Thoughts on XPCS from the Surface Perspective

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In this talk, I will briefly review some of our recent work related to using X-ray Photon Correlation Spectroscopy (XPCS) to probe ion and electrolyte motions and polymer chain dynamics in polymer electrolytes under bias [1]. I will then discuss possible opportunities for using grazing incidence XPCS (GI-XPCS) as a probe of dynamics in both the small angle (SAXS) and wide angle (WAXS) regimes. In the SAXS regime GI-XPCS open opportunities to study the dynamics of domains in phase separated polymers and blends for photovoltaics (PV) and polymer batteries. In the wide-angle regime, there are possible opportunities to investigate ion dynamics in thin films of interest in PV and electrochemical energy storage.

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Toward Functional Nanocomposites: Kinetic Pathway Rules

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Blends with three or more components exhibit unique entropy-driven behaviors and opened up a viable pathway to obtain systemic mobilities. We have shown that supramolecular nanocomposite containing small molecule, nanoparticle and block copolymer-based supramolecules self-assembles analogous to high entropy alloys. That is the system can form hierarchical assemblies with significant formulation flexibility without compromising structural fidelity. Our recent efforts focus on investigating the kinetic pathway. By combining various scattering and electron microscope techniques, we mapped out the kinetic pathway to form hierarchical composite films that have exhibited very interesting properties. These studies clearly demonstrated that *in situ* solution scattering techniques are able to map out how each building block gets organized and are able to overcome several limitations of liquid cell TEM.

APS WK#5: Fundamentals and Applications of High Energy Diffraction Microscopy

Organizers: Marm Dixit, Michael Sangid, and Jun-Sang Park

High-energy x-ray diffraction microscopy (HEDM) has provided new insights into grain-scale measurements of the 3D bulk microstructure and elastic strain, which can be coupled with environmental, thermal, or mechanical loading. The primary goals of this workshop are to bring researchers together to share their experiences using HEDM and discuss needs and ideas of the user community for the HEXM beamline after the APS-U. A combination of talks will include (i) discussions of the fundamentals of the techniques, beamlines, and reconstruction software to support HEDM, (ii) advancements of HEDM, including employing dynamic measurements or sub-grain measurements, such as diffraction tomography, Bragg coherent diffraction imaging, and dark field x-ray microscopy, and (iii) discussion of the applications of HEDM to solve fundamental science questions in materials science, including irradiation, thermo-mechanical loading, and electro-chemistry. During the workshop, we will discuss thoughts and ideas for new experiments in preparation for the HEXM beamline (20-ID) after the completion of the APS upgrade, including necessary software development efforts, the use of machine learning for data analysis, pseudo-real-time zoom-in experiments, etc.

Diffraction Tomography to Unravel the Hierarchical Structure of Biomineral Composites

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Biomineral composites such as bone have complex hierarchical structures. Bone for example is built from collagen fibrils and apatite-like nanocrystals that, together with non-collagenous biomolecules and water, form structures across length scales from the nm to the mm [1]. The structure of these materials thus needs to be understood in three dimensions and across several length scales. To this end, techniques like powder diffraction tomography are particularly well suited and have been used to study several types of biomineral composites [2-6]. The tomographic resolution is determined by x-ray beam size and high energy x-rays will in general be beneficial in part because of the reduced potential for beam damage. The orientation distribution of smoothly textured components can be resolved by measuring diffraction data not only as a function of position and rotation of the specimen but also a tilt – an approach called tensor tomography that we extended to mineral nanocrystals in addition to small angle scattering [7,8]. Thereby the orientational organization of components can also be mapped in 3D.

These techniques provide detailed local insights into complex materials such as biomineral composites whilst retaining the full 3D material context. This in turn enables much deeper understanding of the materials structure.

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[2] Frølich, S. *et al. J. Appl. Cryst.* **49**, 103-109 (2016).
[3] Birkbak, M. E., Leemreize, H., Frølich, S., Stock, S. R. & Birkedal, H. *Nanoscale* **7**, 18402-18410 (2015).
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[8] Grünewald, T. A. *et al. Science Advances* **6**, eaba4171 (2020).

Current and Future Status of Point-focused High-energy Diffraction Microscopy (pf-HEDM)

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The behavior of a polycrystalline material depends not only on the aggregate response of each individual grain, but also on the local intragranular stress concentrations that often dictate the initiation of plastic deformation and damage. Yet very few experimental techniques can quantify intragranular stresses across bulk, three-dimensional volumes. In this work, point-focused high-energy diffraction microscopy (pf-HEDM)—i.e., far-field HEDM with a point-focused "pencil" beam—is used to characterize intragranular deformation across bulk, deformed, polycrystalline titanium specimens. *Ex-situ* and *in-situ* results reveal the heterogenous stress distributions inside individual grains and across grain boundaries. In this talk, we give an overview of the different approaches for analyzing pf-HEDM data sets, compare pf-HEDM results with conventional far-field/near-field HEDM measurements, and discuss the potential for pf-HEDM at the Advanced Photon Source post-APS-U.

In-situ Characterization of Material Transformation Dynamics in Additive Manufacturing Processes

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High-speed synchrotron x-ray imaging and diffraction are powerful tools for characterizing material transformation dynamics (especially beneath the surface of the melt pool) during laser powder bed fusion additive manufacturing process. In this talk, I will present the key data and insights my research group obtained on (1) melt pool fluctuation/instabilities (including both geometry of the melt pool and melt flow within the melt pool), (2) defects formation and evolution, and (3) solidification dynamics. I will also briefly introduce the defects mitigation approaches we developed based on the new mechanisms we discovered and the new insights we obtained from the *in-situ* characterization study. At the end, I will give my thoughts and ideas for first experiments at the upgraded beamlines.

Assessing Polymorphism of Garnet Solid Electrolytes with High Energy Diffraction Microscopy

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Assessing grain level behavior in polycrystalline solid electrolytes is crucial to understand the filament formation and short-circuit behavior of these materials. Here, I will discuss a coupled far-field high-energy diffraction microscopy and tomography approach for assessing the chemo-mechanical behaviour for dense, polycrystalline garnet (Li7La3Zr2O12) solid electrolytes. Mechanical state mapping of all the grains in bulk solid electrolytes during cycling of a symmetric Li | LLZO | Li cell showed that failure in garnet solid electrolytes is initiated locally and is probably a stochastic process. The presence of a trace, secondary cubic polymorphic phase can lead to local transport and mechanical gradients within the solid electrolyte. We observe a strong correlation between stress hot and cold spots with the regions showing high microstructural variation and presence of a secondary cubic polymorph. The combination of real- and reciprocal-space imaging experiments provides evidence of a strong coupling between field-driven ion transport and the mechanical response of grains.

Dark Field X-ray Microscopy Opportunities: Linking Length Scales to Allow for Contextualized Zoom-in Studies

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With the increasing need for high fidelity data to capture the mechanisms of deformation within polycrystalline materials, high energy x-ray diffraction offers the rare ability to non-destructively probe the grain and sub-grain microstructure, often *in-situ*. The combination of high energy x-ray diffraction microscopy (HEDM) and dark field x-ray microscopy (DFXM) is presented in this talk as a tool to facilitate zoom-in studies and provide high spatial and angular resolution data in targeted grains, embedded within the context of the surrounding microstructure. Two use cases are presented, where: i) large spatial gradients in elastic strain are linked to a nearby coherent twin boundary in a nickel-based superalloy, and ii) the local microstructure at triple junctions is shown to be heterogenous along individual triple junctions and, in general, more misorientated than standard grain boundaries. By combining HEDM, DFXM, and careful experimental planning, targeted zoom-in studies are shown to be possible which allow for non-destructive measurements of intragranular lattice curvature and elastic strain in deeply embedded grains, with ~100 nm spatial resolution, while also capturing the surrounding grain averaged microstructure and elastic strains.

Rapid Anomaly Detection of Structural Deformation in HEDM Data

Antonino Miceli[1], Weijian Zheng[2], Hemant Sharma[1], Peter Kenesei[1], Jun-Sang Park[1], Nicholas Schwarz[1], Ian Foster[2], and Rajkumar Kettimuthu[2]

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We have developed a new method for rapid anomaly event detection which was inspired by our model retraining work. Our approach provides users with an anomaly event score for new HEDM datasets, which is calculated using an uncertainty quantification (UQ) score. The UQ score measures the difference between a baseline dataset and new datasets. Our framework leverages an image representation model and clustering algorithms to accomplish this task. The representation model plays a crucial role in transforming the dataset into compact, semantic-rich representations of visually salient characteristics. This method for rapid event detection is based on the pre-processing and clustering of peak patches in the baseline dataset, followed using the pre-trained representation model to generate representation vectors for the new datasets as the material microstructure evolves. By calculating the UQ score, our approach provides users with a reliable indicator of anomalous events such as changes in diffraction peak characteristics. We have successfully applied this method in an HEDM experiment on a Ti-7Al alloy sample with *in-situ* loading to detect the onset of plastic deformation in real-time, where the characteristics of diffraction peaks would change. As compared to traditional approaches for the determination of the onset of plastic deformation utilizing microstructure reconstruction, this method is fully automated, computationally faster by up to 50 times, and works for up to 7 times sparser datasets.

This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science user facility at Argonne National Laboratory and is based on research supported by the U.S. DOE Office of Science-Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

An Overview of Microstructure Characterization Techniques Using High-energy X-rays after the Advanced Photon Source – Upgrade (APS-U)

Jonathan Almer[1], Peter Kenesei[1], Chihpin Andrew Chuang[1], Leighanne Gallington[1], John Okasinski[1], Jun-Sang Park[1], Hemant Sharma[1], and Sarvjit Shastri[1]

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The Advanced Photon Source has been a world leader in developing novel microstructure characterization techniques that use high-energy (> 50 keV) x-rays to investigate materials in their bulk form. In the past decade, several tomographic techniques using absorbed or scattered beam to obtain a 3D view of a sample have been realized. Unique thermo-mechanical sample environments have been combined with these techniques to provide an unprecedented view into how the microstructure evolves with stimulus. For instance, a suite of grain-resolving techniques such as high-energy diffraction microscopy can non-destructively provide 3D information – individual grain orientation, location, morphology, and grain-averaged strain – about a polycrystalline sample with thousands of grains in the illuminated volume. Scattering tomography technique has been an important tool for characterizing the local microstructure variation in nanocrystalline materials. The 3D information extracted from these techniques have been instrumental in material model development and validation at the mesoscale.

The APS-U project presents an exciting opportunity to significantly improve the spatial and temporal resolution of these mapping techniques with enhanced x-ray beam coherence and brilliance. For instance, the newly-constructed High Energy X-ray Microscope (HEXM) beamline will push the spatial resolution of HEDM into sub-micrometer range. Real-time zoom-in and zoom-out capabilities to obtain a more detailed map of the local microstructure will be realized through novel hardware design and software that leverage high-performance computing and novel reconstruction algorithms.

Application of HEDM to Study Aerospace Materials

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High-energy x-ray characterization methods hold great potential for gaining insight into the behavior of materials and providing comparison datasets for the validation and development of mesoscale modeling tools. A suite of techniques has been developed by the x-ray community for characterizing the 3D structure and micromechanical state of polycrystalline materials; however, combining these techniques with *in situ* mechanical testing under well characterized and controlled boundary conditions has been challenging due to experimental design requirements. In this presentation, we describe advanced *in situ* loading environments that are under development for community use at the Advanced Photon Source and the Cornell High Energy Synchrotron Source. Example 3D datasets that have been collected using this hardware and their application for the study of aerospace materials will be discussed.

Application of HEDM for Nuclear Structural Materials Research

Xuan Zhang[1], Dominic Piedmont[1,2], Jun-Sang Park[1], Peter Kenesei[1], Jonathan Almer[1], Matthew Kasemer[3], Ezra Mengiste[3], Mark Messner[1], James F. Stubbins[2], and Meimei Li[1]

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Given the extreme operating environments for nuclear reactor structural materials, it is critically important to understand their response to various structural loading conditions. At best, this should lead to microstructure-property correlation where grain and subgrain level deformation mechanism are capture and related to bulk materials performance. However, there is a discontinuity of the length scales under common investigations of the materials, with mechanical testing providing insight to the bulk behavior while electron microscopy giving nano- to micro-meter scale information. This work presents a series of grain scale (meso-scale) characterization of deformation responses in irradiated materials to provide a direct link between the discontinuous length scales previously observed. Using high energy synchrotron x-rays, high energy x-ray diffraction microscopy (HEDM) nondestructively probes mm-size samples to obtain grain-resolved information before, after, and during uniaxial tensile loading. The resulting data allows for observations of the evolution of grain rotations and residual strains as a function of deformation, and the formation of subgrains in individual grains within polycrystalline aggregates. These results were obtained for Fe-9wt%Cr samples that were neutron-irradiated to different doses at different temperatures, and samples that were not irradiated for comparison purposes. Experimental results will be compared to computational results from Crystal Plasticity Finite Element Modeling (CPFEM) simulations.

APS WK#6: New Opportunities in Chemistry and Materials Sciences with Anomalous X-ray Scattering

Organizers: Mrinal Bera and Matthew Tirrell

Anomalous x-ray scattering provides an unparallel non-destructive tool to determine the element-specific structure of matter in dimensions ranging from sub-nanometers to hundreds of nanometers. Although anomalous scattering is known for more than four decades the very weak nature of anomalous signals in comparison to the non-resonant ones has made the technique very challenging and at the same time too specialized that only a few experts around the world were using it. The availability of bright energy tunable x-ray sources from APS, and the recent development in the optimized ASAXS instrument at NSF’s ChemMatCARS had made it possible to bring this specialized technique to non-expert users. This workshop is focused on bringing current and prospective users of anomalous x-ray scattering to discuss the new opportunities in chemistry and material sciences. Discussions will be focused on using the smaller and improved coherent x-ray source after the scheduled APS upgrade to develop time-resolved and grazing incidence anomalous scattering capability.

Advanced Materials to Decarbonize Future?

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One of the greatest scientific and engineering challenges of the 21st century is to develop sustainable energy technologies to replace fossil fuels that are currently the main sources of global energy. Among various emerging technologies, energy conversion and storage systems have shown tremendous potential to be the alternative of fossil fuels due to their ability to harvest renewable energy, e.g., solar and wind in the form of chemical bonds. In general, energy can be stored or converted into chemical bonds through photo/electrochemical processes, e.g., batteries, carbon dioxide reduction reaction (CO_2RR), oxygen reduction reaction (ORR), oxygen and hydrogen evolution reaction (OER and HER) and utilized as the main energy source in the form of electricity or fuels. However, a real activity improvement for these technologies requires novel and advanced materials with unique properties (e.g., electronic, structural, and physicochemical properties) that are currently a bottleneck. We at *Electrochemical Energy Materials and Devices Laboratory (e^2MDLab)* seek to advance clean energy technologies by having a dual focus: (i) fundamental understanding in the various aspects of advanced materials, photo/electrocatalysis and surface chemistry along with (ii) leading innovation in the area of device fabrication. In this workshop, I will present our recent activities on developing cost-effective and energy-efficient sustainable energy technologies to replace fossil fuels and achieve net-zero carbon economy.

Morphology of Block Copolymer Films Determined by Resonant Soft X-ray Scattering

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Small angle x-ray scattering (SAXS) is a powerful tool for studying the morphology of block copolymers in reciprocal space. However, SAXS cannot be used for studying extremely thin films (comparable to the domain size of the copolymers), neither can it be used to study the morphology of void-containing block copolymers. We demonstrate the utility of Resonant Soft X-ray Scattering (RSOXS) in these systems.

ASAXS Facility at NSF’s ChemMatCARS

Mrinal K. Bera[1]

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NSF's ChemMatCARS located in Sector 15 of the Advanced Photon Source (APS) is a national user facility that offers an exceptional experimental infrastructure to researchers worldwide in the fields of small molecule crystallography, liquid interface scattering, and anomalous small-angle x-ray scattering (ASAXS). ASAXS, one of the three techniques available at ChemMatCARS, is a cutting-edge characterization tool that has undergone rapid advancements in hardware and software. It can provide element-specific structural information for matter ranging from a few nanometers to hundreds of nanometers. This presentation will cover the current capabilities of the ASAXS facility, recent studies conducted using the facility, and future capabilities that will utilize smaller and more improved coherent x-ray beams made available after the ongoing APS upgrade.

Long-range Ordering of Electrolytes Probed with Anomalous X-ray Scattering

Abdullah Kahraman[1], Mohammadhasan Dinpajooh[1], Shawn M. Kathman[1], Greg K. Schenter[1], Christopher J. Mundi[1], Mrinal K. Bera[2], John L. Fulton[1], and Elisa Biasin[1]

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Despite intensive investigation, a complete understanding of the arrangements of ions in concentrated aqueous solutions is still lacking and necessary to understand fundamental phenomena such as ion solvation and transport, as well as nucleation and crystallization. In particular, many open questions remain about the long-range structure of aqueous salt solutions (1-10 nm). Members of our group have shown that to the intermolecular structure arising from the long-range arrangement yield a 'prepeak' at small scattering angle ($Q<1.5$ Å^{-1}), with characteristic position and intensity depending on the type and charge of the ionic species, and on the concentration [1,2]. Atomistic molecular dynamics (MD) simulations have shown that the cation−cation interaction contributes the most to the prepeak signal, which can also be reflected in the oxygen-oxygen correlations, while cation−anion and anion−oxygen pairs contribute destructively (anticorrelation) to the prepeak [2,3]. Benchmarking these calculations is currently impeded by the impossibility of disentangling the different atomic pair contribution to the measured scattering signal, an impediment which we can overcome with anomalous x-ray scattering (AXS). In this talk, I will show recent AXS measurement at beamline ChemMatCARS at the Argonne Photon Source of $ErBr_3$ and $SrBr_2$ in aqueous solution and compare them with MD simulations.

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Opportunities in Understanding Macromolecular Dynamics by Integrating ASAXS and Liquid-phase TEM

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I will discuss my group’s recent efforts on liquid-phase transmission electron microscopy (TEM) studies of macromolecular dynamics at the nanometer resolution in their solution environment. The first system is the fluctuation and fingering dynamics of membrane proteins in lipid bilayers, where liquid-phase TEM imaging in real-space allows us to measure protein mechanics parameters and lipid-protein interactions. The second system is nanogels dispersed in water undergoing *in-situ* heating with concurrent liquid-phase TEM imaging. We convert the TEM contrast intensity maps to maps of local density, revealing a hierarchy of structural heterogeneities in these nanogels. I will conclude with perspectives on how the nondestructive nature and composition sensitivity of ASAXS can provide additional critical insights in these macromolecular systems.

Using ASAXS of Heavy Element (I)-loaded Block Copolymer Micelles to Investigate Fundamental Behavior of Novel Polymer Lung Surfactant Therapeutic

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Animal-derived lung surfactants (LS) annually save 40,000 infants with neonatal respiratory distress syndrome (NRDS) in the US. Lung surfactants have further potential in treating about 190,000 adult patients with acute respiratory distress syndrome (ARDS) each year. To this end, the properties of current therapeutics need to be modified. Although limitations of current therapeutics have been recognized since 1990s, there has been little improvement. To address this gap, our laboratory has been exploring a radically different approach where, instead of lipids/proteins/peptides, synthetic block copolymers (BCPs) are used as the active therapeutic ingredient. This endeavor has led to an identification of a promising polymer-based lung surfactant candidate (BCP nano micelles). BCP micelles produce extremely high surface pressure under high compression because BCP micelles have a strong affinity to the air-water interface. A detailed study is underway to understand the exact molecular origin of this behavior. X-ray reflectivity (XR) and grazing incidence x-ray diffraction (GIXD) are essential for establishing how morphological characteristics of BCP micelles affect their surface mechanical (high surface pressure-generating) properties; however, the low x-ray contrast between the polymer particles and water leads to uncertainty in the analysis. Therefore, we want to explore heavy element (I)-loaded BCP micelles to enhance the x-ray contrast. ASAXS measurements will be used to quantify the spatial distribution within the BCP micelle core to allow for proper analysis of the XR and GIXD data. By obtaining results for loaded and unloaded BCP micelles, we can draw more confident conclusions about the fundamental behavior of the lung surfactant therapy with the hope of ultimately translating this research to improvements in human health outcomes.

Polymerization Induced Microphase Separation Approaches to Ion-containing Nanostructured Materials

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We have used polymerization induced microphase separation (PIMS) strategies to generate nanostructured materials by carrying out a polymerization of a mixture of a monofunctional and difunctional monomers such as styrene and divinyl benzene in the presence of a macromolecular chain transfer agent such as a trithiocarbonate end-functionalized polylactide in the absence of solvent. An initially homogenous solution microphase separates upon conversion of the monomer mixture, and then the crosslinked network chemically fixes the nanostructured material. In the case of polylactide as the macromolecular chain transfer agent, subsequent chemical etching leads to disordered, bicontinuous, nanoporous solids. We have expanded this general approach to other functionalized macromolecular chain transfer agents and have used a PIMS approach to generate nanostructured material that containing ionic groups in one of the domains. This was accomplished by using appropriate protecting groups in the functionalized macromolecular chain transfer agent to give “pre-anionic” or “pre-cationic” functionalized polymers. This allows the PIMS approach to be utilized for the generation of ionic materials post deprotection that have potential utility in electrochemical, separation, and adsorbent applications. In this presentation, I will discuss our recent work in the preparation of ion-containing nanostructured monolithic materials and extension of this approach to the scalable preparation of similarly structured microspheres by utilizing suspension polymerization methods.

Synchrotron-enabled Nanocellulose Research: From Basic Science to New Circular Solutions for Improving Water-food-infrastructural Nexus

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The Hsiao group at Stony Brook has been using a wide range of synchrotron x-ray scattering and spectroscopic techniques to investigate many fundamental aspects of nanocellulose, the nanoscale aggregate of elementary cellulose microfibril (the building block of plant cells). The investigated topics included: (i) the cross-sectional shape and dimensions as well as the aggregation behavior of cellulose microfibrils in suspension, (ii) the re-assembly of nanocellulose into high-performance fibers and membranes through hydrodynamic alignment, (iii) the ion-induced gel-transition of nanocellulose scaffolds, where ions act as screening or cross-linking agents depending on the valency, (iv) nanoscale dynamics of metallic nanoparticles in networks of charge stabilized nanocellulose. We believe the ASAXS technique will be particularly useful to determine the nature of bonding between cross-linking metal ions and nanocellulose, as well as the synthesis of metallic nanoparticles within the nanocellulose scaffold by nucleation and growth pathways. Recently, our team has developed a zero-waste approach to prepare nanocellulose from biomasses of diverse origins. In this approach, the processed effluent can be efficaciously neutralized to produce plant fertilizers. The demonstrated technology has many far-reaching impacts to provide new circular solutions to improve the nexus of food-water-infrastructural systems and combat climate change.

Anomalous Small-angle X-ray Scattering (ASAXS) Studies of Counterion Distribution Surrounding Soft Biomolecular Assemblies

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The structure and function of charged biomolecular materials such as DNA, proteins and lipid assemblies in aqueous solutions are intricately connected to the distribution of counterions that surround them and neutralize their charge. Anomalous small angle x-ray scattering (ASAXS) is the obvious nm-scale technique for analyzing such ionic distributions. We utilized ASAXS to deduce the distribution of Rb^+ surrounding functional biomaterials: DNA-coated proteins and twisted ribbon assemblies of a peptide amphiphile. On one hand these studies reveal some limitations of ASAXS as a standalone technique because of the limited q-range of the weak signal from the counterions. On the other hand, ASAXS not only gives insights into ionic distributions, but also reveals nm-scale details of the macro-ion substructure such as the extension of the charged and uncharged segments. We will discuss these aspects along with possible complementary methods for making the ASAXS analysis more robust.

Programming Multicomponent Colloidal Crystal Structures Using DNA

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To access materials with new functional properties, synthetic strategies are needed that can independently program composition and structure. Multicomponent colloidal crystals comprised of more than one type of functional nanoparticle building block are a promising class of materials that can exhibit new and enhanced tunable properties in comparison to their single-component counterparts. Colloidal crystal engineering with DNA is a powerful strategy to program such structures. In this approach, nanoparticle building blocks are functionalized with a dense shell of oligonucleotide ligands with programmable interactions that drive their assembly into larger structures. The DNA shell has programmable sequence, length, interaction strength that can be tuned independently from the identity of the nanoparticle core. The independent nature of the nanoparticle composition and DNA shell is used to encode both ordered and random substitution in colloidal crystals with otherwise identical parent lattice symmetry and crystal habit. The tunability of DNA interaction strength can be further employed to establish a one-pot synthesis route for core-shell colloidal crystals, and by employing DNA junction dendrimers new lattice symmetries and anisotropic control over lattice parameter in a single crystallographic direction have recently been accessed. The structure of these colloidal crystals has been previously investigated using SAXS, but potential new opportunities emerge in understanding multicomponent colloidal crystal structures using ASAXS.

ASAXS Cataloguing of the Molecular Organization of Biological and Abiological Matter in Hybrid Membranes

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Hybrid phospholipid/polymer membranes organize biological lipids and synthetic polymers into molecularly mixed or phase-separated polymer-rich and lipid-rich domains. These materials hold great potential as bioinspired separation membranes, drug delivery systems, or as platforms to build artificial cells as they harness the chemical diversity of polymers and the biocompatibility of lipids. In a series of papers of the Leal lab we have characterized these systems by SAXS and multiple imaging techniques, and we found that they display synergetic structural, mechanical, as well as heat and mass transport properties. Our hypothesis is that this behavior can be modulated if we control the size and identity of the polymer-rich and lipid-rich domains and the interface between them. However, normal SAXS and most imaging tools do not convey information about the chemical composition of the phase-separated domains. ASAXS evaluates the dependence of the scattering length of a given element if the energy of the incident x-ray beam is near the absorption edge of this element. This can potentially be very useful to elucidate the chemical complexity of domains that emerge during hybrid membrane co-assembly.

ASAXS for Understanding Ion Transport in Confinement

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Solid-state ionic channels with dimensions around and less than 1 nm provide emerging opportunities to modulate the desolvation and transport of ions based on their differences in Lewis acidity and ionic radii for separation. To reconstruct the ion transport pathway, it is critical to resolve the spatial distributions of co-existing ions of different species in the same confined channels in operando or at different snapshots. Here I will introduce ASAXS as a powerful method to correlate with x-ray diffraction and transmission electron microscopy to provide both elemental and structural information about ions and the solid host at the same time.

Counterion Association around Nanoscale Macroions and the Consequent Self-assembly, Phase Transition, and Chiral Recognition Behaviors

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Between traditional simple ions and large colloidal particles, we found that there exists a transitional stage – macroionic solutions. In this regime the solutes show solution behaviors fundamentally different from the other two categories. The moderate size and charge disparities between macroions and their counterions result in lose counterion association around macroions. Using 3-nm-size, structurally well-defined molecular clusters with accurately tunable charges as models, ASAXS provides the opportunity to quantitatively determine the number and distribution of metal counterions around central macroions, which helps to explain the strong attraction among such hydrophilic macroions and their consequent interesting solution behaviors – for both microphase (self-assembly) and macrophase phase separations. In dilute solutions, they tend to reversibly self-assemble into single-layered 2-D nanosheets, which eventually form stable, hollow, spherical "blackberry" structures with their sizes accurately tunable by the strength of counterion-macroion interaction. This self-assembly demonstrates interesting self-recognition behavior, and even chiral discrimination feature among enantiomeric macroions, or when chiral counterions/co-ions are present, commonly seen in biological systems. Macrophase separations result in hydrogel and coacervate phases, both are common for polyelectrolytes but rare for inorganic molecules. We expect ASAXS technique can provide fundamental explanations on these phenomena.

ASAXS Analysis of Random and Blocky Model Semi-crystalline Ionomers

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Ionomers are generally defined as copolymers containing a relatively low content (i.e., less that about 15 mol%) of charged monomer units distributed between runs of non-ionic monomer units. In a sufficiently non-polar matrix, strong electrostatic forces often cause the ion-pairs to aggregate into distinct morphological features (i.e., multiplets having characteristic dimensions near 1nm) that are easily observable by SAXS. In addition, SAXS of ionomers often show a pronounced small-angle upturn proposed to be due to long-range heterogeneities in the distribution of the ions. Since the late 1980's, ASAXS has been shown to provide valuable insight into the morphological origins of complex ionomer scattering. However, many questions specifically related to semi-crystalline ionomers remain unanswered. Recently, we have developed a widely applicable procedure to prepare blocky ionomers by post-polymerization functionalization in the semi-crystalline gel state. In this presentation, we will demonstrate how random and blocky ionomers of the same ion content can yield very different scattering behavior. For example, the ionomer peak in our model random ionomers (e.g., sulfonated syndiotactic polystyrene) is much more prominent than that observed for an analogous blocky SsPS. Similar results are observed for random and blocky sulfonated PEEK ionomers. To add to the complexity, the crystalline component in these ionomers is also profoundly affected by the random vs. blocky microstructure. In this presentation, we hope to explore the ability of ASAXS to discriminate crystalline and ionic contributions to the unusual scattering behavior and to explore how ASAXS can be used to gain insight into the local and long-range ordering of ionic domains.

Where are the Metals?

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At Oregon State University, we have a benchtop SAXS that we use daily to study inorganic molecules, metal-oxo clusters, nanoparticles, and biological macromolecules. We use this instrument in our own research projects and via collaboration. We also use ASAXS as a complementary tool. I will describe the use of ASAXS in a recent collaborative project, and the proposed use of ASAXS in a recently funded project.

DNA-metal hybrid complexes are fascinating building blocks for DNA origami. Exploiting the precise and predictable behavior of the double helix, one can create polyhedra, extended lattices, cages and nanomachines. In a collaboration with Professor Miguel Galindo (U. Granada, Spain), we compare the interactions of silver with a natural DNA complex, and with a deaza-modified DNA complex in which the a CH group replaces the N7 atom, and consequently metal can replace the canonical hydrogen-bond. Benchtop SAXS (Cu-Ka) monitored the nanostructures in solution with titration of silver-ions. Titrating Ag into the two forms (modified and unmodified) showed increase in size in both cases, but with notable differences in shape. The modified DNA complex grew into long chains with Ag addition, and the natural DNA complex showed a smaller size increase, without growth of long chains. Using ASAXS at APS, we then measured the same solutions at 20 different energies within 1 keV and up to the silver K-edge (25.51 keV). These data provided detailed information about the location of the Ag. The Ag located inside the modified DNA, replacing H-bonding of the canonical base pairs. On the other hand, size increase of the natural DNA with Ag titration was attributed to bonding on the outer phosphate groups.

Our team was recently awarded a grant to determine how self-sorting of similar metals into oxocluster compounds can be exploited in metal-metal separations, and we intend to use ASAXS in these studies. Differentiating co-crystallization of metals in separate oxoclusters from statistical mixing of metals into the same cluster is very challenging. In addition, crystallization biases towards the highest-symmetry clusters. Finally, solution-based techniques are non-innocent in promoting metal-scrambling (i.e. ionization mass spectrometry), or cannot simultaneously provide composition and topology information. I will describe how we intend to use ASAXS to determine which metals assemble into which cluster topologies in multimetal solutions, towards understanding oxocluster-based Ln separations, Zr-Hf separations and noble metal separations.

Complex Oxide Nanocrystals, Nanocomposites Films, and Exploring the Potential of ASAXS

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Nanocomposite metal− insulator− metal (MIM) capacitors are of interest due to the possibility of reducing the number of discrete components in printed circuit boards, and alternatively using embedded or directly printed capacitors in conjunction with integrated circuits. The prospect of designing a nanocomposite dielectric, by combining colloidal nanoparticle fillers and polymer hosts, is a long-standing concept that lends itself very well to the idea of tunability of the mechanical and electrical properties. However, nanocomposite films often fall short of providing an enhancement over the properties of the individual components. Continued efforts to understand the dispersion of colloidal nanoparticles in the continuous polymer host, and in particular the interfaces involved, will aid in advancing nanocomposite film technology. Our work in solution processing of inorganic oxide dielectrics and multiferroics, using a modified sol-gel approach allows for the preparation of a variety of formulations that can be treated as inks for deposition as layers and/or for the design of novel nanocomposite films. It is of compelling interest to explore whether ASAXS can be used in the characterization of these systems.

Using ASAXS to Explore Ordering in Soft Materials

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The determination of higher order structuring in polymeric systems is paramount to elucidating the fundamental structure property relationships that allow materials to be tailored for specific applications. However, there are many instances of polymer systems that lack either the contrast required to differentiate adsorbed small molecules from a surrounding matrix or the regular ordering required for many conventional characterization techniques. The focus of these works involves studying nanoscopic ordering in polymer materials using Anomalous Small Angle X-ray Scattering (ASAXS) as a means of circumventing challenges that would typically come with determining the structure of systems such as these. ASAXS was used to probe two different systems: the first being the three-dimensional packing of metal ions surrounding carboxylate functionalized cellulose nanocrystals (CNCs) and the second being the distribution of diselenide containing crosslinks in the amorphous regions of dynamic liquid crystal elastomers (LCEs). The furthered understanding of how these ASAXS active species order within CNCs and dynamic LCEs will offer valuable insight into the structure property relationships that will allow these polymeric systems to be useful in applications such as water separations and trainable materials respectively.

High-entropy Alloy and Oxide Nanoparticles from Flame-based Aerosol Synthesis

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This presentation will briefly describe a unique process that enables one-step continuous synthesis of nanoparticles (typically polycrystalline hollow nanoshells) of high-entropy oxides, incorporating five or more different cations in a single phase. This approach also allows synthesis of metallic high-entropy alloys as nanoparticles on various supports. We will present representative examples of the various high-entropy materials we have prepared by this method. We are applying these materials in both thermal catalysis and electrocatalysis. These high-entropy materials provide an enormous space for designing new materials and have other important advantages such as improved high-temperature stability. However, even when thermodynamically stable at high temperature (where entropic contributions are more heavily weighted) these materials may be metastable at lower temperature, and therefore susceptible to phase separation. We are interested in exploring whether ASAXS can provide valuable insights into distributions of elements in these materials. For example, surface segregation of specific elements, either in the freshly prepared materials or during their use, is of great interest in catalytic applications.

Understanding Solvation Structures in Electrolytes for Electrochemical Energy Storage

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Electrochemical energy storage is an enabling technology as humanity transitions to a carbon neutral economy. It is very important to understand the nature of ion solvation within electrolyte as the strength of the ion-solvent interactions play a strong role in dictating the efficacy of charge and mass transfer and stability at electrode-electrolyte interfaces for electrochemical energy storage [1]. We have adopted a multimodal approach to quantifying solvation including molecular dynamics (MD simulations, x-ray absorption spectroscopy (XAS), various optical spectroscopies and total x-ray scattering or pair distribution function (PDF) measurements. It is becoming increasingly apparent there that there exist nm – 10s nm scale local structures or aggregates in many interesting electrolytes [2]. To probe these nanoscale heterogeneities, we use small angle x-ray scattering (SAXS) and increasingly anomalous SAXS (ASAXS), as this method can provide insight into partial PDFs. In this talk I will discuss recent results [3] on nm scale Zn domains in various concentrations of $ZnSO_4$ in H_2O-acetonitrile mixtures that show an increasing tendency to phase separate into Zn-rich and Zn-poor domains, where ASAXS provides compositional insight. These are promising electrolytes for aqueous Zn batteries.

[1] "Energy storage emerging: A perspective from the Joint Center for Energy Storage Research", L. Trahey et al., PNAS **117**, 12550-12557 (2020).
[2] "Beyond Local Solvation Structure: Nanometric Aggregates in Battery Electrolytes and Their Effect on Electrolyte Properties", Z Yu et al., ACS Energy Lett. **7**, 461−470 (2021).
[3] EN Antonio, MJ Counihan, S Ilic, M Bera, S Tepavcevic, MF Toney, in preparation.

Selective Rare Earth Elements Recovery from Homogeneous Aqueous Solutions by Self-assembling Lanthanide Binding Tag Peptides

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Rare earth elements (REEs) possess unique chemical and physical properties that are applicable in a wide range of industrial applications, such as electronics, catalysis, clean energy, batteries and magnetics. Currently, the separation and purification of REEs rely on solvent extraction, which are fast and inexpensive for the handling of large quantities of materials, but solvent extraction is energy intensive and environmentally unfriendly. We aim to develop new extraction methods that seek to avoid the use of organic solvents for the separation of REEs. We have designed a set of self-assembling peptides based on Lanthanide Binding Tags (LBTs) where self-assembly is driven by ion coordination and crosslinking. We have used anomalous small angle x-ray scattering (ASAXS) measurements to determine the distribution of trivalent cations on the self-assembly structures. We demonstrate that ASAXS can directly measure the number of ions per peptide and quantify selectivity of binding between Terbium and Lutetium. These values were also confirmed by results obtained by inductively coupled plasma optical emission spectroscopy as well as ultraviolet absorption spectroscopy. The ability of the self-assembled structures rich in trivalent cations to then sediment makes possible the use of low energy sediment separation and microfiltration to isolate the desired REEs from undesired elements present in solution.

Foldable Semi-ladder Polymers: Novel Aggregation Behavior Investigated by Using SAXS Scattering Technique

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We develop cross-conjugated weak acceptor-weak donor copolymers as electroluminescent materials. These materials exhibited unexpected high efficiency in organic light emitting transistor. An impressive external quantum efficiency (EQE) of 6.9% in solution-processed multi-layer OLET devices was achieved. Detailed studies in optical properties, DFT calculation and SAX scattering experiments indicated that these copolymers form coiled foldamers with intramolecular H-aggregation, which favors charge transport and minimize exciton quenching.

Applications of ASAXS for Nanoparticle Element Mapping and Biomarkers

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Anomalous small-angle x-ray scattering (ASAXS) can provide element-specific scattering signals, therefore element-specific structural information. This information is not easy to obtain from conventional x-ray scattering and other structural tools. In this presentation, I would like to talk about some ongoing research on using conventional and anomalous SAXS to map the element distribution in bimetallic nanoparticles. In another project, we are interested in measuring long range distances between residues in biomolecules using gold clusters as biomarkers and ASAXS as the technical tool. Some simulation work will be discussed.

Joint WK#7: Real-time Analysis of Synchrotron Light Source and Nanoscale Research Center Data using AI/ML for APS-U First Experiments

Organizers: Nicholas Schwarz, Subramanian Sankaranarayanan, Mathew Cherukara, and Chengjun Sun

The APS and CNM are in the position to help solve some of the most challenging and novel scientific questions facing the energy needs of the nation. The design of new materials to manipulate classical and quantum information with high fidelity and ultralow power consumption, enabling systems for efficient energy storage, transportation, and conversion that will drive the emerging economy based on renewable energy are just a few examples. Addressing these scientific opportunities will be aided by the intrinsic capabilities of APS-U era facilities along with technological advances in detectors and new measurement techniques in x-ray and electron microscopies.

These advances in sources and detectors (x-ray & electron) will result in orders of magnitude higher data rates, and increased complexity from multi-modal data streams. Conventional data processing and analysis methodologies become infeasible in the face of such large and varied data streams. The use of AI/ML methods is becoming indispensable for real-time analysis, data abstraction, and decision making at advanced synchrotron light sources and nanoscale centers. AI/ML will play a key role in the realization of real-time data analysis capabilities for APS-U first experiments.

This workshop is organized to discuss the state-of-the art and potential applications of AI/ML for APS-U first experiments. It provides an opportunity for academics, laboratory and facility staff, researchers, and students from x-ray & electron characterization, hardware design, and computer science communities to exchange ideas and think creatively about new approaches to edge AI/ML applied to next-generation AI-driven experiments at synchrotrons and nanoscale centers.

Topics include, but are not limited to:

- Real-time, on-the-fly processing and analysis
- Smart *in-situ* and *operando* experiments (electron and x-ray)
- Ultrafast phenomena and dynamics
- AI/ML-assisted workflows
- Digital Twins for electron and x-ray characterization
- Data infrastructure for synchrotron and nanoscale user facilities
- AI-accelerators for fast training and inference

Enabling Real-time Artificial Intelligence-guided Photon Correlation Spectroscopy at CSX

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Advances in detector technology and accelerator design have helped x-ray photon correlation spectroscopy (XPCS) become an essential technique found at almost any x-ray synchrotron. However, the increased coherent flux, improved detector time resolution, and higher user demand have created bottlenecks during and after the experiment that affect publication rates. To address this, many beamlines are providing some form of automatic analysis for all XPCS user. However, these revolutionary detector and source advances generate additional complications for straightforward, standardized XPCS data reduction. Advanced detectors help to increase the dynamic time resolution but are also more sensitive to source and electrical noise. At the same time, new user communities are becoming increasingly interested in using XPCS to study a variety of materials (polymers to quantum materials). A flexible endstation with various geometries that can support in-situ experiments is needed, as well as a variable incident energy to gain the necessary scattering contrast for chemical/electronic specificity. Such capabilities can create instabilities in the sample or beamline optics that adversely impact the ability to perform XPCS or other coherent scattering experiments. At NSLS-II, we have developed a few generalized artificial intelligence (AI) tools to help address these issues and to improve/augment standard analyses. We will discuss these tools and show how they may be utilized using open-source software supported by a large and diverse scientific computing community.

Artificial Intelligence and Machine Learning Aided Prompt Analysis of Powder Diffraction and PDF Data

Simon J. L. Billinge[1]

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Hard x-rays tend to make experiments easy. They are penetrating allowing *in situ*, *operando* and spatially resolved measurements. Large regions of reciprocal space can be covered rapidly opening the door to high real-space resolution total scattering measurements. Absorption is lower making corrections easier, and resulting beam damage of the sample is less of a worry. These things tend to make us greedy though. We now want to put operating batteries in the beam and study spatially resolved labs-on-chip, do real-time autonomous experiments and use computed tomography to see diffraction from cross-sections of bulk samples. These developments, powered by wonderful source and detector developments, present major challenges on the data analysis side. Now we are putting heterogeneous devices in the beam and getting signals from different parts of them. We have bad powder averages (spotty data) because we can't spin the battery, and single crystal spots coming from some component in the setup that happens to be in the way of the beam. We have unknown and unexpected phases coming and going, and want to extract tiny signals from large backgrounds. I will take this opportunity to discuss some of the data analysis, algorithmic and computational developments that are helping us to overcome these challenging situations and not only recovering from "bad data," but also turning bad data into good data. Spotty powder patterns have more information in them than smooth powder rings. Normally, data that contain more information would be thought as "better" than data with less, but it is considered bad because we don't have great ways to extract that information. I will describe some new approaches, algorithmic, statistical, machine learning and otherwise, that are helping us move the goalposts in this domain, which can open up new opportunities for studying complex heterogeneous samples with hard x-rays.

Understanding Relaxation Dynamics Beyond Equilibrium Using AI-Informed X-ray Photon Correlation Spectroscopy

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Understanding and interpreting dynamics of functional materials *in situ* is a grand challenge in physics and materials science due to the difficulty of experimentally probing materials at varied length and time scales. X-ray photon correlation spectroscopy (XPCS) is uniquely well-suited for characterizing materials dynamics over wide-ranging time scales, however spatial and temporal heterogeneity in material behavior can make interpretation of experimental XPCS data difficult. We have developed an unsupervised deep learning (DL) framework for automated classification and interpretation of relaxation dynamics from experimental data without requiring any prior physical knowledge of the system behavior. We will demonstrate how this method can be used to rapidly explore large datasets to identify samples of interest, and we will apply this approach to directly correlate bulk properties of a model system to microscopic dynamics. Finally, we will discuss how DL classification of dynamics can be applied at the beamline to help guide experiments, and track changes in dynamics in near real time.

Towards Real-time Data Processing and Analysis of X-ray Emission Spectra Using AI/ML: Argonne X-ray Emission Analysis Packages

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The APS-U and the latest development of advanced x-ray emission spectrometer enable the plausible x-ray emission mapping in conjunction with the microprobe x-ray fluorescence mapping, time-resolved and operando experiments. These experiments generate big data, which requires real-time data processing and analysis. The Argonne X-ray Emission Analysis Package (AXEAP) has been developed to process and analysis x-ray emission spectroscopy (XES) data collected with a two-dimensional (2D) position sensitive detector. AXEAP is designed to convert a 2D XES image into an XES spectrum and quantitative analysis in real time using both machine learning and genetic algorithm. AXEAP is capable of making raw data transformation at a rate similar to data collection, allowing real time comparisons during data collection, reducing the amount of data stored from gigabyte-sized image files to kilobyte-sized text files. In addition, AXEAP designed finds a set of theoretical parameters that induce high-quality fit of the experimental spectrum with minimal program user intervention. AXEAP is written in MATLAB and Python and can run on common operating systems, including Linux, Windows, and MacOS. Furthermore, the AXEAP will also enable the any application by utilizing the position sensitive energy detection technique, such as energy dispersive x-ray absorption spectra.

Towards Autonomous Discovery of Thin Film Functionalities

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The classic design of experiments can be a very time-intensive process which requires experienced advanced planning alongside data processing, modeling, and interpretation by expert scientists. To help accelerate the design of experiments, we developed an integrated, machine-intelligent experimental system which enables simultaneous dynamic tests of electrical, optical, gravimetric, and viscoelastic properties of materials under a programmable dynamic environment. The underlying software controls the experiment and performs on-the-fly extensive data analysis and dynamic modeling, real-time iterative feedback for dynamic control of experimental conditions, and rapid visualization of experimental results. The system operates with minimal human intervention and enables time-efficient characterization of complex dynamic multifunctional environmental response of materials. It provides a viable platform for artificial intelligence-centered material characterization, which, when coupled with an autonomous synthesis system (will briefly discuss), could substantially accelerate discovery of new multifunctional materials.

This research was conducted at the Center for Nanophase Materials Sciences, which is a US Department of Energy Office of Science User Facility.

Towards Autonomous Discovery of Thin Film Functionalities

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The classic design of experiments can be a very time-intensive process which requires experienced advanced planning alongside data processing, modeling, and interpretation by expert scientists. To help accelerate the design of experiments, we developed an integrated, machine-intelligent experimental system which enables simultaneous dynamic tests of electrical, optical, gravimetric, and viscoelastic properties of materials under a programmable dynamic environment. The underlying software controls the experiment and performs on-the-fly extensive data analysis and dynamic modeling, real-time iterative feedback for dynamic control of experimental conditions, and rapid visualization of experimental results. The system operates with minimal human intervention and enables time-efficient characterization of complex dynamic multifunctional environmental response of materials. It provides a viable platform for artificial intelligence-centered material characterization, which, when coupled with an autonomous synthesis system (will briefly discuss), could substantially accelerate discovery of new multifunctional materials.

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X-ray Nano-imaging of Epitaxial Thin Film Functional Oxides via Cluster Analysis

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Scanning x-ray nanodiffraction enables *in-situ*, non-destructive imaging of local structural distortions across an extended spatial region of thin samples. Functional properties of oxide thin films strongly depend on nanoscale structural properties, yet localized lattice distortions remain challenging to detect and pinpoint, due to their weak diffuse scattering. Here, we discuss the application of machine learning in two examples of synchrotron experiments: 1) unsupervised clustering to isolate the low-intensity diffuse scattering in as-grown and alkaline-treated thin epitaxially strained SrIrO3 films, and 2) non-linear least squares modeling of phase coexistence a in a multiferroic heteroepitaxial system. Our findings demonstrate the potential to study electrochemical reactions at defect sites identified through clustering in operando experiments and to facilitate real-time analysis of complex microelectronic devices.

Programmatic and Deep Learning Analysis Pipelines for 4D-STEM Materials Science Experiments

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Many materials science studies use scanning transmission electron microscopy (STEM) to characterize atomic-scale structure. Conventional STEM imaging experiments produce only a few intensity values at each probe position. However, modern high-speed detectors allow us to measure a full 2D diffraction pattern, over a grid of 2D probe positions, forming a four dimensional (4D)-STEM dataset. These 4D-STEM datasets record information about the local phase, orientation, deformation, and other parameters, for both crystalline and amorphous materials. However, 4D-STEM datasets can contain millions of images and therefore require highly automated and robust software codes to extract the target properties. In this talk, I will introduce our open source py4DSTEM analysis toolkit, and show how we use these codes to perform data-intensive studies of materials over functional length scales. This includes measurements of macroscopic properties such as crystal phase, orientation, and local deformation maps, and microscopic properties such as atomic structures in 2D and 3D measured with ptychography and other phase contrast imaging mode. I will also demonstrate some applications of modern machine learning tools, to perform measurements on electron diffraction patterns where property signals have been scrambled by multiple scattering of the electron beam. All our analysis, simulation, and machine learning codes and datasets are freely available for download, as we try to adhere to FAIR data principles.

Static and Dynamic Critical Phenomena in Rare Earth Separations

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Synchrotron-based x-ray scattering techniques enable characterization of complex solutions, including those used in liquid-liquid extraction of critical materials, such as rare earth elements. Static structure, measured with small angle x-ray scattering, and dynamic behavior, measured with x-ray photon correlation spectroscopy, provide insight into the deleterious liquid-liquid phase transitions encountered in this important industrial process. Here, we share research performed at the APS on using these techniques to study critical phenomena associated with that phase transition, gaining insight into how to improve process design. We also discuss how beamline robotics have enabled higher-throughput investigations of phase diagrams. Additionally, simulations of analogous systems using machine learning-based coarse graining methods are helping us bridge experimental and simulation lengthscales and timescales. We comment on how future improvements of the APS-U, combined with advances in coarse-grained computational methodology, will further narrow the gap between simulation and experiment.

Deploying Machine Learning-based Segmentation for X-ray Diffraction Images at Synchrotron Facilities

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The processing of images in scientific user facilities can be challenging due to the vast amount of data generated by experiments and simulations. Moreover, creating and implementing algorithms for real-time processing and analysis, while accounting for image artifacts, is difficult because of the computing requirements of the processing algorithms. To tackle these difficulties, a collaborative effort among multiple Department of Energy national laboratories has led to the development of the "MLExchange" project, which is a Machine Learning framework that uses interactive web interfaces to improve and accelerate data analysis. With MLExchange, users can easily upload, visualize, label, and train networks. The resulting models can then be deployed on actual data, and both the results and models can be shared with other scientists. The MLExchange web-based application focuses on image segmentation, enabling the training, testing, and evaluation of multiple machine learning models on hand-labeled x-ray powder diffraction data. This platform offers an intuitive interface that enables users to identify and separate artifacts using a variety of machine learning algorithms and deep-learning neural networks. In addition, these tools have the potential to overcome the limitations of traditional image segmentation techniques, particularly for complex images with varying contrasts.

APS WK#8: Hard X-ray Imaging Techniques for Biological and Environmental Research: Current Status and Future Upgrades

Organizers: Olga Antipova, Zou Finfrock, and Luxi Li

Over the past 25 years, use of synchrotron-based x-ray techniques has revolutionized many scientific disciplines, including biology, medicine, materials engineering, and environmental research, among others. APS after the upgrade will become the one of world's brightest storage-ring based x-ray source delivering high energy, high brightness, and high coherence x-ray beams. All these characteristics will position the APS to be one of the best x-ray light sources for imaging applications!

Biological, environmental, geological, and material science samples come with heterogeneous composition and characteristics which are impossible to evaluate without x-ray imaging tools. The APS facility of Argonne National Laboratory offers variety of x-ray microscopy instruments, which offers different capabilities, including high spatial resolution, flexible sample environment, sensitivity, and additional imaging modality. Over years at APS, these instruments served the biological and environmental science community to provide comprehensive structural and functional analysis of a large array of specimens, big and small, from tiny microbes to soil samples with microbial colonies, from pollen samples to wood sections undergoing fungal decay, from single cell to a breathing beetle. In all cases, proper sample preparation, *in-situ* environment, appropriate beamline selection and efficient use of beamtime is a key to success.

Beamlines, such as 8-BM, 25-ID, 13-ID, 2-BM, 2-ID-D/E, 7BM, 26-ID, and 32-ID, provide increasing resolution, various modalities, and allow for integrated sample measurement and comprehensive identification of micro features within large samples. This workshop will demonstrate ongoing progress in multi-scale x-ray microscopy research, including data collection, sample handling and guided modification, as well as developments in sample holders design and visualization software, which all together will significantly improve user experience with multi-beamline imaging. We expect to familiarize the broader user community with available x-ray microscopy options at APS and provide ideas for efficient data collection strategy on current APS as well as for upgraded APS beamlines.

Overview of X-ray Imaging at APS

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X-ray Microscopy (XRM) is a powerful tool to study structure and elemental composition of biological, environmental, and material science samples. Synchrotron x-ray source allows high-resolution measurements in flexible environment, while combination with other synchrotron techniques enables comprehensive multi-modal investigation of sample composition, properties and imperfections. Currently, Advanced Photon Source offers seven instruments with XRM capability (8-BM, 20-ID, 13-ID, 2-ID-D/E, 9-ID-B, 26-ID, 2-BM, and 32-ID), which together provide large range of available resolutions and imaging modes. Optimization of the workflow between these beamlines may significantly improve data collection and user experience. APS Upgrade will open possibilities for even higher resolution imaging and expansion of modalities of existing beamlines for significantly more time-efficient and complex measurements. These enhancements will increase beamlines throughput and expand APS user community.

Imaging Modalities for Understanding the Chemical Exchange and Physical Interactions in the Rhizosphere

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The complex dynamics of root-microbe interactions in the rhizosphere drives recognizable spatial structure variations. However, knowledge of the specific factors that lead to their development and sustain them for plant health and productivity is sparse. We are developing a unique functional imaging technique that exploits native sense-and-respond circuits of plant growth-promoting rhizobacteria (PGPR) to monitor chemical exchange between the plant root and microbe during the different phases of colonization. Several native PGPRs will be turned into biosensor cells, and root colonization will be evaluated with Arabidopsis, Camelina, and poplar plants. Genetic variants of Arabidopsis with gain or loss of function will provide drastically altered local environments, resulting in colonization patterns that differ from those observed previously. An orthogonal x-ray imaging approach will provide high resolution elemental analysis of the local environment, and imaging throughput in general will be accelerated by automation and AI-driven analysis. In addition, we propose to advance the throughput of current bioimaging capabilities using confocal microscopy that leverage imaging chips developed with BER funding with automation, and an artificial intelligence-guided image analysis strategy. This combined HTP-AI bioimaging capability, along with advanced analytical techniques offered by APS and EMSL, will capture the dynamic chemical shifts and colonization patterns in the rhizosphere.

Results from poplar root rhizosphere characterization using tomography (micro-tomography at 2-BM) and XRF (Bionanoprobe at 2-ID-E) at the Advanced Photon Source will be discussed.

Chemical Imaging of Atmospheric Particles

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Atmospheric aerosol affects the climate directly by scattering and absorbing sunlight and indirectly by participating in warm and cold cloud formation. Particle size distribution and their chemical composition influence the optical properties of aerosol and their ability to form warm and cold cloud formation. The vertical distribution of different atmospheric aerosol species and their atmospheric processing can impact the atmospheric thermal structure, cloud dynamics and regional to global circulation systems. Measurements of vertical distribution of aerosol properties at various altitude are required in order to better understand the effect of aerosols on climate. Detailed measurements of single particle aerosol composition using chemical imaging techniques as a function of altitude are limited but needed. To improve the understanding of impacts of the vertical distribution of aerosol chemical composition on radiative forcing of aerosol, we perform a detailed physicochemical characterization of aerosol particles sampled during different field campaigns. We utilized the high-resolution microscopy and x-ray spectroscopy techniques to probe their physicochemical properties. I will highlight results from recent field studies.

Development of a New User Program Supporting Biological and Environmental Community after the APS-U

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Synchrotron light sources have provided x-ray-based tools that supported a wide range of research in biological, geological, geochemical, and environmental sciences for decades. The ongoing generational upgrade of the Advanced Photon Source (APS) facility takes advantage of a new light source design, better instrumentation, and novel methods. When completed, the upgraded APS will be one of the world's brightest light sources, delivering x-rays up to 500 times brighter than today. The upgrade project also includes the building of new feature beamlines to make use of the increased brightness and coherence of the x-ray beams, and various enhancements to most of the existing beamlines. The high energy will allow users to probe unaltered large bulk samples with scientific relevance. The high brightness will provide macroscopic fields of view with nanometer resolution. The high coherence will enable highest spatial resolution even in most heterogeneity environment. All these characteristics will position the APS to be one of the best x-ray light sources for imaging applications, revolutionizing many scientific disciplines. To fully take advantage of the state-of-the-art facility, we are developing a new user program – eBERlight, providing an integrated platform, dedicated support from experts in the field, offering multimode approach to study biological and environmental systems. The program will also leverage additional Argonne resources, help users with sample preparation, data collection and data analysis.

Fragmentation of Soil Moisture in Soil Pores Detected by Dual-energy X-ray CT

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Soil pore structure plays a key role in transport and fate of soil organic and inorganic chemicals, gases, microorganisms, as well as defines rates of biogeochemical reactions and microbial activity. Marked heterogeneity of the soil solid and pore spaces and complexity of the pore networks lead to formation of zones with enhanced microbial activity, with occurrences and properties of such zones being highly irregular in space and time. Such zones are commonly referred to as “hot spots” and “hot moments” and their formation requires sufficient supply of water and oxygen to ensure enhanced microbial functioning. The water distribution consistent with observed “hot spots” and “hot moments” occurrences cannot be explained by a classical capillary model of soil water retention, which assumes sequential filling and draining of pores according to their size distribution. The classical model is also not capable to explain high spatial diversity of microbial communities at pore scale. A meniscus water retention model has been developed in the past decade alternatively to the capillary model to explain low mobility of soil microorganism within the pore networks. This model is free of assumptions about incremental saturation/drainage of different pore-size classes. Which of the two models is more appropriate is still debated due to the absence of methods for soil water quantification at pore scale. While visualizations of water distribution within the soil pore network have been conducted for decades, its quantification remains rather challenging. We developed an approach for quantifying pore saturation based on changes of iodine mass attenuation within increasing beam energy after introducing 10% KI solution into the soil. This approach has been implemented to quantify redistribution of water in soil pores at 5 levels of soil water saturation. Image analyses showed: (i) surprisingly high fragmentation (discontinuity) of soil moisture in highly connected pore systems; and (ii) partial saturation of multiple pore-size groups within a wide range of soil water contents. These results support the meniscus model and reject the capillary model of soil water retention, and better explain the spottiness of microbial activity in soils at a pore scale.

Nano-imaging to Tackle Mercury Transformations and Methylation by Bacteria in the Environment

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Mercury (Hg) is a pollutant of concern on Earth, particularly because it converts into methylmercury (MeHg), a strong human neurotoxin. MeHg is mainly produced in the environment by sulfate-reducing bacteria (SRB), and is then biomagnified and bioaccumulated in the aquatic food web, thus resulting in health issues for the consumers at the top of the food web. Untangling the biotransformation processes of Hg by these microorganisms is thus a key to understand the release of MeHg in ecosystems.

The occurrence of *hgcA* and *hgcB* genes is required for bacteria to methylate Hg, but the various Hg chemical forms involved in Hg methylation are still unknown. Our aim is to determine these Hg species as well as the Hg cellular distribution to clarify the processes involved in Hg transformations. For that, we focus on an original model SRB strain *Pseudodesulfovibrio hydrargyri* BerOc1 that is able to methylate Hg and demethylate MeHg. Our approach mainly combines High Energy Resolution Fluorescence Detected X-ray Absorption Near Edge Structure spectroscopy (HERFD-XANES) at Hg L_{III}-edge and cryo nano-hard x-ray fluorescence imaging to identify Hg species and Hg localization, respectively. Results showed heterogeneous levels of Hg accumulation between bacterial cells, and multi-modal imaging combining cryo x-ray fluorescence microscopy and cryo optical fluorescence microscopy can be carried out to clarify the origin of these variations.

Variable-humidity X-ray Fluorescence Microscopy and X-ray Computed Tomography

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A wide variety of both natural and synthetic materials have moisture-dependent properties that can vary substantially depending on the ambient relative humidity (RH). Under high RH conditions, moisture sorption can cause swelling, plasticization, and fracture at interfaces in composites. The effects of moisture can be especially challenging to study in composite materials with small micrometer components. Synchrotron x-ray microprobes and x-ray computed tomography (XCT) can readily be used to study materials at these small length scales. The highly penetrating nature of x-rays and open layout of beamlines opens the possibility to also employ *in situ* environmental chambers. To study the effects of moisture using these techniques, we have built *in situ* RH chambers for Advanced Photon Source (APS) XCT beamline 2BM and x-ray fluorescence microscopy (XFM) beamline 2IDE. The chambers utilized the beamlines kinematic mounts. The environment inside of the RH chambers were continuously controlled from 0 to 100% RH using a gas flow from an external RH generator. The XCT RH chamber was used to study the moisture-induced swelling and shrinking in wood and wood-adhesive bondlines. The XFM chamber was used to study moisture-dependent diffusion of mineral ions and Cl-labeled organic molecules through individual wood cell wall layers. Current challenges and future opportunities will also be discussed.

X-ray Imaging of Soil Aggregates and Sediment Cores to Understand Environmental System Function

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Environmental and ecosystem system function is intimately tied to biogeochemical cycling of the major elements within terrestrial and aquatic environments. Microorganisms, plants, and soil and sediment constituents biogeochemically interact with and affect each other within terrestrial and aquatic environments and ecosystems, exerting great control on the partitioning of elements and chemical compounds between the air, water, and land. In turn, such biogeochemical interactions have a major impact on critical environmental phenomena such as nutrient availability to living organisms, contaminant fate and transport, water quality, and greenhouse gas emission. Besides being opaque, which make them particularly challenging to study, environmental media such as sediments and soils are dynamic and spatially complex. To better understand terrestrial and aquatic ecosystem function, in combination with a variety of biogeochemistry lab-based approaches, we have used the APS to investigate soils and sediments collected along elevation gradients along terrestrial-aquatic interfaces from uplands to wetlands. X-ray based characterization approaches we have used include bulk and spatially resolved Fe and S XAS within soil cores collected along these elevation gradients. Additional 3D x-ray tomographic measurements of these soil cores to determine soil structure and water and air distributions within soil pores and plant roots have been made. We have also worked to develop an approach to use quantum dot-tagged microorganisms to image their 3D distribution within soil aggregates in response to water inundation. I will present results from these experiments and describe opportunities to make better use of them at the APS-U. Finally, I will also discuss opportunities for applying x-ray tomographic imaging approaches at the APS-U to compliment MONet efforts at the Environmental Molecular Science Laboratory at Pacific Northwest National Laboratory.

XRF-imaging of Cd in a Hyperaccumulator Plant Species *Sedum alfredii*

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Contamination of Cd in soils poses a serious threat to both crop productivity and human health. Hyperaccumulator plants can tolerate and accumulate high concentrations of heavy metals, and thus have potential for use in phytoremediation of contaminated soils. Elucidation of the mechanisms involved in Cd hyperaccumulation in plants may facilitate the rational design of technologies for the cleanup of Cd-contaminated soils. *Sedum alfredii* is one of a few Cd hyperaccumulators identified up to date. XRF-imaging of Cd in plants of *S. alfredii* suggests an efficient vacuolar sequestration of Cd in the parenchyma cells may represent the key process responsible for Cd homeostasis and tolerance in shoots of *S. alfredii*. A highly competitive interaction between Cd and Ca was observed in this plant species. Ca deficiency significantly increased Cd contents in shoots of the plants, particularly in the young leaves, and triggered phloem remobilization of the metal from old and mature tissues to the new growth tissues. A highly efficient phloem transport system was afterwards observed for the Cd remobilization from old stems and leaves towards young and new growing tissues in plants of *S. alfredii*. Meanwhile, we found that exogenous Cd treatment significantly reduced the colonization of powdery mildew in the young leaves of *S. alfredii*. Interesting, we also found that infection of powdery mildew significantly increased Cd accumulation in the leaves of *S. alfredii* as compared with the controls. By micro-XRF imaging of Cd in the powdery mildew-infected leaves, we further found that a very high amount of Cd was accumulated in the infected-zone of leaves, and the results by nano-XRF showed that Cd was mainly accumulated in the cell wall of the powdery mildew-infected epidermal cells, which was more than 100 times higher than that in the healthy cells. Meanwhile, root uptake, xylem transport and phloem remobilization of Cd was significantly induced in plants of *S. alfredii* by the infection of powdery mildew. The above results suggest that the plants of *S. alfredii* was able to tolerate and accumulate very high Cd levels mainly in the stem and leaf parenchyma cells, while high translocation and remobilization of Cd to young tissues may help to prevent the infection of pathogen such as powdery mildew.

Processing X-ray Fluorescence Tomography Data with XRFtomo

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X-ray fluorescence tomography allows scientists to map elemental distributions in three dimensions and recover internal information without physically disturbing a given sample. An x-ray light source, positioning instruments, and a detector are used for data acquisition, but software is required to perform image registration and to reconstruct a 3D volume from a set of 2D projections. To facilitate such 3D data analysis and reconstruction, we have developed a python package named XRFtomo based on a data analysis workflow presented earlier [1]. XRFtomo brings together a variety of image processing tools used for preparing, processing and reconstructing 3D volumes of samples imaged using a synchrotron-based x-ray fluorescence (XRF) microprobe or nanoprobe at the Advanced Photon Source (APS).

The general workflow of XRF tomography involves acquiring a series of 2D scans at a range of angles at an XRF beamline. These projections are processed in MAPS [2] or XRF-Maps (a recently developed software for XRF data analysis) for both spectrum fitting and elemental concentration quantification, exported as hierarchical data format (HDF) files, and then imported to XRFtomo. XRFtomo bridges the gap between data acquisition and visualization by providing tools to adjust for misalignment in the imaging process and tools for running reconstructions using TomoPy [3], all with the use of a graphical user interphase (GUI) or command line. This program can output cross-section images, aligned projections, sinograms, metadata, and it automatically saves user configuration and parameters for rapid processing the next time the program is launched. The images it outputs serve as inputs for 3D visualization software used to generate volumetric renderings and animations.

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A Laminography Technique for Scanning Biological Samples

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Laminography [1] is a special kind of x-ray tomography used for scanning flat samples or large samples with minimal number of the sample cutting procedures to reach necessary x-ray attenuation levels yielding high quality and resolution 3D imaging results. Compared to the standard tomography setup where the sample would be cut into pillars, the laminographic geometry uses slab-shaped samples mounted on a tilted rotary stage (in tomography, the stage is parallel to the beam). A laminography imaging system has been implemented at sector 2-BM of the Advanced Photon Source and already demonstrated high-quality imaging results for biological samples such as the mouse brain, leaves, wood, insects. Conventional tomographic scanning of such samples demonstrated significantly lower quality due to the beam blockage of the sample for many projection angles. We have also implemented GPU-accelerated functions for laminographic reconstruction of huge data volumes. The new functionality has been added to the TomocuPy [2] software package used at several beamlines at the APS and other synchrotrons. The developed laminography technique and software toolbox may become a routine tool at many beamlines of the APS-U source. There is an ongoing work on implementing a laminography setup at the XRF instrument at sector 2-ID-E. There are also plans to implement the rotation stage tilting mechanisms at nano-CT instruments at sector 32-ID equipped with the Transmission X-ray Microscope, and with the Projection X-ray Microscope available after the APS Upgrade.

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Use of Multi-scale Hard X-ray Microscopy for Evaluation of Archival Tissues from Animals Exposed to Radioactive Particles

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Biological samples repositories containing FFPE samples from humans and animals exposed to radiation are an irreplaceable resource for studies of effects of exposure to radioactive materials. However, the historic fixation processes such as use of Bouin's fixative and work with tissues that were FFPE embedded for over 30 years represent challenges to extraction of information using standard immunohistochemistry approaches. X-ray fluorescence microscopy (XFM) allows that 2D maps of distribution of different chemical elements be used as biomarkers of radiation exposure. In this study, we demonstrate the feasibility of XFM to evaluate FFPE specimens that were generated in the 1980s.

We used XFM to produce 2D elemental maps of the lung and lymph node tissues of a beagle dog that inhaled previously radioactive aluminosilicate microparticles to which yttrium-90, a radioisotope released during nuclear reactor accidents, was adsorbed. We used low-, medium-, and high-resolution XFM and characterized the distribution of aluminosilicate particles by their chemical signature and found the corresponding tissue response to their presence, again by its chemical signature.

Use of SXRF and LAICPMS to Visualize Dynamic Ca Phenotypes in Plants: Characterizing the Role of Cation/H^+ Exchangers in Anoxia Tolerance

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Calcium has many essential roles in plants: it is a component of the cell wall, an enzyme cofactor and a ubiquitous second messenger in signal transduction. Calcium pumps and exchangers located in multiple membrane systems orchestrate calcium homeostasis. Most calcium pumps are low capacity, high affinity effluxers, but a distinct group, known as the cation/H^+ exchangers (CAXs), have high capacity and low affinity, which indicates involvement in signaling. There are four CAXs in plants. We developed transgenic plants that lack all four and found that they are resistant to anoxia: an economically important abiotic stress (a component of flooding). It may be possible to significantly increase flood tolerance of food crops by selectively manipulating these Ca pumps.

Using elemental imaging (both SXRF at the XFM beamline at NSLS-2 and laser ablation inductively couple plasma mass spectrometry, LAICPMS in our own laboratory) and a time resolution of a full leaf image every 1.5-2 hours after exposure to anoxia in parallel grown plants, we imaged how wild type and quadruple knock out mutants (qKO) reacted to anoxia stress, to understand how CAXs orchestrate stress signaling. We found that in addition to Ca, multiple elements remobilized, particularly phosphorus and zinc, and that loss of turgor manifests as an increase in chorine. Our results suggest that qKO does not react to stress in the same way as wild type – if at all. In normal plants, Ca leaves the leaf hairs and into leaf cells, a prominent feature of the stress response, whereas in qKO, no remobilization was observed.

Importantly, we were not able to definitively capture normal remobilization events for Ca with the 1.5-2 hour frame rate: CAXs help maintain steep a Ca concentration gradient between the cytosol and other organelles, so events are transient. Although in plants remobilization is slow, it still occurs in minutes, rather than hours.

Imaging transient remobilization phenotypes remains a challenge, and in this talk I will show our results and discuss how our proposed enhancements in elemental imaging could begin to close the gap between still and moving elemental images.

Genetics of Resiliency to Cavitation in Metaxylem of Grasses

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Xylem is an essential component of the plant vascular system that transports sap comprising water and minerals from roots to shoots. Xylem consists of large hollow dead cells known as vessel elements. The sap flows between the vessel elements through pits - specialized cell wall regions that lack secondary wall thickenings and contain modified primary walls called the pit membrane. The rate of sap flow through the xylem depends on the morphology and abundance of pits. Although large pits with thin membrane could be advantageous in mesic environments by increasing the sap flow to leaves and higher rate of photosynthesis, such pits could prove detrimental in arid climates. During drought, transpiration of water from leaf surface creates negative pressure inside vessel elements that can not be compensated by water supply from roots. This negative pressure induced formation of air cavities inside vessel elements causing embolism, which blocks sap flow. The air-water menisci from an embolized vessel are more likely to propagate to neighboring water-filled vessels through pits with large and thin membranes, thus further blocking sap flow. On the contrary, smaller pits with thicker membranes have lower propensity for propagating the air-water menisci. Correlation between the embolism spread and pit morphology makes the latter an important trait for development of drought-tolerant plants. However, our ability to engineer pits is limited by the lack of knowledge about genes that control pit morphology. Identification of these genes is slow because imaging embolism formation and spread is challenging. Our project focuses on developing techniques for imaging embolism in grass internode under drought stress conditions. This technique will enable analysis of cavitation in genotypes with altered pit morphology and engineering pits with reduced capacity for conducting embolism to neighboring cells. Plants with slower embolism spread are expected to produce higher biomass in arid climates.

Full-field Imaging of Insects and Other Small Animals

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Insects can be viewed as exquisite microfluidic systems: they pump air, blood, and food through their bodies, all within one small package. Compared to engineered systems, they are far smaller, controllable, and efficient than anything that humans have designed. How do insects produce these physiological flows? In this talk, I'll discuss our studies of insect respiratory, circulatory, and feeding systems, which integrate a range of methods including synchrotron imaging, material testing, and classical physiological techniques. My focus will be on how insects actively ventilate their tracheal system: these small animals take advantage of hemolymph pressurization as well as passive material properties to deform tracheal structures and use functional compartmentalization to control internal flows. I will also discuss how insects feed using multiple pumps in the head (in animals like mosquitoes) as well as how they move blood within their tubular heart and open body cavity.

Synchrotron X-ray Fluorescence (SXRF) Spectroscopy to Measure Trace Metal Stoichiometry of Individual Phytoplankton Cells

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Marine phytoplankton play a major role in the global carbon cycle. They require iron and other trace metals to grow, yet these nutrients are in scarce supply in more than a third of the global ocean. The trace metal content of phytoplankton cells varies in response to nutrient availability in the environment. Measuring the elemental composition of these microalgae requires low detection limits, sub-micron spatial resolution, simultaneous determination of multiple elements, features of synchrotron x-ray fluorescence spectroscopy (SXRF). Measurements of marine algal stoichiometry at 2-ID-E are used to compare different trace metal requirements of different taxa and to characterize the biological fraction of marine particulate matter. Considerations for sample collection and preparation will be covered, as well as how upgrades to APS are anticipated to expand analyses to include phytoplankton taxa that are currently unmeasurable.

An XRF Study in Mechanisms of Chromium Removal from Industrial Storm Water Using Peat Medium

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Treatment processes for metals in industrial storm water can be cost prohibitive. Therefore, passive remediation strategies using natural materials and microbial processes have the potential to provide affordable solutions for removing metals from aqueous waste streams, which is important from regulatory and environmental quality perspectives. Our research explores the key chemical, biological and physical processes promoting removal of hexavalent chromium (Cr) from an industrial storm water treatment system by association with granular organic peat media. Samples were collected from an industrial-sized installation in Howell, MI, USA, where Cr-laden storm water is treated in large, flow-through tank reactors filled with a peat sorbent material. We sampled one reactor in four different locations at four depths for a total of 16 solid-phase peat material samples after 1 and 3.5 years. Chemical digestions show total Cr concentrations ranging from 400-900 mg/kg peat after 3.5 years dependent on depth and location. X-ray Fluorescence Microprobe (XFM) data reveal that Cr is heterogeneously distributed within the remediation media with both diffuse and “hot spot” features on the micron to 10s of micron scale and is highly correlated with Fe and Zn. Additionally, X-ray Absorption Near Edge Structure (XANES) results show both Cr(III) and metallic Cr-bearing particles in the same sample often as rind-like features accumulating on the surface of peat particles over time.

Correlative X-ray Tomographic Imaging and Chemical Analyses to Better Understand Soil Biogeochemical Processes

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At the Environmental Molecular Sciences Laboratory (EMSL), we combine x-ray imaging techniques with different chemical analyses methods to better understand soil biogeochemical processes occurring in 3D space on different spatial scales. On the soil core scale, we study the influence of soil porous microstructure on the stability and transport of soil organic matter (SOM). We employ a combination of x-ray computed tomography imaging for soil pore network characterization, hydraulic experiments to determine the mobility and desorption parameters of SOM, and various chemical analysis tools to extract the different soil carbon (C) pools, measure total organic C and total nitrogen contents and determine SOM composition (organic compound classes). Results on the comparison of soil properties and their influence on the stabilization and transport of SOM is presented. The utilization of pore network geometry data and SOM chemistry information to predict diffusion-limited soil respiration in different soils using reactive transport modeling is also discussed.

On the soil aggregate (mm and micron) scale, we investigate how chemistry, mineralogy, and porosity controls organic C distribution, water-flow dynamics, and consequently the formation of intra-aggregate microsites by performing full 3D characterization of the structure and chemistry of soil aggregates. Finally, we work to expand 2D chemical information to 3D space using multimodal characterization and artificial intelligence tools. Preliminary results from the latter efforts are also presented.

Decentralization of Synchrotron X-ray Fluorescence Microscopy: Recent Advances in Lab-based μXRF

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Synchrotrons accelerate and bend electron beams in order to create tangential, high flux photons across a wide energy range. While synchrotrons are quite difficult to access with very expensive beamtime, there are several powerful analytical modalities accessible through this approach including x-ray crystallography, infrared microscopy, powder diffraction, x-ray absorption spectroscopy, and others. Here we discuss x-ray fluorescence microscopy (XFM), another powerful application associated with synchrotrons, and how recent advances in lab-based μXRF (micro x-ray fluorescence) spectroscopy can be used to inform proper synchrotron design of experiment and substitute for difficult to access synchrotron beamtime. Lab-based μXRF instruments now allow decentralized access to high spatial resolution elemental mapping of samples down to 5 μm spot excitation diameter. Data will be presented comparing synchrotron-generated elemental maps to lab-based μXRF for several different sample types including cofactor migration tracking within biological tissue sections, element accumulation and distribution in plants, and minerology mapping.

CNM WK#9: Nanomaterials and Sustainability

Organizers: Renaud Bachelot and Gary Wiederrecht

The current use of current fossil fuels and the mining of ores for many technologies is producing climate change, environmental damage, and pollution. Furthermore, a large number of elements of the periodic table, even if rare and in short supply, are included in devices we use daily, leading to considerable supply chain and recycling challenges. Sustainable solutions must be urgently found.

In this workshop, we explore the role that nanoscience can have in this field. Researchers are exploring many new types of nanostructured materials made of sustainable materials for a variety of targets. As far as the nanomaterials community is concerned, more and more research groups are working on the development of carbon-based and organic functional materials whose increasing use is expected to lead to low-cost, efficient sustainable technologies. One example is the bio-inspired assembly of functional nanostructures for CO_2 reduction, green hydrogen production, and solar energy conversion.

However, the goal and feasibility of such endeavors remain to be assessed. New issues result in the exploration of new fields, with the risk of steering a business-as-usual scenario with scientists probing new areas without sufficient consideration of supply and economic limits. In this workshop, we also explore the need for researchers to assess their research programs against criteria that take into account the global considerations (from an economic, biophysical or climatic standpoint).

Working on limits means working with limits. This is a timely issue to scientifically address.

This one-day workshop will address this issue in a global way. It will consist of two kinds of talks: talks about recent research activities involving sustainable nanomaterials and talks addressing broader sustainability issues for researchers to consider.

Nanomaterials, Manufacturing, and the Science of Scale-up

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Materials to enable next generation technologies are increasingly in the nanoscale whether for flexible electronics, quantum computing, energy storage materials and other novel applications. Nanoscale manufacturing includes both top-down and bottoms-up methods and is subject to the same sustainability requirements as other categories of materials.

Evolution of synthesis, safety and characterization of nano-materials will be discussed in context of the applications requiring those materials.

Two case studies in MERF will be presented to highlight strategies for scaling up nanoscale materials. One is upscaling synthesis of ultrasmall PtNi nanocage catalysts for fuel cells by using a conventional batch method. The other is ultrafast synthesis of M-phase VO_2 nanoparticles/rods for preparing smart window films by developing a continuous flow hydrothermal reactor. With well-controlled flow and transport, continuous flow process is evolving as the suited upscaling technique for manufacturing high-quality nanomaterials. The opportunities, e.g., ML/AI enhanced process automation, and existing technical challenges will be briefly discussed.

Charge Transport Mechanism in Photoconductive Metal Organic Frameworks

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Metal organic frameworks (MOFs), built from inorganic and organic linkers, represent an emerging class of porous crystalline materials that have demonstrated many potential applications encompassing energy conversion and storage, gas separation and storage, chemical sensor, and drug delivery. Recent reports of electrical conduction in MOFs expand their applications in devices such as supercapacitors, electrocatalysts, chemiresistive sensors, and batteries. However, the charge transport mechanism that guides the rational design of highly conductive MOFs remains underexplored; yet it is essential to further promote these materials for the above-mentioned applications.

In this talk, I will present our recent progress in fundamental understanding of charge transport mechanism in a series of MOFs and the correlation of the metal nodes and organic linkers with their photophysical property and photoconductivity. We found that structural preference in M-THQ MOFs (M = Fe, Ni, Cu and Zn; THQ = tetra-hydroxybenzoquinone) is controlled by metal node identity where Cu prefers a square planar coordination which leads to a 2D Kagome type structure. Fe, Ni and Zn prefer an octahedral sphere which leads to a 3D structure. Fe-THQ has the smallest band gap and highest photoconduction as well as a long-lived ligand to metal charge transfer state due to the mixed valence state revealed by time resolved optical and x-ray absorption and terahertz spectroscopy. On the other hand, charge transport mechanism is controlled by the size of the organic linker, where some MOFs prefer through space transport while others undergo through bond charge transport mechanism. These results demonstrate the importance of the building blocks in tuning the photophysical and photoconductive properties of MOFs.

Image Exciton and Charge Transport with Ultrafast Microscopy in the Quantum Regime

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At the most fundamental level, transport of energy carriers (such as electrons and excitons) in the solid state is determined by their wavefunctions and the interactions with the lattices and the environment. Wave properties of these particles have profound consequences in their transport. However, the conventional and steady-state measurements of transport assume these energy carriers as classical particles. The key difficulties in probing transport in the quantum regime in real materials lie in the fast (picosecond or shorter) dephasing processes and the nanoscale localization lengths. Thus, to image the motion of charges and excitons in their natural (quantum) time and length scales, experimental approaches combining spatial and temporal resolutions are necessary, which requires a paradigm shift from conventional spectroscopy and microscopy methods.

To address this challenge, my research group has pioneered the combined use of optical microscopy and ultrafast spectroscopy tools to image transport of charge carriers and excitons from the nanoscale to the mesoscale and over a wide range of temperatures. In my talk, I will discuss our recent progress on imaging the hot carrier transport in hybrid perovskites, quantum exciton transport in perovskite quantum dot superlattices, and exciton phase transitions in moiré superlattices of two-dimensional transition metal dichalcogenides. These results provide fundamental understandings of how excitons and charge carriers migrate in materials and how these processes can be manipulated quantum mechanically. The unique ability to measure and control coherent pathways are critical for both solar energy and quantum information applications.

Manufacturing Fuels and Chemicals Using Plasmonically Concentrated Light

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My laboratory is exploring green routes to the synthesis of fuels and valuable chemicals using visible light. This technology relies on metal nanostructures that function as visible-light-harvesting antenna that concentrate light energy down to the nanoscale in the form of collective electronic oscillations. This concentrated source of energy drives multielectron, bond breaking, and bond formation reactions on the surface of the metal nanostructure. A striking example of this phenomenon is the conversion of CO_2 to form C_1–C_3 hydrocarbons on gold nanoparticles under visible light. I will describe the use of plasmonically concentrated light energy for i) achieving important transformations using milder conditions, ii) altering the inherent catalytic properties of a metal and modulating product selectivity, iii) driving thermodynamically uphill reactions where free energy is harvested from light and stored in the form of energy-rich bonds, and iv) boosting electroconversion.

Transforming Next Generation Photovoltaics with Semiconductor Nanostructures

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Silicon photovoltaics are regarded as part of green energy technology. However, they carry significantly longer (as high as 3 years) energy payback time. Semiconductor nanostructures are finding new ways to design light energy conversion devices (e.g., thin film solar cells and light emitting devices). The thin film design enabled through low temperature processing decreases the energy payback time. The decreased consumption of energy during the manufacture and the lessened use of semiconductor materials lowers the overall carbon footprint with energy payback time less than a year. The early studies focused on the synthesis of various semiconductor nanostructures and exploration of their size dependent optical and electronic properties. Careful engineering efforts in recent years have led to their integration in high efficiency thin film solar cells. Metal halide perovskite solar cells, in particular can now deliver efficiencies greater than 26%, thus matching the power conversion efficiency of silicon solar cells. Recent developments in utilizing semiconductor quantum dots for light energy conversion devices and how they can influence decreasing carbon footprint will be discussed. Efforts are needed to address the stability issues, to assess environmental impacts and to transform current practices of energy utilization.

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Nanotechnologies and Twin Transitions: Insight into Critical Materials Challenge

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Nanotechnologies have a decisive contribution to the twin transition. Indeed, the improvement of the solar cells performance of the battery storage capacity is a major challenge to met the objective of a Net Zero Carbon society. In the meantime, Nanotechnologies are creating the hardware (sensors, data storage systems, actuators etc…) needed for the digitalization of the society. Nowadays, there is a race for performance of these device to allow them to replace the older technologies and the research for new materials is very active. The emergence of nanotechnology is partly responsible for the extension of the palette of metals used by Humanity. A smartphone requires twice more elements than all life-forms on Earth do[1], [2].

Limiting the challenge of the Green and digital revolutions to the simple cost-performance paradigm would be somehow repeating the mistake of the Oil Age during which the resource was considered as infinite and the impact on the environment had been long time neglected. Making the twin transition successful requires to change the mindset of innovators (from lower TRL) to a binary trade-off (price-performance) towards multi-criteria decision making [3]. In this seminar, the different risks and impact associated with the massive increase in the metal extraction will be presented. Risk assessment at the level of devices will be presented and a multicriteria decision support system will be introduced showing the importance role and importance of the perception of the final user.

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Industrial Perspectives on Nanomaterials and Sustainability: Opportunities and Challenges

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Nanomaterials represent a tremendous opportunity to accelerate technological innovations that are being developed for more sustainable energy utilization and for chemical and energy conversion processes. As industrial steps, separation and conversion processes can often require large inputs in energy and resources to implement, representing numerous opportunities for nano-enabled technologies to be deployed to reduce these inputs, resulting in enhanced industrial sustainability. Nanomaterials are also key components in many sustainable technologies, such as fuel cells and electrolyzers.

Through three use cases from nanoscale polymeric membranes for enhanced gas separations, advanced hierarchical catalysts for chemical conversions, and nanoscale catalysts that are enabling the hydrogen economy, some important industrial opportunities and challenges will be discussed.

Semiconductor Nanomaterials for Bio/ecoresorbable Electronics

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A key goal in most microsystems technologies is to achieve stable operation over long periods of time, without physical or chemical change. Recently developed classes of semiconductor nanomaterials create an opportunity to engineer the opposite outcome, in the form of ‘transient’ devices that dissolve, disintegrate or otherwise disappear at triggered times or with controlled rates. Water-soluble classes of transient electronics serve as the foundations for applications in zero-impact environmental monitors, 'green' consumer electronic gadgetry and bioresorbable biomedical implants. This presentation describes some foundational concepts in polymer chemistry, materials science and assembly processes for eco/bioresorbable electronics in 1D, 2D and 3D architectures, the latter enabled by approaches that draw inspiration from the ancient arts of kirigami and origami. Recently demonstrated device example range from temporary cardiac pacemakers designed to operate during recovery from a surgical procedure to passive colorimetric microfliers engineered to monitor key environmental parameters.

Artificial Photosynthesis through Purple Membrane Re-engineering with Nanomaterials

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Natural photosynthesis has evolved as a mechanism that allows green plants and microorganisms to turn carbon dioxide (CO_2) and water into energy storage organic molecules harnessing power of sunlight. Bio-inspired artificial photosynthesis was developed by scientists to turn carbon dioxide and water into energy-dense fuels, such as hydrogen and methane, and value-added chemicals [1]. The fusion of biological pathways with synthetic inorganic materials offers avenues for sustainable clean energy production [2-5]. In our work, we use a cell-mimic strategy to develop an artificial photosynthesis paradigm for carbon dioxide reduction by integrating a biotic material, a purple membrane isolated from *Halobacterium*, with abiotic semiconductor TiO_2 nanoparticles. In these biohybrids, a membrane protein, bacteriorhodopsin, functions as a photosensitizer that injects light-excited electrons into the conduction band of TiO_2 and retains its native biological function of visible light-driven proton pump. Thus, photoinduced electrons and protons accumulated within a confined nano-bio architecture act in concert, allowing catalytic reactions via proton-coupled multielectron transfer PCET process at significantly reduced potential requirements. The nano-bio architecture converted CO_2 into CO and CH_4 under white light in water at pH7 and room temperature with ascorbate as a sacrificial electron donor [6]. Our study provides an alternative toolkit for designing photosynthetic processes to mitigate environmental footprint of CO_2 emissions and production of clean fuels and value-added chemicals.

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Towards Developing Green Nanolubricants for Automotive and Oil-gas Industries

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Oil-based lubricants are widely used in the lubrication industry due to their ability to reduce friction and wear losses while being durable. However, the disposal of oil waste, which may contain hazardous additives, poses a significant environmental and health concern. To mitigate this issue, recent development in solid lubricants based on two-dimensional (2D) materials offer a promising alternative. These lubricants have shown excellent wear and friction properties while producing no hazardous waste and requiring only a small amount. Furthermore, they can be easily recoated at lower cost and are durable.

At Argonne, we have developed several solid lubricants based on 2D materials in combination with nanoparticles, which have played a critical role in achieving low wear and ultralow friction, including superlubricity (near zero friction) at the macroscale. The intricate nature of tribochemistry at nanoscale plays a pivotal role in the formation of a tribolayer thereby reducing friction and wear. I will discuss the mechanism in detail along with a few examples of the work carried out in close collaboration with industry for applications in the metal stamping and oil and gas indutries. This demonstration opens the door to further advancements in realizing oil-free solid lubricants in various real-world applications, helping to achieve the decarbonization goal in the lubrication industry.

Thermal Transfer Management Using Nanomaterials

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The thermal conductivity of nanostructures and nanostructured materials differs significantly from the macroscopic laws of bulk materials. Mastering the heat dissipation enables the creation and conceptualization of nanocomposite or nanomaterials for specific thermal management purposes. For lattice thermal conductivity alone, multiple interesting non Fourier phenomena have been explored recently such as thermal rectification [1,2], phonon filtering [3], phonon diffraction and interference [4,5], as well hydrodynamic effects [6]. These exotic phenomena opens the way for new application. For instance, thermal rectification enables the creation of smart material that can dissipate heat or insulate depending on the ambient conditions, diffraction of phonons allows focussing heat on a specific spot to heat it or on the contrary shield it from heat. Phonon filtering on the other end may be useful in the field of phononic computing where information is carried by phonons.

In this presentation, these particular thermal transport phenomena at the nanoscale are explored using atomistic simulations. Amorphous/crystalline Silicon nanocomposites and nanomaterials are used, thus one can achieve thermal management without requiring the use of complex crystalline structures or the use of raw materials.

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Implications of Nanoscale Amorphous Metal Oxide Electrode Materials for Lithium-ion Batteries

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Intercalation-type metal oxide electrodes are promising negative electrode materials for safe and stable operation of rechargeable lithium-ion batteries due to the reduced risk of Li plating at low voltages. Nevertheless, lower energy and power density along with cycling instability remain a bottleneck for their implementation, especially for desirable fast charging applications. Here, we summarize our recent progress in utilizing amorphous metal oxide nanostructures (e.g., TiO_2 and Nb_2O_5) for enhanced electrochemical properties. Examples include the effects of crystallinity, electrochemically-induced amorphous-to-crystalline (a-to-c) transformation, and radiation-induced a-to-c transformed electrodes.

APS WK#10: Training Workshop on X-ray Spectroscopy Data Analysis with Larch (Data Analysis Tools for X-ray Spectroscopy) and AXEAP (Argonne X-ray Emission Analysis Package)

Organizers: Shelly Kelly, Matthew Newville, Inhui Hwang, Mikhail Solovyev, and Chengjun Sun

With the upgraded spectroscopic beamlines at APS-U era, it is essential to achieve the real-time interpretation of the spectroscopic data and the capability to change experimental conditions during a beam run correspondingly. This one-day workshop will focus on x-ray absorption and emission spectroscopy data analysis with Larch (Data Analysis Tools for X-ray Spectroscopy)[1] and AXEAP (Argonne X-ray Emission Analysis Package)[2], respectively.

Larch is an open-source library and set of applications for processing and analyzing x-ray absorption and fluorescence spectroscopy data and x-ray fluorescence and diffraction image data from synchrotron beamlines. Larch aims to provide a complete analysis toolkit for x-ray absorption fine-structure spectroscopy (XAFS), including both x-ray absorption near-edge spectroscopy (XANES) and extended x-ray absorption fine-structure spectroscopy (EXAFS). Larch also provides visualization and analysis tools for x-ray fluorescence (XRF) spectra and XRF and x-ray diffraction (XRD) images as collected at scanning x-ray microprobe beamlines.

Argonne X-ray Emission Package (AXEAP), a singular purpose software package for processing x-ray emission (XES) images collected with a 2-dimensional position sensitive pixel array detector, has been developed. AXEAP can rapidly convert XES image files into a spectral form by applying parallel computation and unsupervised machine learning to compute vast amount of image data. Special focus has been placed on designing user-friendly-interface for processing multiple edges, non-resonant and resonant x-ray emission image analysis, in order to make data processing quick and easy. AXEAP is free software and is written in MATLAB, armed with powerful libraries and toolboxes. The software runs on all common operating systems such as Linux, Window, and Mac.

The workshop will start with an overview of spectroscopic beamlines and a brief introduction to XAFS[3], followed by the demonstration of the Larch in the morning; in the afternoon, we will provide outline on x-ray emission techniques, then provide the demonstration of XES data analysis with AXEAP.

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Argonne X-ray Emission Analysis Package1 (AXEAP1) and AXEAP2: A Comprehensive Solution for Processing and Analyzing X-ray Emission Spectroscopy (XES) Data

In-Hui Hwang[1], Shelly D. Kelly[1], Maria K. Y. Chan[2], Mikhail A. Solovyev[1], Sang-Wook Han[3], Eli Stavitski[4], John P. Hammonds[1], Nicholas Schwarz[1], Xiaoyi Zhang[1], Steve M. Heald[1], and Cheng-Jun Sun[1]

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The Argonne X-ray Emission Analysis Package 1 (AXEAP1) has been developed to calibrate, process, and analyze x-ray emission spectroscopy (XES) data collected with a two-dimensional (2D) position-sensitive detector. AXEAP1 employs calculations and unsupervised machine learning to convert a 2D XES image into an XES spectrum in real-time, making it possible to compare the processed data during collection.

To further address the challenge of x-ray emission spectrum data analysis, we introduce a new XES data analysis method based on Genetic Algorithm (GA) and implement it as a standalone application, Argonne X-ray Emission Analysis 2 (AXEAP2). Our approach finds a set of parameters that match the experimental spectrum with minimal intervention and has been applied to analyze the non-resonant Kβ x-ray emission spectrum (XES) of 3*d* transition metals such as Mn, Co, and Ni oxides. AXEAP2 is capable of reproducing the experimental spectrum and providing insights into the electron spin state, 3*d*-3*p* electrons exchange force, and Kβ emission core-hole lifetime. AXEAP1 and AXEAP2 are written in MATLAB and run on Windows OS.

Introduction to Resonant and Non-resonant Hard X-ray Emission Spectroscopy: Principles and Uses

Mikhail A. Solovyev[1]

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This talk is a general introduction to resonant and non-resonant x-ray emission techniques as it relates to capabilities of the 25-ID beamlines at APS. It is meant to give general background that will help with understanding the techniques and their utility. It will also provide information on the x-ray emission instruments at the beamline, such as benefits and drawbacks, as well types of samples the instruments were designed for. Examples of data and their interpretation will be provided to show the kind of information that can be acquired as well as the limitations of the techniques.

APS WK#11: Time-resolved X-ray Opportunities toward APS-U

Organizers: Xiaoyi Zhang and Donald Walko

The Advanced Photon Source (APS) is unique among the U.S. synchrotrons in offering high single-pulse brightness and large inter-bunch spacing, which is advantageous for time-resolved studies. The enhancement of the coherence especially at high x-ray energies at the upcoming APS upgrade motivates the development of new time-resolved x-ray spectroscopy, scattering and imaging techniques. This workshop will be focused on discussing with user communities new/enhanced time-resolved capabilities that leverage APS-U capabilities and their scientific applications.

(1) Time-resolved Multi-Modal Imaging & Diffraction Instrument (MMID). MMID will be upgraded and moved to a dedicated station at 7-ID. The MMID will provide nanoscale multimodal imaging capability that is designed to address urgent questions on structural dynamics in quantum materials and microelectronic devices.

(2) Time-resolved high energy x-ray total scattering and microscopy with atomic pair distribution function (TR-PDF) analysis. The TR-PDF will significantly broaden time-resolved structural investigations of nanocrystalline and amorphous materials used for catalysis, optoelectronics and solar energy conversion. This capability will enable study of light-induced non-equilibrium short-range atomic responses via TR-PDF analysis in time and space domains.

(3) X-ray transient absorption spectroscopy (XTA) combined with novel synchronous and asynchronous X-ray Multi-Probe (XMP) data acquisition techniques. We have developed XMP based XTA techniques that allow us to perform XTA measurements in all x-ray operational modes at APS and APS-U. The XMP-XTA technique enables the visualization of multiple transient states along the full reaction path simultaneously during photochemical and electrochemical reactions, which is extremely useful in studying complex energy conversion systems with multiple reaction steps and mixtures of intermediate species.

Ultrafast Atomic Pair Distribution Function Analysis

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The atomic pair distribution function method is growing in popularity as an approach for studying local structure in nanomaterials, amorphous materials, molecular materials and liquids, as well as a growing interest in the study of local symmetry breaking in bulk crystals. It is a direct measure of the local structure in the vicinity of an atom. As such, it is a very interesting representation of the structure in the context of time resolved measurements, because if the local bonding state or coordination of an atom is changed through photoexcitation, the PDF gives a direct measure of that change, and how the change propagates out in time from the location where it occurred.

Despite this, to date there has been very little work in measuring ultrafast PDFs (ufPDFs). The reasons are technological rather than scientific. First, the resolution of the PDF in real space is directly determined by the measured range in momentum, Q. To get quantitatively reliable PDF high Qmax values of greater than 20 inv. angstroms are required, and this requires good fluxes of short wavelength x-rays (> 20 keV) to be used. Second, it is required to measure this wide range of reciprocal space quantitatively with low backgrounds and linear detector response. These limitations are now being addressed with latest generation large area 2D detectors and the developing of hard-x-ray free electron lasers.

I will describe the PDF and how it could, in principle, be used in an ultrafast time resolved context. I will then describe our recent attempt to obtain moderate resolution, quantitatively reliable, PDFs in an ultrafast PDF experiment at LCLS at SLAC. The initial results are very promising, which opens the door to much more extensive quantitative time resolved local structural studies.

Excited State Trajectories in Photoactive Transition Metal Complexes Probed by Ultrafast Laser, X-Ray Spectroscopies, and Scattering

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Many photochemical events start from initial light-matter interactions that cause atomic and electronic displacements in the excited states away from the energy minima of their potential energy surfaces. When certain photochemical events, such as bond breaking, intersystem crossing and electron/energy transfer taking place within the periods of key vibrational modes, the excited state energies are determined by the trajectories defined by the actual nuclear movements that may lead to different reaction pathways and outcome. Examples will be given in the work of tracking excited state pathways for transition metal complexes on the time scales from femtosecond to a few picoseconds, such as excited state Cu(I) and Pt(II) dimer complexes. Using fs broadband transient spectroscopy and fs x-ray solution scattering, coherent vibrational wavepacket motions can be examined.

From the time evolution of key vibrational modes in the Pt dimer complexes, particularly the Pt-Pt stretching mode, we mapped out excited state trajectories on potential energy surfaces of Pt-dimer complexes for light conversion, including coherent nuclear motions. These studies were carried out in a series of model platinum dimer complexes in solution and their electron donor acceptor complexes, featuring rich photochemistry and a set of intricate excited state potential energy surfaces on time scale previously unattainable.

For the time evolution of the structural dynamics of Cu(I) complex, the experimental results revealed the Jahn-Teller distortion that transforms the symmetry of the molecule from the D_{2d} in the ground state to D_2 in the triplet metal-to-ligand-charge-transfer (MLCT) state along the two key cooperative coordinates, the Cu-N distances and the angle between the two phenanthroline ligand planes. The detailed structural trajectories have been reproduced by quantum mechanical calculations to map out the actual excited state nuclear motions from the Frank-Condon structure to an intermediate triplet state and finally the triplet MLCT state.

Nanomagnetism in a Thermal Gradient: Domains and Magnetization Gradients

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The development of spintronic devices incorporating a thermal gradient has led to a number of presently unanswered questions about how the magnetism of thin film layers evolves in thermal gradients. In the particular example of magnetic rare-earth garnet thin films, a temperature gradient can produce the spin-Seebeck effect leading to questions about how the magnetic moment, its nanoscale depth dependence, and the distribution of magnetic domains depends on the temperature and thermal gradient. Experimentally the thermal gradient can be reproducibly and precisely established using ultrafast optical excitation. We have recently conducted a time-resolved x-ray diffraction study probing the thermal properties of garnet superlattices and determined the magnitude of interfacial thermal conductances [1]. The thermal properties were probed using structural x-ray reflections of the garnet layer and can be combined with structural studies of other layers in the heterostructure. The upgrade to the APS will make it possible to conduct time-resolved magnetic diffraction studies of the magnetic – rather than structural – reflections and to probe the evolution of the magnetism under non-equilibrium thermal conditions. Methods developed at the APS [2] combine ultrafast excitation and nanobeam diffraction and can provide sufficient resolution in both time and space to resolve magnetic domains and their evolution in the thermal gradient. Comparisons with smaller-magnitude steady-state gradients can be obtained by using thin-film resistor layers as heaters. The magnetic contrast in the diffracted intensity is on the order of percent [3]. The increase in brilliance due to the APS upgrade makes thin-film magnetic scattering studies possible using repetition rates matching the laser excitation.

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New Insights into Nanocrystalline Energy Materials by Time-Resolved Pair Distribution Function Analysis

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The electronic, optical, and catalytic properties of nanocrystalline solar energy materials are closely related to the dynamics of their excited-state electronic carriers. These dynamics are affected by the short-range atomic imperfections, resulting in charge trapping and nonradiative relaxations. To control their properties and fully realize their potential, a deeper understanding of local atomic properties is needed in nanocrystalline materials in relation to their excited-state responses.

To investigate the role of local atomic structure on the excited-state responses, we have been developing a time-resolved total x-ray scattering tool at the Advanced Photon Source. This capability enables the investigation of local atomic properties, including the short-, mid- and long-range order, in nanocrystalline materials at sub-nanosecond timescales, providing insight into the coupling between the nanostructure and the photocarriers.

In this talk, I will present two scientific examples of the transient total x-ray scattering approach, enabling a time-resolved pair distribution function (TR-PDF) analysis. Specifically, I will discuss the study of non-isotropic lattice deformations in distorted lead chalcogenide nanocrystals and nanocrystalline bismuth vanadate thin-films. Through these examples, I will demonstrate the potential of TR-PDF analysis in providing new insights into the atomic-level structure and dynamics of nanocrystalline energy materials, which could ultimately inform the design of more efficient solar energy materials.

Mechanistic Investigation of Photochemistry and Photophysics at Transition Metals and Post-Transition Metals

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The powerful combination of ultrafast optical transient absorption spectroscopy with element-specific time-resolved x-ray and/or gamma ray techniques at synchrotron facilities can provide a comprehensive picture of complex photochemical mechanisms. In this talk, I will present three recent examples of such work from my group, beginning with our investigation of the Cu(I)-catalyzed [2 + 2] photocycloaddition reaction. By observing the intermolecular dimerizations of two model cyclic olefins from femtosecond to microsecond timescales, we have found that this photocatalytic reaction may be directed along strikingly disparate trajectories through only very minor changes to the structure of the substrate. Next, I will present our work identifying the timescales, intermediates, and branching ratios for the competing photochemical and photophysical relaxation pathways of the aqueous ferrate(VI) ion, a remarkable example of an air-stable hexavalent iron complex that is an excellent source of oxidizing potential in both catalysis and energy storage applications. Finally, I will conclude by discussing our progress toward nuclear resonance (i.e., Mössbauer) pump-probe spectroscopies using our recent measurement of time-resolved nuclear forward scattering from photoexcited tin(II) oxide as a proof-of-principle example.

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Unraveling Magnetic and Electronic Behavior at Ultrafast and Ultrasmall Limits

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Ultrafast laser control of magnetic and correlated materials has emerged as a fascinating avenue of manipulating magnetic and electronic behavior at femtosecond to picosecond timescales. Ultrafast manipulation of these materials has also been envisioned as a new paradigm for next generation memory and data storage devices. Numerous studies have been performed for both magnetic metallic systems as well as complex oxides to understand the mechanism underlying laser excitation. However, it has been recently recognized that spatial domain structure and nanoscale heterogeneities can play a critical role in dictating ultrafast behavior. In this talk, I will focus on utilizing time-resolved x-ray scattering and nanodiffraction studies to study spatial texture dependent dynamics in magnetic multilayers and correlated systems. I will describe our recent experimental studies using emerging synchrotron techniques and free electron laser. In magnetic multilayers, we uncover a symmetry-dependent behavior of the ultrafast response. Labyrinth domain structure with no translation symmetry exhibit an ultrafast shift in their isotropic diffraction peak position that indicates their spatial rearrangement. On the other hand, anisotropic domains with translation symmetry do not exhibit any modification of their anisotropic diffraction peak position. I will also show spatially dependent ultrafast response measured at APS for complex oxides such as rare-earth nickelates. This intriguing observation suggests preferential, texture-dependent paths not only for the transport of angular momentum, but also for structural rearrangements. These emerging nanodiffraction and imaging methods open up opportunities to access material behavior at ultrafast and ultrasmall limit and provide us with a unique way to study and manipulate spin, charge and lattice degrees of freedom.

Interfacial and Bulk Defect Resolution Using Ultrafast Diffraction and Scientific Machine Learning

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Materials defects are ubiquitous and play a key role in materials' functional properties. However, there has been a lack of non-contact, non-destructive defect quantification tools to resolve complex defect profiles when multiple types of defects are present. Here we introduce an alternative approach for defect quantification, using the fact the phonons – major heat carriers in insulators and semiconductors – are sensitive to defect scattering: phonon-frequency-resolved relaxation time and transmittance are known to contain direct and quantitative knowledge of materials' bulk and interfacial defect structures. However, frequency-resolve phonon relaxation and transmittance are long considered not measurable. Recently, we design an integrated experimental-machine-learning framework to extract such quantities in one dimension by using machine-learning to analyze time-resolved diffraction patterns: ultrafast diffraction offers high-dimensional data in time-momentum space where phonon thermal transport is reflected on the atomic vibrations and thereby diffraction intensities, and scientific machine learning is used to solve an inverse thermal transport problem and extract those frequency-resolved phonon transport with significantly increased reliability [1]. By generalizing the work to higher spatial dimension, we anticipate the work might serve an alternative pathway for non-contact, quantitative defect resolution.

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Advancing Time-resolved X-ray Absorption Spectroscopy Towards APS-U

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The introduction of laser pump-probe technique to the field of x-ray absorption spectroscopy (XAS) has allowed to develop the ultrafast time-resolved XAS (TR-XAS) in the configuration of laser pump-x-ray probe. With the elemental-specific and oxidation-state and site-sensitive characteristics of XAS, TR-XAS enable us to concurrently interrogate the multiple time-scale electronic and structural evolution of materials upon photoexcitation with the picosecond time-resolution at the atomic level. This knowledge plays a key role in the design, fabrication, and application of materials for photovoltaics, optoelectronics, and photocatalysis. Although TR-XAS has achieved a great success in the decades of development and operation at APS 11-ID-D, now its new advancement becomes indispensable as the TR-XAS program has been relocated to a new beamline APS 25-ID-E and APS upgrade (APS-U) is upcoming, which open doors to new, previously inaccessible TR-XAS capabilities. In this talk, the TR-XAS program at the new beamline APS 25-ID-E will be presented, including the resources, beamline layout, capabilities, and scientific applications. As well, the future development of TR-XAS combined with novel synchronous and asynchronous x-ray multiple-probe (XMP) data acquisition techniques will be discussed.

Tracking Chemical Reactivity Across Multiple Timescales with X-ray Spectroscopy

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For light-induced reactions in liquids, chemistry often occurs across a wide range of timescales, from the femtosecond regime of the initial electronic excitation out to the microsecond regime (or longer) where one finds diffusion controlled bimolecular reactions. APS-U will provide a factor of two more x-ray flux in fine-spaced fill patterns that are optimal for tracking these processes with pump-probe methods and promises new insight into the mechanistic details governing this chemistry. In this talk I will describe our studies on the UV degradation of iron(II) hexacyanide in water, a system that has been known to be light sensitive for over a century, but for which details are still lacking, but relevant, for a wide range of research areas such as aqueous flow batteries, synthesis of Prussian-blue analogs for radionuclide recovery from nuclear wastewater, prebiotic chemistry on early earth, and environmental cyanide contamination from industrial pollution. Our pump-probe XAS studies at the Fe K-edge, coupled with QM/MM molecular dynamics simulations, have revealed insight into fluxional behavior of reaction intermediates and our pump-probe nonresonant XES studies of the full Fe 1s emission spectrum have provided insight into the spin state and covalency changes of intermediates. Future studies with APS-U can take advantage of the more efficient data collection rate and explore larger parameter space, such as varying counter ions, incorporating solvent mixtures, or varying temperature, concentration, or pH. I will also mention some ideas for overcoming challenges with APS-U for pump-probe studies, such as the elongated x-ray pulse duration and slow pixel area detectors.

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Unraveling the Mechanistic Pathways of Earth-abundant Photosensitizers and Solar Fuel Catalysts through Time-resolved X-ray Spectroscopy

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The search for sustainable ways to store and distribute energy is one of the most urgent scientific challenges in view of the rapid depletion of fossil fuels, environmental pollution and resulting climate emergency [1]. A solution to the undergoing energy crisis can only be obtained through implementation of renewable sources and new low-polluting fuels [2]. Solar-driven water splitting provides an efficient means of meeting our energy demands and storing energy in the form of a clean fuel (H_2) and oxidant (O_2) [3]. Hydrogen as an energy carrier further provides an attractive alternative to fossil fuels with its combustion producing only heat and water. The prospect of developing a hydrogen economy and using hydrogen as a carbon-free fuel has motivated the discovery of effective and robust catalysts and photosensitizers that can lower the energy barriers to hydrogen production. Approaches similar to natural photosynthetic modules have further been developed to efficiently couple photosensitizers which involve transient one-electron excited states to multi-electron, proton-coupled earth-abundant HECs [4].

It is however important to remark that despite significant efforts, key insights on the photo-induced electron transfer dynamics, photogenerated intermediates and influence of the various ligands on the activities and electronic properties of earth-abundant photosensitizers and solar fuel catalysts have been limited. In this context, time-resolved x-ray absorption with x-ray emission spectroscopy are powerful tools for visualizing the "real-time" electronic and geometric changes involved in a photocatalytic system with picosecond-microsecond time resolution. This talk will demonstrate the reaction pathways of several earth-abundant photocatalytic complexes, examined in unprecedented detail with picosecond time resolution. The mechanistic pathways followed by these light-harvesters and catalysts with spectroscopic and kinetic characterization of the different intermediates towards the hydrogen evolution pathway and H-H bond formation will be explained. Results shown will enable the rational design of molecular light-harvesters and hydrogen-evolving photocatalysts that can perform beyond the current microsecond time scale and suggest ways in which the ligand structures can be adjusted to improve the emission lifetimes and catalytic efficiencies.

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Catching Atoms in Action in Functional Materials Using Time-resolved Synchrotron Techniques

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In functional materials electronic and atomic structures are closely correlated. However, our knowledge about their temporal correlations is still limited. The APS-upgrade will open up new horizons for catching atoms in action together using time-resolved multimodal synchrotron x-ray techniques. When atoms start to move inside or through crystalline materials, it will cause structural disorders, phase transitions and amorphization. Whereas in non-crystalline materials, atomic motions will lead to short- or medium-range order reconfigurations. In this talk, we will explore future opportunities in studying atomic motions in some functional materials using time-resolved XRD/PDF techniques. Perspectives and challenges will be discussed.

Transient Lattice Dynamics of 0-, 2-, and 3-D Metal Halide Perovskites

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Solution-processed metal halide perovskite compositions offer scalable synthesis as well as highly desirable optoelectronic properties. As such, these materials offer significant prospects for use in light absorption and emission technologies including solar cells, light emitting diodes, and lasers. We report studies of optical pump, transient X-ray diffraction probe paired with temperature dependent diffraction and optical studies that interrogate the response of the lattice in these materials upon illumination. Materials studied span 0-, 2-, and 3-D where in some cases, surprising evolution of lattice symmetry is observed as well as phase metastability. The findings offer insight regarding optical response of these materials and present opportunities.

Time-resolved Multimodal Imaging and Diffraction at Upgraded APS

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The APS upgrade enables time-resolved x-ray diffraction imaging with unprecedented spatial resolution and signal-to-noise ratio. Combining *in-situ* local electrical and optical stimulation and probes, dynamical structure-property relationships can be directly measured at nanoscales. In this talk, I will present the enhancement plan for the nanodiffraction imaging instrument at Sector 7. Its potential applications will be presented using examples of phase transitions in quantum materials driven by electrical and optical stimulation.

Joint WK#12: Microelectronics: Materials, Design, Devices, and Characterizations

Organizers: Yuzi Liu, Hua Zhou, and Yue Cao

Novel materials and design to break the limit of current semiconductor devices are urged in order to meet the increasing requirement in microelectronics in beyond Moore's computing era. The emerging concept of stacktronics attracts great interests in research communities in recent years due to the unique properties of various 2D materials and the approach of stacking which could be implemented for device fabrications in large scale. The concept of neuromorphic computing has created a new paradigm of energy efficient infrastructures and unique computing approach has caught great attention in the last decade. A suite of promising materials and devices were reported and demonstrated the great potentials for applications. However, there are still many critical questions regarding fundamental material properties, innovative device design, device working mechanism and reliability. The architecture-level understanding and the integration of the new microelectronics devices with existing semiconductor technologies remain much less explored. The efficiency and effectiveness of the new proof-of-concept devices rely on fundamental understanding of material transformation while the device in operation. It urgently calls for operando observation and microscopic characterization in different length scales.

This workshop will discuss widely what state of art of microelectronics design and fabrications, the emerging proof-of-concept devices and performance evaluation, the high throughput characterization platforms and computational tools available and in needs at national facilities, including the cross platform *operando* imaging capabilities (synchrotron x-ray and electron beam) to tackle the fundamental challenges in capturing material evolution in working devices. The workshop will gather the experts in fields of inverse design, materials and device fabrication and evaluation, condensed matter physics and characterizations to discuss the opportunities to move forward in the field of microelectronics.

Towards an Expanded Palette of Materials and Mechanisms for Neuromorphic Computing

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The metal-insulator transitions of electron correlated transition metal oxides provide an attractive vector for achieving large conductance switching with minimal energy dissipation. However, given the sparse and disconnected current knowledge of neuromorphic materials, a fundamental understanding of descriptors of neuromorphic function formulated in terms of intrinsic material properties, and the influence of atomistic defects on mesoscale domain evolution in the presence of external applied fields is currently lacking. Using VO_2 and $M_xV_2O_5$ compounds as model systems, I will detail our efforts to develop a systematic understanding of how compositional modifications through substitutional or interstitial doping alter transformation characteristics such as the transition temperature, magnitude of switching, energy dissipation, and hysteresis.

The inclusion of dopant atoms strongly modifies the free energy landscapes in terms of relative phase stabilities, transformation barriers, and pathways; thereby profoundly altering the coupling of lattice, electronic, and spin degrees of freedom in a non-trivial manner. I will particularly focus on the three distinct mechanisms: (a) discovery of diffusive dopants that provide a distinctive new way to alter the dynamics of electronic transitions; (b) cation shuttling and polaron oscillation as a means of engendering metal—insulator transitions; and (c) lattice-anharmonicity-driven mechanisms in compounds with stereochemically active lone pairs.

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Unveiling Fractional Quantum Anomalous Hall States in R-stacked Twisted MoTe2

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The discovery of the fractional quantum Hall effect (FQHE) revolutionized our comprehension of quantum phases of matter and opened up new avenues for fault-tolerant topological quantum computation. However, the necessity for low temperatures and high magnetic fields imposes significant technical constraints on its practical application. In this talk, we present our findings on a zero-field counterpart of FQHE, the fractional quantum anomalous Hall effect (FQAHE), in R-stacked twisted MoTe2. The observation of FQAHE at high temperatures and without the need for magnetic fields highlights the immense potential of this material platform for advancing topological quantum computation.

Dynamic Processes in Strontium Cobaltite Heterostructures

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Transition metal oxides (TMOs) possess variable oxygen stoichiometry which can be the cause of distinct changes to physical and electronic properties. One such TMO, strontium cobaltite ($SrCoO_x$), has two structurally and electrically distinct phases – the insulating orthorhombic brownmillerite ($SrCoO_{2.5}$ – BM-SCO) and conducting cubic perovskite ($SrCoO_{3-\delta}$ – PV-SCO) – that reversibly transition via a topotactic pathway with the insertion or removal of oxygen. In the thin film form, this topotactic transition occurs while preserving high quality epitaxial films, making this material system of interest for resistive memory switching applications. Here, BM-SCO based-heterostructures on strontium titanate (STO) and $(LaAlO_3)_{0.3}(Sr_2TaAlO_6)_{0.7}$ (LSAT) (001) substrates are investigated in order to understand changes to the oxide and at different interfaces under oxidizing / reducing conditions and while under applied potential. The results of x-ray diffraction (XRD) and x-ray photon correlation spectroscopy (XPCS) studies will be discussed along with the potential of such materials in the development of improved resistive switching devices in epitaxial heterostructures.

Nanoscale Imaging of *Operando* Semiconductor Systems through Time-resolved Hard X-ray Diffraction Microscopy

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The unique imaging power of nano-focused synchrotron hard x-rays can be harnessed to provide non-destructive methods for 3D visualization of crystallographic phase and strain in solid-state materials. This gives access to understanding extremely subtle lattice perturbations (<10^-4 dc/c) near defects or interfaces within fabricated heterostructures that can be located potentially microns away from surfaces without sectioning the sample. The use of time-resolved coherent synchrotron illumination synchronized to external stimuli can further augment this approach to understand excitation-driven energy flow and dynamic structure-function relationships across broad classes of current and emerging microelectronics device architectures and other material systems. Current work and future directions enabled by the near-term completion of diffraction limited storage rings such as the Advanced Photon Source Upgrade (APSU) and correlative data synthesis with quantitative electron microscopy methods will be explored in the context of recent results.

X-ray Metrology for the Semiconductor Industry

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Modern microelectronics continue to get smaller and more three dimensional to increase the performance and energy efficiency. These complex 3D nanostructures contain a variety of different materials that are integrated together. The details of the nanoscale chemistry and shape determine how these nanodevices function and how they are fabricated. The semiconductor industry is dependent on metrology methods to accelerate the development of new process nodes and to monitor and control the fabrication process. The current metrology methods are struggling to provide the information needed on the latest 3D nanodevices. We will report on several x-ray-based methods developed by NIST and applied to gate all around nanosheets, 3D-NAND, and next generation lithography. We will also discuss key requirements for the semiconductor industry for new metrology methods.

Semimetal Technology for 2D Semiconductor Electronics

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2D semiconductors have emerged as promising candidates for the channel materials in future ultimately scaled transistor technologies. A number of challenges still remain in terms of both material processing and device technologies. The weak interlayer coupling and the unique mesoscopic physics of semimetal/2D semiconductor heterostructures can potentially address some of these fundamental challenges, giving rise to viable pathways towards scalable and high-performance electronic device technologies based on 2D semiconductors. This talk will summarize our recent research efforts on the material processing and device technologies for semimetal/2D semiconductor electronics. First, I will discuss a wafer-scale semi-automated dry transfer process for monolayer CVD transition-metal dichalcogenides (TMDs) utilizing the weakly coupled interface between semimetal (Bi) and TMDs. Second, our recent progress of semimetal contacts (Bi, Sb) to 2D TMDs for high performance n-type field effect transistor (nFET) technologies will be covered. The thermal stability of these contact technologies will also be evaluated. Finally, I will talk about our computational efforts on the searching of pinning free semimetallic p-type contacts to 2D TMDs.

Developing High Performance Piezoelectric Oxide Thin Films for Acoustic Filters in 5G Wireless Communications

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High-speed and low latency 5G wireless networks are essential to enable exciting applications such as autonomous vehicles, internet of things and virtual reality. However, the current speed of 5G network is largely limited by the hardware in radio frequency front end modules in the mobile devices. The speed of the wireless network is determined by the bandwidth of the acoustic filters, which serve the key function of selecting the desired frequency bands and filtering out unwanted signals. The bandwidth of the acoustic filters is proportional to the electromechanical coupling coefficients of the piezoelectric thin films used in these devices. Therefore, developing high performance piezoelectric thin film is critical to achieve high-speed 5G wireless communications.

In current commercial acoustic filters, AlN based piezoelectric thin films are the dominant materials. However, the low electromechanical coupling coefficients of AlN is limiting the bandwidth of acoustic filters. To improve the coupling coefficients, Sc-doped AlN are widely studied by leading companies and researchers in the field. Another candidate is $LiNbO_3$ piezoelectric thin films with much higher coupling coefficients. However, the direct growth of $LiNbO_3$ thin film is very challenging, hindering the commercial applications of this material. Recently, our team has reported giant piezoelectric coefficients in $NaNbO_3$ thin films with nanopillar structures [1]. In this talk, I will show the initial demonstration of large electromechanical coupling coefficients of $NaNbO_3$ in acoustic resonators. Potential time resolved *in situ* x-ray diffraction under applied electric field to understand the working mechanism of acoustic filters at ~ GHz frequency will also be discussed.

[1] Huajun Liu, et al. *Science*, 369, 292 (2020).

Complex Oxides for Brain-Inspired Computing

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Information processing, learning and memory in animal brains serves as an inspiration for artificial neural networks. The design of energy-efficient hardware for implementing the various aspects of intelligence and integrable with Si CMOS circuitry is in early stages. In this talk, we will give examples of complex oxide semiconductors that can be synthesized with near-atomic scale structural and compositional precision towards design of artificial neurons, synapses and their interconnections. Basic research needs in metastable materials intersecting physics, neuroscience and computer science will be pointed out.

Towards Developing Energy-efficient Electronics Based on Diamond Heterointegration with Semiconductor Materials

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Diamond possesses several unique properties, including high phonon energy, low trap density, and high thermal conductivity, making it an ideal substrate for forming heterojunctions through Van der Waals interactions. Our research has focused on integrating diamond with semiconductor materials such as GaN for efficient thermal management as well as two-dimensional (2D) materials such as graphene and MoS_2 to create heterojunction devices with exceptional performance. For instance, we have achieved a very high breakdown current density of $10^9 A/cm^2$ from devices fabricated using graphene on diamond. Additionally, by integrating n-type MoS_2 with p-doped bulk diamond, we have successfully formed p-n junctions demonstrating excellent diode characteristics. This approach of integrating diamond with 2D materials offers new opportunities for developing novel nanoelectronic devices. However, further research is needed to understand the mechanism of charge transport at the interface and the effect of surface chemistry on the performance of these devices.

Memristors with Thousands of Conductance Levels for Analog Computing

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The analog data deluge issue nowadays call for multipurpose analog computing platforms with great reconfigurability and efficiency, namely, field-programmable analog arrays (FPAAs) [1]. FPAAs as the analog counterpart of field-programmable digital arrays (FPGAs) open opportunities for fast prototyping analog designs as well as efficient analog signal processing and neuromorphic computing. Memristors may be the ideal building blocks for FPAAs if they are truly analog with many conductance levels, not just for lab-made devices, but more importantly, devices fabricated in foundries. We have recently demonstrated 2048 conductance levels, a record among all types of memories, achieved with memristors in fully integrated chips with 256 × 256 memristor arrays monolithically integrated on CMOS circuits in a standard foundry [2]. We have unearthed the underlying physics that previously limited the number of distinguishable conductance levels in memristors and developed electrical operation protocols to circumvent such limitations. These results reveal insights into the fundamental understanding of the microscopic picture of memristive switching and provide approaches to enable high precision memristors for various applications.

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APS WK#13: A Decade through the Looking Glass: X-ray Scattering on Quantum Materials in Pulsed and Persistent Magnetic Field

Organizers: Zahir Islam, Ulrich Welp, and Antonino Miceli

With APS-U rising on the horizon, this workshop aims to highlight a portfolio of high-field diffraction experiments on quantum materials to inform future studies and experimental needs. In a global arena with powerful techniques at other new as well as upgraded hard x-ray sources equipped with high-field magnets, it is timely to exchange ideas on how best to leverage complementary opportunities. Of particular interest is an incisive look into difficult-to-access phase space, means to leverage subtle diffraction contrasts, and concurrent multi-modal measurements. Furthermore, discussions on ways to go beyond measuring 'average' properties by imaging to obtain spatially resolved information are anticipated.

Simulation of the Temperature Distribution in Heterogeneous Samples or Devices due to X-ray Beam Heating

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Heating effects of samples subject to high-power x-ray beams are in particular important for superconductors below the transition temperature. Motivated by the x-ray diffraction study of the doped topological insulator $Sr_xBi_2Se_3$, we performed simulations of the heat diffusion equation for the sample setup, including attached leads and effects of the sapphire wafer the sample is mounted on.

In this talk I will briefly describe the experimental setup and measurements for the $Sr_xBi_2Se_3$ sample and go over the model and simulation results. I will describe the computational approach to some detail and show some potential extensions.

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X-ray Diffraction Under Large Magnetic Fields: The Case of Piezomagnetism in Uranium Dioxide

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5*f*-electron spin systems exhibit strong spin-lattice coupling and electronic correlations and are predicted to host new emergent phenomena. One recent example is the observation of piezomagnetism and magneto-elastic memory effect in the antiferromagnetic Mott-Hubbard insulator, UO_2 [Daniel J. Antonio et al., Piezomagnetic switching and complex phase equilibria in uranium dioxide. Communications Materials 2, 17 (2021)]. Here, we give a short overview of piezomagnetic behavior in this material with a focus on x-ray diffraction studies of oriented UO_2 crystals under strong pulsed magnetic fields. We show how the high-resolution single crystal diffraction allows us to study details of subtle unit-cell distortions below and above the structural and magnetic phase transition in this material. We show that direct microstructural observations of the piezomagnetic and switching effects are being a direct consequence of the non-collinear 3**k** magnetic order that breaks time-reversal symmetry in a non-trivial way. We also observe the presence of magnetic domains with distinct magnetic-field evolution in the magnetically ordered state of UO_2, both when the field is applied repeatedly in a single direction and when the field direction is alternated.

Resonant Inelastic X-ray Scattering Under Magnetic Field

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Resonant Inelastic X-ray Scattering (RIXS) provides excitation spectra in quantum materials by measuring their momentum- and energy-dependences which leads to the discovery and understanding of new phenomena [1]. Ir compounds have received much attention because of rich emergent phenomena [2]. Tuning quantum ground states using a magnetic field can help us better understand the phase diagrams of Ir compounds. In this talk, I present the RIXS technique and its application in studies of square-lattice and honeycomb-lattice iridates under a magnetic field [3,4]. Spin excitation spectra by RIXS showed that the isotropic Heisenberg coupling governs the spin dynamics of antiferromagnetic Sr_2IrO_4 [3]. Magnetic field aligns an antiferromagnetic domain Sr_2IrO_4 and provides a way to revisit the spin excitations in terms of the transverse and longitudinal responses, revealing a deconfinement behavior. Honeycomb iridates (Li_2IrO_3 Na_2IrO_3) belongs to a first class of materials that has emerged as a prominent candidate for a topological phase of the Kitaev quantum spin liquid (KQSL) [4-6]. Magnetic field tunes between competing quantum ground states of honeycomb iridates and RIXS probes dynamic spin correlations of a field induced magnetic phase.

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Future Pathways of Dark Field X-ray Microscopy: Magnetism, Charge Order, and Beyond

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The development and implementation of Dark Field X-ray Microscopy (DFXM) has opened new pathways of studying spatial heterogeneities within condensed matter systems. I will present recent studies of weak-scattering systems (e.g. thin films and neuromorphic devices) that demonstrated necessary steps to studying more exotic phenomena such as magnetic structures and charge density waves. Existing low-temperature capabilities offer innovative means of DFXM imaging of quantum materials (QM) in magnetic fields. The upgrades of APS-U will offer orders-of-magnitude enhancements of this flourishing technique to many more scattering phenomena in condensed matter systems and further our understandings of the mesoscopic interactions in QM.

Nonuniform Superconducting States

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I will review two oscillating superconducting states which were in the focus of extensive research activity over several decades: (i) helical state in magnetic superconductors caused by indirect interaction between the moments mediated by superconducting electrons, and (ii) state with periodic modulation of the superconducting order parameter caused by strong exchange field acting on superconducting electrons known as Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state. I will discuss the exciting physics behind these states and recent developments in their theoretical and experimental investigations.

Nanocalorimetry Instrumentation Development for X-ray Science Applications

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Advancements in calorimetry (nano) sensors and measurement techniques have enabled highly sensitive heat capacity measurements along with fast heating/cooling rates for samples below sub-milligram in mass. The calorimeters typically operate from room temperature down to liquid-helium temperatures. Each calorimeter cell consists of low power thin film heaters and a thermometer on a thin dielectric membrane. Calorimetry can be combined with many other sophisticated techniques including x-ray (scattering, imaging) and electron microscopy (scanning, tunneling). The unique capability for concurrent studies of bulk thermodynamic properties coupled with structural, chemical, or atomic properties makes a powerful analytical tool for a diversity of systems encompassing functional materials and single-crystal samples subject to thermal cycling. In this talk, we will summarize our R&D efforts on novel calorimeter designs and batch fabrication of the state-of-the-art calorimeters (nano) for thermodynamic measurements with a goal to build novel multimodal synchrotron instrumentation.

X-ray Study of the Valence Transition of $CeOs_4Sb_{12}$ in Pulsed Magnetic Fields

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Valence transitions, where f electrons undergo a transformation from quasi-localised to itinerant, are associated with a change in unit cell volume. Perhaps the most famous and dramatic example of this is the $\gamma - \alpha$ transition in cerium and its alloys, which for elemental cerium is accompanied by an isostructural collapse of the unit cell volume often reported to be as large as ~15 % [1]. The Ce-based compound $CeOs_4Sb_{12}$ has previously been shown using resistivity, magnetostriction, and contactless conductivity (PDO) measurements to undergo a valence transition with a very unusually-shaped phase boundary in the field-temperature phase diagram [2, 3]. In this talk I will discuss the results of single-crystal x-ray diffraction measurements in pulsed magnetic fields of up to 30 T performed to directly study the change in lattice parameter associated with this valence transition. Such a setup is vital to study the high-field region of the phase diagram. We observe a clear signal indicating a change in lattice parameter upon crossing the phase boundary. Furthermore, we report a small tetragonal distortion from the previously reported cubic structure, the observation of which is made possible by the high sensitivity of the backscattering geometry used.

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New Science Opportunities at the High Magnetic Field X-ray Facility at CHESS

Jacob Ruff[1], on behalf of the HMF Project Team[1,2,3]

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The High Magnetic Field (HMF) beamline currently under construction at CHESS will enable x-ray scattering and spectroscopy studies in persistent magnetic fields as high at 20T. The end station will feature a wide-angle conical superconducting solenoid which allows diffraction experiments at angles as large as 50 degrees. The beamline will be capable of delivering bright x-ray beams with wide tunability for many types of experiments – energy ranges from 2.7 keV to 72 keV will be available, with control of incident beam polarization and bandwidth. Sample temperatures as low 2K will be available for users. In this talk, I will review the science drivers, beamline design, planned capabilities, and current progress of construction of the HMF beamline. HMF is a partnership between CHESS, the MagLab, and the University of Puerto Rico, which is scheduled to become available to users in January 2026. The HMF beamline project is supported by the National Science Foundation, Mid-Scale Research Infrastructure Program, under award DMR-1946998.

Single-crystal Diffraction Below 1K: Looking for Symmetry-breaking Distortions in a Rotational Symmetry Breaking Superconductor

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The discovery of a rotational symmetry breaking, or nematic, state in the superconducting doped topological insulator $M_xBI_2Se_3$ (M = Cu, Sr, Nb) indicates a multicomponent superconducting order parameter which is topological in nature. Many questions remain in this family of materials. In particular, the nematic axis of twofold symmetry is always pinned along one of three rotationally equivalent directions in the threefold symmetric basal plane in the rhombohedral crystal. Crystallographic strain has been proposed as the origin of the choice of pinning axis, but different techniques disagree on the presence of strain, the temperature at which symmetry-breaking occurs, and whether or not nematic domains exist in a single crystal. I will summarize recent data in this family of materials and discuss our group's recent work performing perhaps the first ever sub-kelvin single-crystal synchrotron diffraction measurements at the APS to look for structural origins of the choice of nematic pinning axis deep in the superconducting state. Our multimodal technique may open up new methods of investigating other unique low-temperature phenomena.

Possibilities for X-ray Diffraction Experiments in Magnetic Field at the APS-U Polar Beamline

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In April 2024, the upgrade of the Advanced Photon Source at Argonne National Laboratory to an MBA reverse bent lattice will be completed. APS-U will offer extremely brilliant and highly coherent beam through the new low emittance source to the user community. This will enable a variety of exciting new possibilities for scattering and spectroscopy experiments by pushing towards extreme pressures and high spatial resolution in combination with polarized x-rays. Polar, the beamline for polarization modulation spectroscopy at sector 4 of the APS will make use of small intense focused beams with high degree of coherence and tunable polarization, with the possibility to combine these with a suite of sample environments including variable temperature, magnetic field, pressure, and uniaxial strain.

At Polar, different magnets will be available for magnetic diffraction or imaging experiments. A versatile, superconducting 2 Tesla magnet will be available for mounting into the diffractometer where it can be combined with low temperature cryostats for sample cooling. It will allow for experiments using mini-DACs and strain cells as function of temperature and magnetic field. The flexible setup enables in-field dichroic reflectivity as well as diffraction experiments with unconstrained in-plane angular access and will make use of micron-sized focused beam. The long detector arm will allow for dichroic Bragg CDI, directly relating sample strain to magnetic properties. 3D dichroic nano-tomography and ptycho-tomography in small magnetic fields will be possible at ambient temperatures. A 9-1-1 Tesla magnet will enable real-space, as well as ptychographic 2D imaging with dichroic contrast at low temperatures using sub-micron focused beams in a transmission geometry, combined with applied pressures or uniaxial strain.

In this presentation, we will provide details about the experimental setup and discuss scientific possibilities and examples.

X-Ray Spectroscopy and Resonant Scattering in Pulsed High Magnetic Fields: A Look Back and into the Future

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First, this presentation takes a look back at a decade of work at the European Synchrotron radiation facility, where the internal development of high duty cycle miniature coils [1] has enabled us to perform photon hungry experiments including nuclear resonant scattering of synchrotron radiation [2] and Fe K-edge XMCD [3,4] in pulsed high magnetic fields for the study of ferrimagnetic and frustrated materials [5,6,7,8]. Later, we developed a low temperature cryostat and a miniature high pressure cell in collaboration with the Laboratoire National des Champs Magnétiques Intenses for their solenoid coil [9], in order to perform x-ray spectroscopy in strongly correlated electron systems in multi extreme conditions of temperature, pressure, and field. In an outlook to the future, I will outline the opportunities offered by the ongoing integration of a pulsed high magnetic field installation contributed through the HIBEF consortium at the High Energy Density Instrument of the European XFEL [10]. To finish, I speculate what the ultimate magnet for a MHz repetition rate free electron laser facility could look like.

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In-Situ Nanocalorimetry: Combining X-ray Diffraction with Thermodynamic Measurements

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Specific heat and x-ray diffraction can provide complementary information about a materials properties and phases. Measuring them simultaneously in particular close to phase transitions allows for a detailed investigation of the material under study. To this end, we have integrated a nanocalorimetry platform into a 4.5T magnet at an x-ray beamline of the APS. With this multi-modal setup we are able to measure the specific heat and x-ray diffraction simultaneously across a broad range of temperatures and magnetic fields. We have benchmarked this setup with the study of Fe2P, a hexagonal transition metal pnictide undergoing both a structural and magnetic phase transition at 217K. Strong magneto-elastic coupling turns the usual 2nd order paramagnet-to-ferromagnet transition into a 1st order one, making this material a perfect candidate to study the interplay between phase transitions. Our multi-modal approach confirms that the structural and magnetic transitions appear at the same temperature. We observe that applying an external magnetic field broadens the structural transition. Additionally, we investigated the hysteresis of the transition in both specific heat and lattice parameter where the precise temperature control of the nanocalorimeter allows to line up the features observed in both quantities. X-ray scans were taken at different temperatures through the transition which reveal peak splitting in the FM phase that persists into the superheated region indicating the appearance of twinning or a domain structure.

High-Field Studies of Charge Density Wave Order on a Kagome Lattice

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Charge density wave order is predicted to form on a kagome lattice with an electron filling close to the saddle-point derived Van Hove singularities in its band structure. This charge density wave order can be unconventional, and, in select regimes of interaction strengths, can theoretically acquire an imaginary component that breaks time reversal symmetry. The resulting orbital flux phase would be an unusual form of magnetic order that forms in the absence of local magnet moments. Such a state has recently been speculated to form in a class of kagome compounds of the form AV_3Sb_5 (A= K, Rb, Cs). Here I will present some of our x-ray scattering work probing the character of the charge density wave state in these compounds. The response of the real component of the charge density order under the application of a magnetic field will be discussed.

Pfeiffer Vacuum Training: Advanced Technical and Theoretical Concepts and Considerations to Further Develop your Vacuum Knowledge

Organizers: Camila Virgen, Ian Malloch, and Maureen Rosenwinkel

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Advanced Technical and Theoretical Concepts and Considerations to Further Develop Your Vacuum Knowledge

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Achieving Ultra High Vacuum (UHV) conditions within a system has proven to be a challenging task due to the limiting mechanisms encountered within such an environment. As vacuum technology continues to improve and more applications call for UHV conditions, being aware of the technology that is required, as well as being capable of interpreting the data provided by a pump down curve have become primary knowledge to working with systems of this nature. Consequently, cleaning procedures and other maintenance methods tend to be overlooked as users assume that the ability to achieve these low pressure levels is only dependent on the capabilities of the pumping technology.

The improvements of vacuum technology over the years have resulted in its implementation onto applications that introduce high radiation and magnetic fields within a UHV environment. Safety measures have been taken and design upgrades made to allow the technology to function as efficiently as it does in standard applications. Apart from vacuum pumps, leak detection and mass spectrometry technology have also been further developed to assist in applications that require UHV conditions. These extremely low pressure environments are becoming the norm for most vacuum systems, resulting in the need for knowledge of UHV systems as well as the spectrometric technology that they implement to be preserved and continuously expanded as more advancements are made within the vacuum industry.

CNM Short Course: Using AI/ML for Modeling and Characterization of Nanoscale Materials

Organizers: Maria Chan, Subramanian Sankaranarayanan, and Henry Chan

This workshop will focus on the application of AI/ML techniques in nanoscience and materials research. Besides research highlights, the workshop will also provide an overview and demo of various AI/ML tools and software developed at the CNM. Examples include:

- Ingrained framework for matching simulated and experimental STEM/TEM and STM images.
- FANTASTX framework for determining atomic structures from STEM, PDF, XAS, XRD, STM, and other experimental data types.
- BLAST framework for fitting interatomic potentials for atomistic/coarse-grained molecular dynamics simulations using Ab Initio and experimental data.
- CASTING framework for inverse design of structures and processing-microstructure optimization using molecular dynamics and kinetic Monte Carlo.
- POLYBOT framework for enabling autonomous experiments guided by AI/ML and digital twins.

Diversity, Equity, and Inclusion Workshop: The Power of Small Disturbances, the Promise of “Domino Dynamics,” and How to Innovate for a More Equitable Future

Organizers: Fanny Rodolakis, Becky Sikes, and Michelle Mejia

The grand challenges we face today - like climate change and inequality - can seem intractable. After all, the systems we live, work, and learn within are imbued with implicit bias and continue to produce inequitable and unjust outcomes. The field of science is no exception. Today, because bias, discrimination, and inequity continue to prevent the full diversity of voices - and their ideas, questions, and solutions - from reaching the world’s megaphones and shaping what happens inside and outside the laboratory, we are necessarily stymying our progress toward a more equitable and sustainable world.

But this doesn't have to be our story.

With the need for innovation more urgent than ever, and a collective imperative to create the conditions where everyone has an equal opportunity to succeed and reach their full potential, small systemic disturbances have the power to create seismic change. And each of us can play an active role in creating those disturbances.

In this session, you’ll hear a guest perspective from Dr. Sonali Mohapatra, Quantum Innovation Sector Lead at the National Quantum Computing Centre, Director of the Prospero Space Fellowship, and Founding Member and Chair of New Voices in Space Working Group on the Scottish Space Leadership Council. Dr. Mohapatra will describe why *now* is the time to innovate the systems in the field of science for greater equity and equitable scientific innovation. Dr. Kristen Liesch - Forbes “D&I Trailblazer” and co-founder and co-CEO at Tidal Equality - will explore how small disturbances and ‘domino dynamics’ have the power to transform our systems and drive a more equitable and innovative future. She will share insight, drawing on the science of behavioral change and the art of social change, and provide practical examples and tactics you can use to create “small disturbances” of your own.

Diversity, Equity, and Inclusion Workshop: Reducing Systemic Biases through Anonymized Application Processes and Machine Learning

Organizers: Fanny Rodolakis, Becky Sikes, and Michelle Mejia

Most resource allocation for observatory time (or money) is done through peer review processes that can be time-consuming and prone to bias. The Space Telescope Science Institute (STScI) has pioneered a dual-anonymous reviewing process and implemented new tools, streamlining mechanisms to reduce bias. This talk will showcase these changes and share some preliminary results on their effects from the most recent award cycles.

Dr. Louis-Gregory (Lou) Strolger is an Observatory Scientist and Deputy Head of the Instruments Division at Space Telescope Science Institute (STScI), and a Research Scientist in Physics and Astronomy at Johns Hopkins University. His scientific research explores supernovae, cosmology, and dark energy, where he primarily works on the nature of supernovae progenitors. Dr. Strolger has been involved in science policy for much of his professional career. Notably, he had a key role in developing the dual-anonymous peer review process for observing time on the Hubble Space Telescope, which has been adopted at many astronomical observatories, and is rapidly gaining interest in physics communities and with federal granting agencies. Find out more on his website: https://www.stsci.edu/~strolger/