

# DRIVING DISCOVERY

## 2017 APS/CNM USERS MEETING

### POSTER ABSTRACTS

A-# = Advanced Photon Source abstracts

C-# = Center for Nanoscale Materials abstracts

ESRP-# = Exemplary Student Research Program abstracts



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APS POSTER ABSTRACTS



## Biology

### A-1

#### A Comparison of Micro-CT Images of the Middle Ear of Two Mammalian Species

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Non-invasive studies of the structure of the middle ear typically involve dedicated commercial x-ray computed tomography (CT) systems. Such studies contribute valuable data regarding the anatomy of the middle ear, and may inform models of middle ear function. Limitations of these systems include insufficient contrast of soft tissues and poor resolution in comparison to scale of vibrations of the middle ear. Imaging using synchrotron x-rays provides visualization of both soft and hard tissues, allowing for non-invasive imaging of the complete system at higher resolutions. Mouse and Guinea Pig temporal bone samples were imaged using coherent synchrotron x-rays with photon energies near 25 keV at the 2-BM beamline at Argonne National Laboratory. These species have contrasting middle ears, the micro-type ear (mouse) and fused malleus-incus (guinea pig). Resolutions achieved were as low as 1.49 micrometers, in comparison to 8.5 micrometers for very high resolution commercial microtomography [1]. Several soft tissue structures could be identified without staining, including suspensory ligaments, muscles, mucosal folds, and the tympanic membrane. These images confirmed reports of malleus-incus fusion in the guinea pig and provide a foundation for future 3D motion measurements.

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### A-2

#### Preserving Elemental Content in Adherent Mammalian Cells for Analysis by Synchrotron-based X-ray Fluorescence Microscopy

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Trace metals play important roles in biological function, and x-ray fluorescence microscopy (XFM) provides a way to quantitatively image their distribution within cells. The faithfulness of these measurements is dependent on proper sample preparation. Using mouse embryonic fibroblast NIH/3T3 cells as an example, we compare various approaches to the preparation of adherent mammalian cells for XFM imaging under ambient temperature. Direct side-by-side comparison shows that plunge-freezing-based cryoimmobilization provides more faithful preservation than conventional chemical fixation for most biologically important elements including P, S, Cl, K, Fe, Cu, Zn and possibly Ca in adherent mammalian cells. Although cells rinsed with fresh media had a great deal of extracellular background signal for Cl and Ca, this approach maintained cells at the best possible physiological status before rapid freezing and it does not interfere with XFM analysis of other elements. If chemical fixation has to be chosen, the combination of 3% paraformaldehyde and 1.5% glutaraldehyde preserves S, Fe, Cu and Zn better than either fixative alone. When chemically fixed cells were subjected to a variety of dehydration processes, air drying was proved to be more suitable than other drying methods such as graded ethanol dehydration and freeze drying. This first detailed comparison for x-ray fluorescence microscopy shows how detailed quantitative conclusions can be affected by the choice of cell preparation method.

## A-3

**Machine Learning Analysis on X-ray Scattering Data of Cellulose Microfibrils**Yan Zhang<sup>1</sup>, Michael Crowley<sup>2</sup>, Jacob Hinkle<sup>3</sup>, Charudatta Phatak<sup>1</sup>, and Lee Makowski<sup>4,5</sup><sup>1</sup> Material Science Division, Argonne National Laboratory, Argonne, IL 60439<sup>2</sup> Biosciences Center, National Renewable Energy Laboratory, Golden, CO 80401<sup>3</sup> Computational Science Center, National Renewable Energy Laboratory, Golden, CO 80401<sup>4</sup> Department of Bioengineering, Northeastern University, Boston, MA 02115<sup>5</sup> Department of Chemistry and Chemical Biology, Northeastern University, Boston, MA 02115

X-ray scattering at the APS is an important tool for observing molecular processes during the deconstruction of cellulose microfibrils due to chemical pretreatment. Nevertheless, application of this tool to biomass degradation is challenging because the heterogeneous nature of the fibrils undergoing deconstruction results in scattering patterns that are difficult to interpret in terms of the molecular processes involved. Here, we apply machine learning approaches on simulated and experimental x-ray scattering intensities to characterize the ensemble of microfibril structures in native and treated samples of cellulose. A set of atomic coordinates for cellulose fibrils of different cross-sectional shapes, size and twist are generated by molecular dynamics using Charmm. Pair-distance distributions of these structures are calculated and scattering intensities are simulated using the Debye formula in cylindrical coordinates. The simulated intensities (organized into a dictionary) are used to fit the experimentally collected intensities (measurements) by determining the relative abundances of the conformations in the dictionary by regression. Principal component analysis as well as spectral clustering analysis demonstrated the redundancy of the dictionary of cellulose structures. Hierarchical support vector machines and neural network methods are applied for cellulose shape classification. A codebook mapping the pair-distance distribution and scattering intensities is trained and generated as the inverse Fourier Transform operator for scattering intensities. The pair-distance distribution function can be calculated fast and accurately by the multiplication of codebook and measured intensity. These methods provide the means to track alterations in the structural ensemble of cellulose fibrils in biomass undergoing chemical deconstruction processes.

**Chemistry**

## A-4

**Cucurbit[6] Binding of Local Anesthetics**

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Pharmacokinetic modeling of bupivacaine partitioning into lipid emulsion reveals for each doubling of the affinity constant ( $K_a$ ), the cardiac blood level falls by half [1]. A 100 fold increase in the  $K_a$  from  $10^3/M$  to  $10^5/M$  would significantly reduce cardiac toxicity. Lipid emulsion acts as solvent with a  $K_a=1500/M$  [2]. True binding agents, sugammadex or calabadiol have  $K_a$ 's of  $10^7/M$  for rocuronium [3].

**Methods:** The macrocycle cucurbit[6]uril was studied using isothermal titration calorimetry to determine its affinity to chirocaine, ropivacaine, and tetracaine. Solutions of bupivacaine with cucurbit[6]uril in hydrochloric acid were prepared, crystals grown by evaporation, harvested into oil in nylon loops, and flash cooled in liquid nitrogen. X-ray diffraction data were measured at the Life Sciences Collaborative Access Team (LS-CAT) beamline 21-ID-D at the Advanced Photon Source at Argonne National Laboratory. Data were measured at a wavelength of 0.708473 Å, and are consistent with the hexagonal morphology of the crystals, with unit cell dimensions of  $a=b=25.172$  Å  $c=20.582$  Å,  $\gamma=120^\circ$ . Data are complete to 0.83 Å resolution and structure determination is ongoing.

**Results:** Cucurbit[6]uril forms very tight complexes with bupivacaine and its enantiomorph chirocaine.

**Discussion:** Cucurbit[6]uril is very selective in its binding of local anesthetics. It may be a useful addition to lipid emulsion for treating bupivacaine induced local anesthetic systemic toxicity (LAST) [4].

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## A-5

### Experimental and Computational Studies of Interfacial Water and Ion Adsorption Structures at Solid-water Interfaces

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Electrochemical energy storage is initiated by the formation of an electrochemical double layer at the electrode-electrolyte interface. A complete understanding of the atomic-scale structure of this layer can help to further develop the energy storage capabilities of many devices including batteries and supercapacitors. While the Gouy-Chapman model predicts a diffuse double layer of ions adsorbed at an electrochemical interface, this structure has not been directly confirmed by experimental observation. Here, we present preliminary *in situ* electrochemical studies of monovalent  $\text{Rb}^+$  and divalent  $\text{Sr}^{2+}$  ion adsorption at the graphene-water interface using low-angle x-ray reflectivity and resonant anomalous x-ray reflectivity. These techniques allow us to measure element-specific Angstrom-scale changes in the interfacial structure [1] as ions adsorb/desorb as a function of applied potential and concentration. This preliminary work demonstrates the feasibility of these techniques to study the formation of the diffuse ion profile and paves the way for in depth exploration of ion charge and size effects on the formation of and storage capacity of the electrochemical double layer.

Additionally, we compare recent density functional theory (DFT) calculations of the  $\text{Al}_2\text{O}_3$ -water interface with x-ray reflectivity studies of the same system to assess the ability of DFT to accurately describe interfacial relaxation in complex environments. Future work will expand DFT and molecular dynamics to calculations of ion adsorption in aqueous solutions at interfaces, such as the graphene-water interface described above.

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## A-6

### Remediation of Pertechnetate ( $\text{TcO}_4^-$ ), Iodide ( $\text{I}^-$ ) and Iodate ( $\text{IO}_3^-$ ) from Groundwater by Organoclays and Granular Activated Carbon: Capacity and Binding Mechanisms

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<sup>99</sup>Tc and <sup>129</sup>I are major long-life fission products during nuclear power generation. Over the years, Tc and I have been inadvertently introduced into the environment from leaks at waste storage facilities and currently are key risk drivers at the US DOE sites. The most common chemical form of Tc and I in liquid nuclear wastes and in the environment is anionic pertechnetate ( $\text{TcO}_4^-$ ) or iodide ( $\text{I}^-$ ), iodate ( $\text{IO}_3^-$ ) and organo-I. They display limited adsorption onto common sediment minerals and are highly mobile making them difficult to capture or to be immobilized. As the stockpile of <sup>99</sup>Tc- and <sup>129</sup>I-bearing nuclear waste continues to increase rapidly, novel sequestration technologies are needed to reduce its potential contamination of the environmental and living organisms.

In this work, inexpensive organoclays and granular activated carbon (GAC) were evaluated for remediation of  $\text{TcO}_4^-$ ,  $\text{I}^-$  and  $\text{IO}_3^-$  from groundwater using batch experimental set-up under atmospheric conditions. For  $\text{TcO}_4^-$ , the adsorption coefficient ( $K_d$ ) values for the organoclays and GAC samples were greater than  $1 \times 10^5$  mL/g, with nearly 100% adsorption. Their adsorption kinetics was fast, completing within 1 hour. The adsorption capacities were >3.2 mg/g over a wide groundwater pH range and under oxic conditions. For  $\text{I}^-$  and  $\text{IO}_3^-$ , the adsorption capacities onto the organoclays and GAC in groundwater under oxic condition were high as well: 30 mg/g for  $\text{I}^-$ , and >100 mg/g for  $\text{IO}_3^-$ .

Further, Tc K-edge XANES and EXAFS spectra of the organoclays and GAC after Tc adsorption were collected using the beamline 20-BM at the Advanced Photon Source (APS) in order to understand Tc speciation and binding chemistry. Both Tc K-edge XANES and EXAFS spectra indicated that the Tc species bound onto these sorbents is  $\text{TcO}_4^-$ , rather than its reduced  $\text{Tc(IV)}$ .  $\text{TcO}_4^-$  is likely bonding with N ligands present in functionalized organic molecules of organoclays or other surface moieties present on GAC. The innovation of this technology is that inexpensive organoclays and GAC can sequester Tc contaminant in the form that it exists naturally in the environment, and we do

not need to first create an artificial reducing environment. These results provide an applied solution for treating  $\text{TCO}_4^-$ ,  $\text{I}^-$  and  $\text{IO}_3^-$  contamination in the environment or in nuclear wastes.

### A-7

#### Advanced Hybrid Battery with a Magnesium Metal Anode and a Spinel $\text{LiMn}_2\text{O}_4$ Cathode

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Two Mg–Li dual salt hybrid electrolytes are developed, which exhibit excellent oxidative stability up to around 3.8 V (vs.  $\text{Mg}/\text{Mg}^{2+}$ ) on an aluminum current collector, enabling the successful coupling of several state-of-the-art lithium-ion intercalation cathodes ( $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoO}_2$  and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ) with magnesium metal anodes. The Mg– $\text{LiMn}_2\text{O}_4$  battery delivers an initial discharge capacity of about 106 mA h  $\text{g}^{-1}$  with a working voltage of around 2.8 V (vs.  $\text{Mg}/\text{Mg}^{2+}$ ), highlighting the highest working voltage of rechargeable batteries with magnesium metal anodes to date.

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### A-8

#### Solvent Effects on the Photoinduced Spin Crossover Process in Fe (II) Complexes

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Understanding the light-induced processes on the molecular level is of fundamental and practical importance for engineering innovative light-driven operating principles for digital processing and communications [1]. As prototypes of synergistically bistable molecular systems, the large family of  $3d^4$ – $3d^7$  transition-metal complexes has attracted much attention due to their spin crossover (SCO) behavior, in which the electronic state of octahedro-coordinated Fe center can be switched from a low-spin (LS) to a high-spin (HS) by light irradiation [2]. The produced metastable HS excited state is hence accompanying with a striking bond-elongation between the Fe center and its first coordinate shell [2–4].

By combing ultrafast optical and x-ray transient absorption spectroscopies, we have investigated the electronic and structural dynamics of the prototypical SCO complex  $[\text{Fe}(\text{mbpy})_3]^{2+}$  ( $\text{mbpy}$ =4,4'-dimethyl-2,2'-bipyridine) dissolved in two simple solvents: water ( $\text{H}_2\text{O}$ ) and acetonitrile ( $\text{CH}_3\text{CN}$ ), respectively. Our findings clearly reveal for the first time the microscopic origin of the solvent effects on the SCO complexes.  $[\text{Fe}(\text{mbpy})_3]^{2+}$  in  $\text{H}_2\text{O}$  exhibits a depopulation of MLCT excited states to the lowest high spin (HS) excited state slower by  $\sim 100$  fs than in  $\text{CH}_3\text{CN}$ . The average ground state Fe–N bond lengths of  $[\text{Fe}(\text{mbpy})_3]^{2+}$  in  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CN}$  are nearly identical, namely  $1.980 \pm 0.002$  Å.

However, the excited state Fe–N bond expansion of  $[\text{Fe}(\text{mbpy})_3]^{2+}$  in two solvents are obviously different and it is  $0.181 \pm 0.002$  Å in  $\text{H}_2\text{O}$ , which is  $\sim 10\%$  less than in acetonitrile ( $0.199 \pm 0.002$  Å). The decay of the HS excited state to LS ground state of aqueous  $[\text{Fe}(\text{mbpy})_3]^{2+}$  was measured to  $\sim 865$  ps, while it is much shorter than that ( $\sim 1295$  ps) in  $\text{CH}_3\text{CN}$ . These observations are attributed to the easier accessibility of smaller  $\text{H}_2\text{O}$  molecule to the intra-ligand grooves of  $[\text{Fe}(\text{mbpy})_3]^{2+}$ , giving a stronger ligand field around the Fe center. Our results prove that the solvent effects could play an important role in the SCO process compared to the complex own structure, and they should provide further insight into the specific solute-solvent interactions occurring in solvated SCO complexes systems.

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### A-9

#### Nickel-surface-doped $(x)\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCoO}_2$ Cathode Particles for Investigating the Effects of High-voltage Surface Protection

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Increasing the energy and power density of lithium-ion batteries is highly desirable for transportation applications, including electric vehicles with extended driving ranges



and lower production costs. Increasing the upper cutoff voltage of commercially available lithium-ion cathode materials such as  $\text{Li}_{1.0}\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  (NMC-622) from 4.3 V to 4.6 V (vs. Li) increases the initial observed cathode capacity by 15–20%. However, most of this excess capacity is lost over just 50 cycles. XAS studies of these materials show minimal differences between the transition-metal local structures of pristine and cycled cathodes, indicating that bulk instability of the delithiated cathode is not the root cause of the observed capacity fade. Instead, this capacity fade is attributable to changes at the cathode surface and/or cathode/electrolyte interphase brought on by oxygen loss and/or electrochemical reactions with the carbonate-based electrolyte.

In order to observe surface-localized changes to the cathode local structure, a nickel-free composite cathode material ( $(x)\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCoO}_2$ ) was coated with a  $\text{LiNiPO}_4$  sol-gel. Subsequent annealing selectively substitutes  $\text{Ni}^{2+}$  into  $\text{Li}^+$ -containing transition-metal-layer sites of the  $\text{Li}_2\text{MnO}_3$  minority component near the surface of the cathode particle, creating a nickel-doped surface layer. Because of the lack of nickel in the core structure and the element specificity of XAS, changes to the local structures of the surface nickel sites can be monitored *in operando*. The nickel-doped surface serves as a model system for investigating the abilities of novel electrolyte additives, fluorinated electrolytes, and subsequent cathode coatings to protect the cathode surface from structural degeneration and resultant capacity fade.

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## A-10 Structural Characterization of Framework-guest Interactions in Metal-organic Frameworks

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Powder x-ray diffraction studies provide valuable insight into the observed behavior of metal-organic frameworks, a promising class of porous, chemically tunable materials. In collaboration with Beamlines 17-BM-B and 11-BM at the Advanced Photon Source, we have employed powder x-ray diffraction to study promising metal-organic frameworks for methane and hydrogen storage [1,2,3,4], carbon dioxide capture [5], and catalysis, allowing for correlation of framework structure with function. Structural characterization of  $\text{Co}_2(m\text{-dobdc})$  ( $m\text{-dobdc}^{4-} = 4,6\text{-dioxido-1,3-benzenedicarboxylate}$ ) [3] and  $\text{Mn}_2(\text{dsbdc})$  ( $\text{dsbdc}^{4-} = 2,5\text{-disulfido-1,4-benzenedicarboxylate}$ ) [4] were critical in identifying these frameworks as promising materials for hydrogen storage. Furthermore, *in situ* studies have proven essential for understanding methane adsorption in  $\text{Co}(\text{bdp})$  ( $\text{bdp}^{2-} = 1,4\text{-benzenedipyrzole}$ ) [1],  $\text{Fe}(\text{bdp})$  [1], and  $\text{Co}(\text{bdp})$  derivatives [2]; and carbon dioxide adsorption in  $\text{mmen-Mn}_2(\text{dobpdc})$  ( $\text{mmen} = \text{N,N'-dimethylethylenediamine}$ ,  $\text{dobpdc}^{4-} = 4,4'\text{-dioxidobiphenyl-3,3'-dicarboxylate}$ ) [5].

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**A-11****Rheo-SAXS to Determine 3D Printing Design Rules for Polymer/Clay Composite Inks**Brittany Rauzan<sup>1</sup>, Sean Lehman<sup>1</sup>, Joselle McCracken<sup>1</sup>, Simon Rogers<sup>2</sup>, and Ralph Nuzzo<sup>1</sup><sup>1</sup> Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801<sup>2</sup> Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801

Polymer/clay composite inks are at the core of 3D printing due to the ability to incorporate stimuli-responsive components that allow for flexible structures that respond in unprecedented ways to external stimuli. Before these structures can be printed, the polymer/clay composites require a thorough understanding of their physicochemical interactions that become exceedingly complex due to the conditions (applied high pressure) during printing. A model system, N-isopropylacrylamide/Laponite with a rheological modifier, sodium pyrophosphate, is studied to understand electrostatic interactions in polymer/clay inks. Rheo-SAXS is used to probe the nano/micro-structure of Laponite to understand flow and printing behavior of inks. Sodium pyrophosphate allows for modification to electrostatic interactions between platelets providing a mechanism to reduce platelet jamming during extrusion, which is not possible in Laponite only ink. 3D printing design rules are established based on electrostatic interactions to harness the innate microstructure of Laponite to develop Laponite inks.

**A-12****Heavy Metal Adsorption at Charged Interfaces: X-ray Scattering and Fluorescence Studies**William Rock<sup>1</sup>, Baofu Qiao<sup>1</sup>, Wei Bu<sup>2</sup>, Binhua Lin<sup>2</sup>, and Ahmet Uysal<sup>1</sup><sup>1</sup> Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439<sup>2</sup> Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637

Solvent extraction—the surfactant-aided preferential transfer of a species from an aqueous to an organic phase—is an important technique used in heavy and precious metal refining and reprocessing [1]. Solvent extraction requires transfer through an oil/water interface, and interfacial interactions are expected to control transfer kinetics and phase stability, yet these key interactions are poorly understood [2]. Langmuir monolayers with charged headgroups atop concentrated salt solutions containing heavy metal ions act as a model of solvent extraction interfaces; studies of ions at a charged surface are also fundamentally important to many other phenomena including protein solvation, mineral surface chemistry, and

electrochemistry. We probe these charged interfaces using a variety of surface-sensitive techniques—x-ray reflectivity (XRR), x-ray fluorescence near total reflection (XFNTR), grazing incidence diffraction (GID), and vibrational sum frequency generation (VSFG) spectroscopy. We integrate experiments with Molecular Dynamics (MD) simulations to uncover the molecular-level interfacial structure.

*This work is supported by the U.S. DOE, BES, contract DE-AC02-06CH11357. The use of the Advanced Photon Source is also supported by U.S. DOE, BES. ChemMatCARS Sector 15 is supported by the National Science Foundation under grant number NSF/CHE-1346572.*

[1] P. Tasker et al. (2003). *Comp. Coord. Chem. II*, 759.[2] W. Rock et al. (2016). *Langmuir* **32**(44): 11532.**A-13****In situ XAS Study of Ru-based Water Oxidation Catalysts Incorporated in Metal-organic Framework**Yuliana Pineda-Galván<sup>1</sup>, Shaoyang Lin<sup>2</sup>, Amanda Morris<sup>2</sup>, and Yulia Pushkar<sup>1</sup><sup>1</sup> Department of Physics, Purdue University, West Lafayette, IN 47907<sup>2</sup> Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

Green plants convert sunlight into chemical energy in the process of photosynthesis, which involves water splitting ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$ ) as a key step. Mimicking this reaction in a manmade device would enable widespread usage of solar energy; however, water splitting needs an efficient and robust catalyst. Ruthenium-based water oxidation catalysts (WOC) are relatively stable and most studied to date systems. The first Ru WOC was “blue dimer”, reported in 1982. Almost two decades later, it was shown that single-site Ru complexes are also capable of water oxidation. Most studies were performed on homogeneous catalysts in solution. Incorporation of such catalysts into photo-electro-chemical assemblies will allow for photo-induced water splitting and will decrease risk of bi-molecular reactions which lead to catalyst degradation.

Incorporating molecular catalyst into metal-organic framework (MOF) could help to achieve these objective. MOFs are porous, highly ordered and tunable structures. In this work,  $[\text{Ru}(\text{dcbpy})(\text{tpy})\text{OH}_2]^{2+}$  incorporated into UiO-67 MOF (“Ru-MOF”) and its homogeneous analog,  $[\text{Ru}(\text{bpy})(\text{tpy})\text{OH}_2]^{2+}$  were studied at water oxidation conditions using x-ray absorption spectroscopy at Ru K-edge. Water oxidation was performed at acidic conditions using both electrochemical oxidation (at 1.8V vs. NHE) and sacrificial oxidant ( $\text{Ce}^{\text{IV}}$ ).

EXAFS analysis of both complexes showed that the structure of catalytic complex does not change much after incorporation into MOF. Ru-MOF catalyst deposited onto conducting electrode was stable during water electrolysis.

XANES spectroscopy indicates that Ru centers are oxidized up to Ru<sup>III</sup> oxidation state [1]. Further studies of Ru-MOF catalysts prepared at different conditions revealed dependence of Ru oxidation state on the size of MOF particles. Smaller particles have more oxidized Ru<sup>III</sup> centers. However, the loading of MOF with Ru has no effect on the oxidation state of Ru.

Unlike Ru-MOF catalyst, molecular [Ru(bpy)(tpy)OH<sub>2</sub>]<sup>2+</sup> was fully oxidized to Ru<sup>IV</sup> oxidation state after electrolysis at 1.8V. EXAFS spectra indicated the presence of species with 1.8Å Ru-O distance, which is consistent with Ru<sup>IV</sup>=O. These findings are in agreement with previous studies of [Ru(bpy)(tpy)OH<sub>2</sub>]<sup>2+</sup> under catalytic conditions using Ce<sup>IV</sup> as oxidant [2].

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- [2] Pushkar, Y., Moonshiram, D., Purohit, V., Yan, L., and Alperovich, I. (2014). *Journal of the American Chemical Society* **136**(34): 11938–11945.

## Condensed Matter Physics

### A-14

#### High-resolution Coherent X-ray Surface Scattering Imaging

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It was demonstrated the feasibility of the Coherent Surface Scattering Imaging (CSSI) in grazing-incidence geometry with a limited success, due to a low coherent flux and short sample-to-detector distance [1,2]. Recently, with high coherent flux at PETRA-III we proved that CSSI yields surface structure reconstruction with 5 nm reconstruction in plane in the transverse direction, with even a single scattering pattern. Compared to the results from the original APS results, the data efficiency is improved by 5 orders of magnitude while a factor of 4 better in plane resolution is achieved. This particular x-ray source was utilized as it retained the required coherent x-ray flux that is congruent to the x-ray source that the Advanced Photon Source will be endowed with once the upgrade is finalized. This result showed the defining impact of coherent flux and proper x-ray optics/detector combination on CSSI.

- [1] Sun, T. et al. (2012). "Three-dimensional coherent x-ray surface scattering imaging near total external reflection," *Nat. Photonics* **6**: 586.
- [2] Miao, J. et al. (2015). "Beyond crystallography: Diffractive imaging using coherent x-ray light source," *Science* **348**: 530–535.

### A-15

#### Microscopic Stress Relaxation of Shear-thickened Colloidal Suspensions Observed by Heterodyne XPCS

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When concentrated colloidal suspensions are sheared beyond critical shear stress, they show shear thickening behavior, where their macroscopic viscosity abruptly increases. When suspensions enter into this shear-thickened state, the particles form strong force network, similar to jamming, which leads to the suspensions no more follow shear profile and also often slip on the shear cells. It makes hard to study stress relaxation of shear thickening macroscopically. Here, by employing x-ray photon correlation spectroscopy (XPCS), we have studied the stress relaxation of a shear-thickened suspension of 340 nm silica suspension with volume fraction of 61% in microscopic perspective. The suspension was loaded in Couette cell, where a cup and a bob are coaxially aligned, and the suspension is loaded in the gap between them. It was first sheared to the shear thickened state, and then shear stopped, after which XPCS was measured over 1,000 seconds. In the shear thickening regime, the suspension was separated into a flowing and a shear-thickened regions. Even after shear stopped, the shear thickened volume still remained jammed, which leads to the difference in velocities of these two different volumes. XPCS could measure their relative velocities. It was observed that the shear-thickened particles are flowing downward during relaxation, which indicates they were initially dilated during shear. The volume fraction of shear thickened volume remained almost constant at near 90% over 1,000 seconds.

**A-16****Coexistence of Superconductivity and Magnetism in  $\text{Ca}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$ : Universal Suppression of the Magnetic Order Parameter in 122 Iron-based Superconductors**

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We examined  $\text{Ca}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$  single crystals with  $x=0.00, 0.35, 0.50$  and  $0.67$  by means of muon spin relaxation and Mössbauer spectroscopy to investigate the electronic and structural properties of these compounds.  $\text{CaFe}_2\text{As}_2$  is a semi metal, which shows antiferromagnetic spin density wave (SDW) order below 167 K [1]. By hole doping via Ca->Na substitution, the magnetic order is suppressed and superconductivity (SC) emerges including a substitution level region, where both phases coexist. We studied the order parameter interaction in this coexistence region and found nanoscopic coexistence of both order parameters. This is proven by a reduction of the magnetic order parameter of 7% below the superconducting transition temperature [2].

We present a systematic correlation between the magnetic order parameter reduction and the ratio of the transition temperatures,  $T_C/T_N$ , for the 122 family of the iron based superconductors [2].

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[2] P. Materne et al. (2015). *PRB* **92**: 134511.

**A-17****Magnetoelectric Coupling in Mixed Multiferroic State of  $\text{Eu}_{1-x}\text{Y}_x\text{MnO}_3$** 

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In the orthorhombic multiferroic systems, the role of the rare-earth elements for appearance of ferroelectric order is still being debated. Whereas  $\text{TbMnO}_3$  is ferroelectric below  $T_C=30$  K, in  $\text{GdMnO}_3$  ferroelectricity appears in a very small temperature range and is established in a wider

temperature range only by an applied external magnetic field. Investigation of the Gd magnetic order using resonant elastic x-ray scattering (REXS) brings this in direct relationship to the order of Gd moments, which is extended by application of magnetic field [1].

Deeper insight into the role of the rare earth is expected from the investigation of  $\text{Eu}_{1-x}\text{Y}_x\text{MnO}_3$ , where  $\text{Eu}^{3+}$  ( $4f^6$ ) and  $\text{Y}^{3+}$  ( $4f^0$ ) ions both are in principle non-magnetic [2,3]. A comparison of the magnetic order of the  $x=0.2$  and  $0.3$  samples show different ordering behavior below the ferroelectric transition temperature  $T_C=30$  K [3]. In the  $x=0.2$  compound, the magnetic structure shows weak ferromagnetism, attributed to a cone-like structure that breaks inversion symmetry and gives rise to ferroelectricity with the polarization along the a-axis. High magnetic field measurements reveal a stabilization of an intermediate canted spin structure, which is also responsible for an increase in spontaneous polarization. Recent high pressure studies on the  $x=0.2$  compound performed at 4-ID-D, APS, show a change in ordering behavior similar pointing towards a stabilization of the cycloidal phase for increasing pressure.

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[2] J. Hemberger et al. (2007). *Phys. Rev. B* **75**: 035118.

[3] A. Skaugen et al. (2015). *Phys. Rev. B* **91**: 180409.

**A-18****In situ XMCD Study of Voltage Controlled Interlayer Coupling in Perpendicularly Magnetized Magnetic Tunnel Junctions**

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Magnetic interlayer coupling, the parallel or antiparallel alignment of ferromagnetic layers in proximity to each other in the absence of external magnetic fields, has been of great interest because it offers a promising way of low energy magnetization switching by electric fields. To clarify the mechanism for the voltage controlled interlayer coupling (VCIC) observed in a perpendicular magnetic tunnel junction (pMTJ) with the structure of Si/SiO<sub>2</sub>/Ta(8 nm)/Ru(10 nm)/Ta(7 nm)/Co<sub>20</sub>Fe<sub>60</sub>B<sub>20</sub> (0.85 nm)/

GdO<sub>x</sub> (3.3 nm)/Co<sub>20</sub>Fe<sub>60</sub>B<sub>20</sub> (1.6 nm)/Ta(7 nm)/Ru(20 nm) [1], we performed an *in situ* experiment where the tunneling magnetoresistance (TMR) and x-ray magnetic circular dichroism (XMCD) were measured simultaneously at beam line 4-ID-C of the Advanced Photon Source. Clear XMCD spectra for the Fe and Co L<sub>2,3</sub> edges were observed at photon energies of 700–730 eV and 770–810 eV, respectively. Surprisingly, a clear XMCD signal was observed at the Gd M<sub>5</sub> edge under zero magnetic field with an average magnetic moment of 0.6μ<sub>B</sub> per Gd, indicating the existence of ferromagnetic order in the GdO<sub>x</sub>. Furthermore, the XMCD hysteresis loops measured at the Gd M<sub>5</sub> edge and Fe L<sub>3</sub> edge showed two distinct transitions at magnetic fields corresponding to the coercivities of the top and bottom CoFeB layers revealed by the TMR measurements. The Gd hysteresis loops also generally resembled the shape of the Fe loops but with the opposite signs, suggesting that the coupling between the Gd ions and the CoFeB is antiferromagnetic and that the moment of Gd ions is induced by the proximity effect from Fe. These results from the simultaneous XMCD and TMR measurements directly confirmed our hypothesis of voltage driven oxidation/reduction in the GdO<sub>x</sub>-pMTJs and the proximity-induced moment of the Gd ions by CoFeB. Our results may lead to a new class of spintronic devices where magnetization switching can be accomplished by voltage controlled interlayer coupling.

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## Environmental Science and Geology

### A-19

#### Mineralogical Characterization, Geochemical Behavior and XFA Study of Rare Earth Elements in Carbonatites

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The leaching potential of the rare earth elements (REE) from carbonatite deposit, a light REE (LREE) mine project

of GéoMéga resources, was investigated using kinetic test (i.e., humidity and weathering cells) in order to predict their geochemical behavior in laboratory conditions. All materials (three lithologies and two ores) were sampled, characterized using different mineralogical techniques (i.e., SEM-EDS, QEMSCAN, XRD, XPS). XAFS is used to study the chemical states and structural environment of REE in all post-dismantlement samples.

In order to understand the effect of iron oxy-hydroxides (goethite and magnetite), phosphates, and carbonates on the mobility of the REE, five mixtures (mixing REE carbonates with the synthesized phases in different proportions) were formulated and subjected to kinetic testing (i.e., mini-alteration cells). The addition of pyrite could accelerate the dissolution of carbonates which could result in a significant release of REE.

Geochemical results showed that the REE contained within various lithologies of the Montviel deposit were leached at very low concentrations (less than 2μg/l) during kinetic testing; thermodynamic simulations also suggest that many REE-bearing secondary minerals might precipitate during weathering.

XAFS results show an important affinity of the REE with phosphates, carbonates, and iron oxides. REE edges show some remaining REE<sup>3+</sup> in secondary minerals which precipitate during kinetic tests such as phosphates and iron oxides. XAFS signal is similar in all samples.

### A-20

#### Microscale Characterization of Mineral Phases and Trace Metals in Coal-mine AMD Precipitates

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A key challenge to designing acid mine drainage (AMD) treatment systems is the need to understand the dynamic evolution of precipitates and the sequestration mechanisms of metals in these precipitates. The passive treatment systems designed to treat AMD usually include modules that promote sequestration of pollutants in neoformed nano- and micro-scale particles (nNP) through precipitation, co-precipitation, and sorption. These nNP, that commonly are Fe-rich phases such as schwertmannite and goethite, can undergo subsequent biogeochemical redox transformations which strongly affect nNP stability and the fate of AMD contaminants associated with them. In the case of coal-mine AMD, detrital nano- and micro-scale

particles (dNP), dominated by clay minerals, are also present as a significant fraction of AMD contaminant load. During interaction with AMD, these dNP can undergo chemical and structural modifications as well as promote crystallization and/or dissolution of nNP [1]. However, the impact of such processes on the fate of AMD contaminants is largely unknown.

In this study, we conducted synchrotron x-ray microanalysis on sediment samples collected at Tab-Simco, an abandoned coal-mine site in Illinois, recognized as one of the highest contaminated sites in the U.S. We simultaneously collected micro-fluorescence ( $\mu$ XRF) elemental and micro-diffraction ( $\mu$ XRD) measurements to decipher the mineralogical residency, distribution, and mobility of contaminants in the AMD sediments [2]. The  $\mu$ XRF elemental maps allowed large areas of AMD sediments to be studied and provided insight into the complex spatial distribution of key chemical elements. Fe was used as proxy for nNP while Ga served as a proxy for Al and clay-dNP since  $\text{Ga}^{3+}$  is incorporated into nonexchangeable framework positions in the phyllosilicate sheets.

Our preliminary results show that segregated areas dominated by Fe-nNP and clay-dNP developed within the AMD sediments. Unexpectedly, contrasting behavior of metals was mapped in the two types of samples. The Fe-rich samples displayed XRD patterns of goethite and jarosite while the XRF spectra were dominated by Fe K with additional peaks for Zn, Cu, and As. The concentration of trace metals was very small. In contrast, the XRD patterns in the clay-rich samples were dominated by quartz with clays also present. These samples had significantly higher concentration of metals and abundant metal-rich hot spots for V, Ni, Cr, Cu, Zn, Pb, and As. These hot spots yield XRF spectra dominated by Fe K with additional peaks from K, Ca, Ti, V, Cr, Ni, Cu, Zn, Ga, Pb, As, Rb, and Sr. These results are interpreted to indicate that, contrary to previous reports, the trace elements are primarily incorporated in detrital clays that coat quartz grains. Overall, this study shows that accurate prediction for the capacity of the AMD sediments to stabilize toxic metals is necessary when designing strategies for effective AMD remediation systems.

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[2] Sutton, S.R., et al. (2017). *Journal of Environmental Quality*, doi:10.2134/jeq2016.10.0401 (2017).

## High Pressure

### A-21

#### Studies of Phase Transitions in $\text{EuFe}_2\text{As}_2$ by $^{57}\text{Fe}$ and $^{151}\text{Eu}$ Nuclear Resonant Scattering under High Pressure

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Nuclear resonant scattering (NRS) is a powerful technique based on Mössbauer active isotopes using synchrotron radiation as an excitation source. NRS includes two techniques—synchrotron Mössbauer spectroscopy (SMS) and nuclear resonant inelastic x-ray scattering (NRIXS). NRS provides valuable information about valence, spin, magnetism and phonon density of states on the microscopic scale. With the discovery of superconductivity in Fe-pnictides, it has been applied to studies of magnetism and lattice dynamics in these systems. Among the many families of Fe-pnictides,  $\text{EuFe}_2\text{As}_2$  shows complex and intriguing phase diagram under moderate pressure (<10 GPa), including magnetism from both Eu and Fe sublattices, valence transition from Eu and structural transitions induced by low temperature and high pressure. NRS studies on magnetism, valence and phonon density states on a single crystal  $\text{EuFe}_2\text{As}_2$  sample by both  $^{57}\text{Fe}$  and  $^{151}\text{Eu}$  isotopes have been performed and results on magnetism, valence, and phonon density of states will be presented to give insight to the nature of the complex phase transitions under hydrostatic pressure.

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### A-22

#### Pressure-induced Reversible Polymorphism of $\text{CaSiO}_3$ Wollastonite

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$\text{CaSiO}_3$  is believed to be one of the most important chemical compounds in the Earth's lower mantle, with the Ca-silicate perovskite (Ca-Pv) phase, featuring octahedrally coordinated silicon, accounting for almost 10% of the mantle rocks by volume below the transition zone depth.

At lower pressures and shallower depths, other, less dense wollastonite pyroxenoid polymorphs with  $\text{CaSiO}_3$  composition, characterized by tetrahedrally coordinated silicon are more thermodynamically stable. Knowledge about transformation mechanisms leading from the low density polymorphs to Ca-Pv, including any possible intermediate structures, would significantly improve our understanding of the silicate densification process, one of the critical factors in controlling mantle convection. Unfortunately, low symmetry of the wollastonite phases, particularly the thermodynamically stable wollastonite-1A polymorph, has crystallographic studies very challenging.

In the current project we examined the behavior of two different polytypes of low-density  $\text{CaSiO}_3$  wollastonite: monoclinic parawollastonite-2M, and triclinic wollastonite-1A, on hydrostatic compression at ambient temperature to maximum pressure of 35 GPa, using synchrotron single-crystal x-ray diffraction. The experiments were conducted at APS experimental station 13IDD. Wollastonite-1A was found to undergo a series of two displacive phase transitions that take place at approximately 9 and 24 GPa and are accompanied by discontinuous increases in density. Crystal structures of the two new triclinic high-pressure polymorphs have been solved from *in situ* single crystal data. The highest pressure phase shows a change in coordination number of silicon from  $^{\text{IV}}\text{Si}$  to a mixture of  $^{\text{IV}}\text{Si}$  and  $^{\text{V}}\text{Si}$ . Wollastonite-2M undergoes a single displacive phase transition at about 25 GPa, which changes the symmetry to triclinic. The structural relationships of all these polymorphs will be discussed and their relevance for cold subduction zone environments will be reviewed.

*The project was supported by the NSF Division of Earth Sciences Geophysics grant 1344942. Development of the ATREX software, used for experimental data analysis was supported by NSF EAR Geoinformatics grant 1440005. Portions of the x-ray diffraction work were conducted using x-ray Atlas instrument at the University of Hawaii, funded by NSF EAR Instrumentation and Facilities grant 1541516. Portions of this work were performed at GeoSoilEnviroCARS (Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation—Earth Sciences (EAR-1128799) and Department of Energy—Geosciences (DE-FG02-94ER14466). Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.*

## A-23

### Python Software Development at GSECARS

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Since the development of high-brilliance synchrotron sources, along with fast and efficient detectors, one of the bottlenecks of efficient usage of beamtime has been

the software used, not only for beamline control, but also for preliminary on-the-fly data analysis, allowing users to quickly make informed decisions on how to proceed with their experiment. This is especially relevant for the typical users of the diamond anvil cell program at GSECARS, performing XRD measurements at high-pressure and high-temperature conditions, which requires simultaneous control of multiple parameters related to the sample position, laser power, pressure, temperature, and synchronization of diffraction and spectroscopic measurements. Therefore, we are making an effort to develop a new GUI based software suite, which aids the user in every aspect along the way. We have chosen Python as the development language so that the code is open source and running/modifying it requires no purchase of software.

We have developed a fully customizable automatic logging procedure, which monitors unlimited user selected EPICS events and registers any experimental information the user needs in a convenient interactive format. This allows the user to quickly go back and find the information about previous measurements, and is especially important when collecting data from a number of detectors in quick succession, which does not allow a person enough time to write down all the essential information. We have developed 2D mapping visualization procedure for the XRD reduction data software DIOPTAS [1], which allows the user to easily and conveniently compare multiple diffraction patterns of different locations on the sample overlaid with its image and connected to the sample stage. Another project we have begun is multi-step ramp heating which allows the user to predefine the laser-heating power as a function of time, and to automatically measure the diffraction pattern and the temperature in selected ranges, including visual snapshots.

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## A-24

### Unravelling the Polyamorphic Sequence of $\text{GeO}_2$ Glass at High Pressure

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Polyamorphism of the classic network-forming glasses such as  $\text{GeO}_2$  and  $\text{SiO}_2$  is of great interest because of industrial applications, Earth science implications [1] and significance

in glass theory [2]. These classic network-forming glasses have recently received renewed intensive investigations both in experimental and theoretical studies [3–7] due to the findings of new intermediate states [8–11]. High-pressure XAFS including the near edge (XANES) and extended (EXAFS) spectra offers critical information on the local and electronic structure of absorber atoms in the fields of materials science, chemistry and biophysics at high pressure or ambient environment [12–14]. We have recently developed a method for acquiring high quality x-ray absorption spectroscopy (XAFS) with long energy range at high pressure using diamond anvil cell (DAC) [11,15]. Using this method, the structural polyamorphs of  $\text{GeO}_2$  glass has been investigated up to 115 GPa, giving rise to five distinct sequent structural polyamorphs in  $\text{GeO}_2$  glass under high pressure. In this presentation, we will also show some recent developments of HP-XAFS in combination with HP-PDF studies.

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## A-25

### High-pressure $\gamma$ - $\text{CaMgSi}_2\text{O}_6$ : Is Penta-coordinated Silicon Common in the Earth Mantle?

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Earth's mantle and crust are dominated by silicates.  $\text{Si}^{4+}$  in Earth's crust and upper mantle minerals resides almost exclusively in 4-coordinated sites (e.g., quartz, pyroxene and olivine), whereas minerals with  $\text{Si}^{4+}$  in 6-coordinated sites dominate the transition zone and the lower mantle (e.g., stishovite, perovskite and akimotoite). Five-coordinated  $\text{Si}^{4+}$  is observed in silicate glasses and melts upon compression as intermediate states and can provide important insight into the transformation mechanisms involved in silica densification. Crystalline silicates with  $\text{Si}^{4+}$  in 5-coordinated sites, though rare, have been previously reported in  $\text{CaSi}_2\text{O}_5$  at ambient conditions, and  $\text{MgSiO}_3$  orthopyroxene at high pressure. Diopside, with formula of  $\text{CaMgSi}_2\text{O}_6$  is a Ca, Mg endmember of pyroxene and has a space group of C2/c in the upper mantle. Previous study reported a new  $\text{P2}_1/\text{c}$  phase of diopside ( $\beta$ -diopside) with a mixture of 4- and 6-coordinated silicon at  $\sim 50$  GPa by single-crystal x-ray diffraction. Here, we show results of a compression study of natural diopside with  $\sim 25\%$   $\text{Fe}^{2+}$ , which also undergoes the transformation to a  $\text{P2}_1/\text{c}$  phase, though the high pressure phase is found to exhibit two separate regions, differing by Si coordination. At pressures above 50 GPa, the  $\text{P2}_1/\text{c}$  phase features  $\text{Si}^{4+}$  in 5- and 6-coordinated sites ( $\gamma$ -diopside), whereas below 50 GPa, on decompression, the mineral transforms to  $\beta$ -diopside phase with  $\text{Si}^{4+}$  coordination changes to 4 and 6. This 5- and 6-coordinated phase is also predicted by density functional theory (DFT) by relaxing  $\beta$ -diopside. Enthalpy calculated by DFT shows that the  $\text{P2}_1/\text{c}$  phases are more stable than the C2/c diopside at high pressure.  $\gamma$ -Diopside is  $\sim 2.5\%$  and  $\sim 7\%$  lighter than akimotoite and bridgmanite. If metastable pyroxene be preserved to the transition zone as suggested by the recent experiments, it is possible that five-coordinated silicates exist in the Earth's mantle and provide negative buoyancy of the subducting slab.



**A-26****Ultra-high Temperature Studies of Materials in Mbar Pressure Range with Combined Pulse Laser Heating and X-ray Diffraction Techniques at GSECARS**

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Recent developments in continuous laser heating techniques, including application of fiber lasers and flat top laser beam shaping optics, result in significant improvement of the quality of x-ray data collected *in situ* at high pressure and temperature in the DAC [1]. Nevertheless, the maximal static temperatures in the laser heated DAC, suitable for reliable *in situ* high pressure synchrotron experiments, is limited. This is especially noticeable in the Mbar pressure range due to fundamentally thin pressure chamber (a few microns) and the lack of insulating layers between laser heated ultra-thin samples and highly thermal conductive diamond anvils. Standard continuous laser heating combined with x-ray diffraction at very high P-T conditions typically results in failure of the diamond anvils due to the relatively long exposure to very high laser powers of ~100W. This is especially true for thin samples containing hydrogen or helium, which can diffuse into the diamond, thus further weakening it. Using a microsecond pulsed laser-heating technique allows one to achieve a few times higher temperatures using less total laser power, due to the high laser power density of each pulse [2].

At GSECARS we have combined double-sided pulse laser-heating with our new CdTe Pilatus 1M detector (Dectris). A frequency-modulated laser beam with pulse widths of one microsecond was synchronized with the x-ray detector and temperature measuring spectrometer (PiMax detector, Princeton). Accumulation of 100k–500k pulses at a rate of 10 kHz (effective time of 10–50 ms) was required to record high quality XRD data with an x-ray energy of 37 keV from relatively low Z samples and sample thickness less than four microns. Application of this technique to study materials at ultra-high pressures and temperatures with an example of Fe<sub>3</sub>O<sub>4</sub> (170 GPa and 4000 K) will be discussed.

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**A-27****High Pressure Behavior of Liebenbergite, the Most Incompressible Olivine-structured Silicate**Dongzhou Zhang<sup>1,2</sup>, Yi Hu<sup>1</sup>, Jingui Xu<sup>1</sup>, Przemyslaw Dera<sup>1</sup>, and Robert Downs<sup>3</sup><sup>1</sup> HIGP, University of Hawaii at Manoa, Honolulu, HI 96822<sup>2</sup> GSECARS, University of Chicago, Argonne National Laboratory, Argonne, IL 60439<sup>3</sup> University of Arizona, Tucson, AZ 85721

Nickel is an abundant element in the bulk earth, and the nickel-endmember olivine, liebenbergite (Ni<sub>2</sub>SiO<sub>4</sub>), is a potential reservoir of nickel in the mantle. In this study, we used high pressure single crystal diffraction to explore the compressional behavior of synthetic liebenbergite sample up to 42.6 GPa at ambient temperature. Over the studied pressure range, the liebenbergite sample retains the orthorhombic *Pbnm* structure, and no phase transition is observed. 3<sup>rd</sup> order Birch-Murnaghan equation of state is used to fit the unit cell volume, lattice parameters, the polyhedral volume and the average bond length within each polyhedron. We find that liebenbergite is the most incompressible olivine-structured silicate that has been studied thus far, and Ni<sup>2+</sup> tends to increase the isothermal bulk modulus of both olivine- and spinel-structured silicates. The stability of liebenbergite at high pressures is likely to be related to the electronic configuration of the Ni<sup>2+</sup> cation. With the recently calibrated Ni equilibrium partitioning coefficient between olivine and melt at different P-T conditions, we calculate the Ni concentration in olivine at different depths using an exhumation model. We calculate the effect of Ni-doping in the density of olivine at the upper mantle conditions.

**Instrumentation****A-28****Approximating the Near K-edge Mass Absorption Coefficients of Ni Using an Ultra-thin Bi-metal Ti-Ni Foil**

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A method for determining the near K-edge mass absorption coefficients for Ni has been developed using an ultra-thin bi-metal Ti-Ni foil. This method uses NIST mass absorption coefficients with 1% uncertainty combined with absorption measurements at multiple energies to estimate the relative thickness of the ultra-thin Ni. Based on this thickness, mass absorption coefficients can be fit for Ni near K-edge energies by incorporating fixed Ti coefficient values from the NIST XCOM (Berger et al. 2010)

database together with absorption measurements at multiple energies. Once determined, these fit coefficients will be used to compute the thickness of a free-standing  $\sim 8\mu\text{m}$ -thick metal foil over the same range of measurement energies. The thickness error determined from the  $\sim 8\mu\text{m}$ -thick Ni foil will be used to assess the fitting error. Comparison of fit coefficients with those of independent investigators shows good agreement at the 1% error level.

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## A-29

### High Resolution Camera for Resonant Inelastic Soft X-ray Scattering Spectroscopy

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Resonant inelastic scattering spectroscopy (RIXS) in the soft x-ray regime is a powerful technique to probe the electronic structure of matter. The technique utilizes energy dispersive spectrometers to disperse a scattered x-ray beam from a sample in such a way as to translate each x-ray energy into a corresponding position on a detector active area. Thus, in these spectrometers energy resolution is dependent on the position resolution of the detectors used. To increase the energy resolution of a detector, either the distance between the dispersive element and the detector is increased or the detector pixel pitch in the energy dispersive axis is reduced.

Researchers at the Lawrence Berkeley National laboratory have demonstrated the technical feasibility of the Spectro CCD, a novel direct-detection, soft x-ray imaging camera with up to 3 times better position resolution than the current commercial offering. The Spectro CCD has been optimized for soft x-ray RIXS spectrometry by employing a  $5\mu\text{m} \times 45\mu\text{m}$  pixel geometry to increase resolution in the energy dispersive axis ( $5\mu\text{m}$  direction) and by utilizing a 10 nm back entrance window to achieve high quantum efficiencies in the soft x-ray regime. The camera performance has been characterized at the Advance Light Source (ALS) 8.0.1 RIXS beamline, with a  $\sim 280\text{ eV}$  ( $C_K$ ) x-ray beam on a graphite sample. The Spectro CCD point spread function for soft X-rays in the energy dispersive axis was measured to be  $4.5\mu\text{m}$ , with a readout noise of 3–6 electrons. The tests demonstrated that individual oxygen  $\sim 520\text{ eV}$  ( $O_K$ ) x-rays can be identified and located with a  $3.5\mu\text{m}$  precision. In addition, the quantum efficiency of the CCD was measured to be greater than 75% in the range from 200 eV to 1 keV. A general overview of the system and the test results will be presented.

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## A-30

### ZEISS MultiSEM: The World's Fastest Scanning Electron Microscope...Again

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Scientific innovation intrinsically requires the development of new tools which offer solutions previously not available to the user community. Such tools have the ability to fuel a dramatic shift in traditional workflows by providing increased speed, precision, and/or automation compared to conventional laboratory instrumentation. Although there generally still exists a competition between overall experimental throughput and probing resolution of a given characterization tool, recent advancements in multi-beam scanning electron microscopy [1] are helping to bridge the divide between nanoscale properties and device level macroscopic properties by providing an imaging platform that preserves spatial context to the physical specimen over many length scales.

Technical details of the simultaneous high throughput and high resolution ZEISS MultiSEM have been described previously for a 61 beam version [2], here we introduce the next generation 91 beam version which offers even greater throughput capability. Coupled with high throughput automated sample preparation using the ATUM device [3,4], brain mapping studies have been accelerated to the point where previously unimaginable sample volumes are becoming routine tasks. Application examples of mouse brain serial array tomography for connectomics studies will be provided.

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**A-31****A Comparative Study on X-ray and Electron Microscopy for Thick Biological Specimens**Ming Du<sup>1</sup> and Chris Jacobsen<sup>2,3,4</sup><sup>1</sup> Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208<sup>2</sup> Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439  
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Investigations on x-ray and electron microscopy starting from the beam-matter interaction point of view could lead to interesting insights in the factors determining the image quality and radiation doses. Here we categorize x-ray and electron probe beams based on the types of interaction events they undergo, and quantitatively model their fractional intensities. This not only provides a perspective on the dependence of image contrast on sample thickness, but also allows one to compare the radiation doses required by different imaging modalities to obtain a specific signal-to-noise ratio or spatial resolution. In the scenario we have studied, x-ray and electron differ in dose efficiency for different regimes of sample thickness. Contrast modes and the use of energy filter (for electron imaging) are also noticed to play a significant role in dose efficiency.

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**A-32****Characterization of Wavefront and Beam Coherence with Grating Interferometry**

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The forthcoming APS upgrade will provide high brilliance and highly coherent x-ray beams. The Optics Group at APS has been actively developing diagnostics tools necessary to characterize and study the coherence and the wavefront under the influence of different x-ray optics. In this work we discuss the latest developments and results obtained using grating interferometry [1].

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**A-33****Extended Range Ultra Small-angle X-ray, Small-angle, and Wide-angle Scattering for Materials Characterization at 9ID Beamline**Jan Ilavsky<sup>1</sup>, Ivan Kuzmenko<sup>1</sup>, Ross Andrews<sup>1</sup>, Fan Zhang<sup>2</sup>, Lyle Levine<sup>2</sup>, and Andrew Allen<sup>2</sup><sup>1</sup> X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439<sup>2</sup> National Institute of Standards and Technology, Gaithersburg, MD 20899

Development of new high-performance materials (e.g., new alloys, ceramics, or polymer materials), is critical for advances in energy production and utilization as well as materials future for every day life. These materials often exhibit complex microstructures spanning multiple length scales that control their performance. In this context, it is important to simultaneously characterize, ideally *in situ* or *in operando*, various facets of the microstructure—for example precipitate shape and size, together with their phase and chemical composition. Advanced Photon Source (APS) with NIST has developed and optimized a combined Ultra-small, Small, and Wide-angle X-ray Scattering (USAXS/SAXS/WAXS) facility currently located at sector 9ID beamline. Data spanning over 5 decades in microstructural size can be collected sequentially in 4 to 6 minutes, from the same volume during one *in situ* experiment. In this poster we present the facility capabilities, access methods available and document experimental capabilities using selected examples of user results. This facility is available through general user program (<https://www1.aps.anl.gov/Users-Information>) to world-wide user community at the APS sector 9ID (<http://usaxs.xray.aps.anl.gov>).

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**A-34****Third-generation ARPES Tool for Band Mapping**

David Laken

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The DA30-L is a third-generation ARPES hemispherical electron energy analyzer. First generation analyzers measured intensity at a single angle, requiring detectors mounted on a movable goniometer. Second generation analyzers, pioneered by Scienta Omicron, measured intensity at varying angles along the slit projected onto a 2D detector. The DA30-L can electrostatically move the electrons into the slit to measure an area of the Brillouin zone without movement of the sample. This provides for higher resolution and faster mapping while simplifying experimental setup.

### A-35

#### APS Upgrade Beam Stability R&D

R. Lill, N. Arnold, A. Brill, H. Bui, J. Carwardine, G. Decker, P. Dombrowski, L. Erwin, T. Fors, R. Keane, T. Pietryla, N. Sereno, S. Shoaf, X. Sun, J. Wang, B. Yang, and R. Zabel  
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We have approached the MBA beam stability R&D in two phases. The first phase, prototyped new, higher risk diagnostics and their interfaces. This R&D includes a Mechanical Motion System (MMS), RF BPM detector and electronics, Grazing Incidence Insertion Device (GRID) x-ray BPM, and new feedback processing electronics. This phase has been completed and has provided the foundation for the next phase of R&D. The second phase of the R&D effort advances the design and integrates all systems required to qualify beam stability. The integrated beam stability testing requires 16 new RF BPMs and 8 new corrector power supplies and interfaces. The integrated beam stability instrumentation has been designed to operate transparent to normal APS operation and was installed and commissioned in September 2016. This testing will greatly reduce risks and qualify many diagnostic, controls and power supply systems and their related interfaces.

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### A-36

#### The APS Detector Pool

Chris Piatak, Nino Miceli, Orlando Quaranta, and Russ Woods  
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The APS Detector Pool provides users with access to many different types of x-ray detectors and related equipment. The most popular devices include: Area Detectors (Pilatus 100K, PixiRad, Mar 165 CCD), Microscopy Cameras (Andor Neo, CoolSnap, Prosilica), and Spectroscopic Detectors (Vortex, Oxford Ge, Amptek CZT), Point Detectors (ATIM Avalanche Photo Diode, Oxford Cyberstar, Mythen silicon strip, PIN Diodes). New detectors for 2017 include ASI Medipix3RX and Dectris Eiger X 500K. It also coordinates equipment loans between beamlines, provides hardware and EPICS troubleshooting, and works with vendors to circulate demo units of next generation detectors.

### A-37

#### Exceeding the Speed Limit: Bringing Zoom Zoom to X-ray Microscopy

Curt Preissner<sup>1</sup>, Junjing Deng<sup>1</sup>, Chris Roehrig<sup>1</sup>, Sheikh Mashrafi<sup>1,2</sup>, Michael Wojcik<sup>1</sup>, Shane Sullivan<sup>1</sup>, Zhonghou Cai<sup>1</sup>, David Vine<sup>3</sup>, Barry Lai<sup>1</sup>, and Stefan Vogt<sup>1</sup>

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The Advanced Photon Source Upgrade (APS-U) will provide over 100 times the coherent flux as the current machine. This large increase in flux will enable a revolution in nanoprobe operation. This poster covers the design details of the Velociprobe, an instrument designed to develop nanoprobe technology for the APS-U. Goals include demonstrating sub-10 nm resolution while scanning a one square micron area in under 10 s. This will be combined with 50 nm resolution fluorescence data. Novel granite air-bearing stages provide an ultra-stable platform for the zone plate scanner and sample stages. Our advanced scanning control scheme uses laser interferometry along with a FPGA-based control algorithm to minimize the influence of disturbances and noise (better resolution) and increase scanning bandwidth (higher speed). The combined result will allow us to acquire high-resolution, multi-modal data, on real samples in drastically shorter times than current instruments.

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### A-38

#### Germanium Strip Detector for Energy-dispersive Diffraction

Russell Woods<sup>1</sup>, Orlando Quaranta<sup>1</sup>, Johnathan Baldwin<sup>1</sup>, Anthony Kuczewski<sup>2</sup>, Joseph Mead<sup>2</sup>, Abdul Rumaiz<sup>2</sup>, Peter Siddons<sup>2</sup>, Jonathan Almer<sup>1</sup>, John Okasinski<sup>1</sup>, Stuart Stock<sup>3</sup>, and Antonino Miceli<sup>1</sup>

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In collaboration with the detector group at NSLS-II, the XSD Detectors Group is developing germanium strip detectors for high-energy spectroscopic applications.

Germanium strip detector combines low-noise readout electronics from NSLS-II with commercial high-quality germanium sensor to provide position and energy resolution. The first-generation detector consists of a 3-mm-thick germanium sensor with 64 strips on a 0.5-mm pitch. An energy spectrum is measured from each strip simultaneously; the energy resolution is 400–500 eV. Currently, the maximum energy is limited to 50 keV, but new readout electronics being developed at BNL and further detector innovation will extend the energy range beyond 100 keV, allowing thicker and/or higher-z materials to be investigated. The XSD Detector group has been responsible for the mechanical design of cryogen-free cryocooler system and the software, which makes the operation of the detector fully automated. Together with scientists from the XSD/MPE Group and Northwestern University, this germanium strip detector has enabled a new x-ray imaging technique based on energy dispersive diffraction. This new technique provides spatially-resolved diffraction data including phase fractions and strains on cm-sized specimens. Applicable to more geometries than standard tomography techniques (e.g., high aspect ratio samples), with target areas including batteries, bone implants and aerospace components. The new imaging mode was accomplished with a slit and single translation across the sample, and applied to a three-dimensional printed bone “phantom” to confirm accuracy. The peak centers from each phase present can also be reconstructed to yield strain information.

### A-39 New Developments in Multi-sensor Silicon Drift Detectors

**Del Redfern, Peter Smith, Mark Gray, and Bob Daniel**  
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In many x-ray spectroscopy applications, it is important to acquire data quickly to shorten the analysis time and maximise the statistical accuracy. This is especially important for synchrotron radiation studies, where highly focused excitation beams may be used to generate thousands of fluorescence spectra during 2D and 3D sample scans. For the x-ray fluorescence detector, this means maximising the solid angle presented while ensuring that the incident count rate remains within a practical range. High speed Silicon Drift Detectors, operated together with the latest generation of digital pulse processors, allow count rates of a few million cps. However, for high solid angle detection systems it is often necessary to use multiple sensors to process the available number of events. The principles behind linear and circular focused sensor arrays are discussed and practical examples and performance data are presented. Recent further developments in fluorescence detector design

have extended the availability of optimised multi-sensor solutions to applications where more demanding geometrical constraints are imposed. Details of these unique developments are presented.

### A-40 12bm Focusing Optics Upgrade – Preparing for the APS-U

**Benjamin J. Reinhart<sup>1</sup>, Chuck Kurtz<sup>1</sup>, Oliver Schmidt<sup>2</sup>, Sungsik Lee<sup>1</sup>, and Randy Winans<sup>1</sup>**

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The focusing optics for beamline 12bm have been upgraded to prepare for the APS-U as well as to improve the metrics of the beamline which before the upgrade was using 1980 optics brought over from Brookhaven that utilized outdated coating technology, older substrate materials, along with shorter mirror lengths.

The 12bm optics upgrade replaced the functional but older 60cm Flat/Toroidal mirrors with 110cm Flat/Toroidal mirrors. This length addition has allowed a larger energy window and hence increased the number of elements that can be explored when running experiments at 12bm. The previous higher limit of the energy range for the focused beam of 23keV has been increased to 30keV. This allows experiments to utilize a focused beam for elements currently under popular demand in the range of 23keV up to 30keV. Another addition due to the optics upgrade was an increase in flux that has doubled at lower energies and increased an order of magnitude at higher energies.

Aside from better substrate material and length, 12bm has also considered the coating of the optics [1]. Having a Pt coating with a 10 nm Al<sub>2</sub>O<sub>3</sub> layer deposited on top of the Pt coating has created a better transition between lower energies to higher energies. Without this extra coating there is a quick drop in reflectivity from the Pt coating around 15keV. The Al<sub>2</sub>O<sub>3</sub> layer acts like a multilayer mirror and keeps the flux from dipping rapidly as it does with just the Pt coating at energies above 15keV (this is calculated with an incident angle around 2.6 mrad).

[1] Steve M. Heald (2011). *Nucl. Instr. and Meth. A*. **649**: 128–130.

*I want to acknowledge the APS Deposition and Metrology groups for providing the coatings and metrology. Use of the Advanced Photon Source is supported by the U.S. Department of Energy, Office of Science, under Contract DE-AC02-06CH11357.*

**A-41****Synchrotron Powder Diffraction Simplified: The High-resolution Diffractometer 11-BM at the Advanced Photon Source**

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Synchrotrons have revolutionized powder diffraction. They enable the rapid collection of high quality powder diffraction patterns with tremendous resolution and superb signal to noise. In addition, the high penetration and exceptional data sensitivity possible at high-energy light sources, like the Advanced Photon Source (APS), allow exploration of trace containment levels, *in situ* sample environments and crystallographic site occupancies, which previously demanded neutron sources. Despite all these advantages, relatively few scientists today consider using a synchrotron for their powder diffraction studies.

To address this, the high resolution synchrotron powder diffractometer beamline 11-BM at the APS offers rapid and easy mail-in access for routine structural analyses with truly world-class quality data [1]. This instrument offers world-class resolution and sensitivity and is a free service for non-proprietary users [2]. The instrument can collect a superb pattern suitable for Rietveld analysis in less than an hour, is equipped with a robotic arm for automated sample changes, and features variable temperature sample environments. Users of the mail-in program typically receive their high-resolution data within two weeks of sample receipt. The diffractometer is also available for on-site experiments requiring more specialized measurements.

This presentation will describe this instrument, highlight its capabilities, explain the types of measurements currently available, as well as recent significant improvements to the instrument's performance. We will discuss plans to improve access and the available sample environments and collection protocols. We are particularly interested in seeking input from potential users within the powder diffraction community.

More information about the 11-BM diffractometer and its associated mail-in program can be found at our website: <http://11bm.xray.aps.anl.gov>.

[1] Wang, J., et al. (2008). *Review of Scientific Instruments* **79**: 085105.

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**A-42****areaDetector: What's New?**

M.L. Rivers

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Recent enhancements to the EPICS areaDetector module will be presented.

- Plugins can now run multiple threads to significant increase performance.
- Scatter/gather capability for plugins to run in parallel.
- ImageJ plugin that uses EPICS V4 pvAccess rather than Channel Access. Provides structured data with atomic update, and better performance than Channel Access plugin.
- ImageJ plugin that allows graphically defining detector readout region, ROIs, and overlays.
- Plugins can now be reprocessed without receiving a new NDAarray for testing effect of different parameters, etc.

**A-43****Vortex Multi-element SDD Detectors: New Performance Data**

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Vortex multi-element SDD spectrometers have been developed for advanced x-ray spectroscopy, such as x-ray fluorescence micro imaging, XANES (x-ray absorption near-edge structure) and EXAFS (extended x-ray absorption fine structure) and x-ray fluorescence micro imaging, fluorescence computed microtomography (fCMT). These applications typically use synchrotron x-ray beams and they require a large solid angle and high count rate.

These multi-element SDD spectrometers are based on 0.5 and 1 mm thick Vortex® SDDs, integrated with advanced front-end Cube preamplifiers, and they feature an excellent energy resolution at extremely short peaking times [1]. The option with unique 1 mm thick SDD provides also significantly increased detection efficiency of x-rays at high energy.

High performance of the multi-element SDD spectrometers could be most fully realized in combination with a modern adaptive processing electronics. Other data concerning the design and performance of the Vortex multi-element SDD detectors will be presented.

[1] S. Barkan, V.D. Saveliev, Y. Wang, L. Feng, E.V. Damron, and Y. Tomimatsu, "Extreme High Count Rate Performance with a Silicon Drift Detector and ASIC Electronics," *Biological and Chemical Research*, Volume 2015, 338–344.

**A-44****Distance Metrology Using a Low-finesse Fiber-optic Fabry-Pérot Interferometer**

**Klaus Thurner, Danilo Marcello Schmidt, and Khaled Karrai**  
attocube systems AG, 80539 Munich, Germany

Our interferometric displacement sensor is based on a folded low-finesse Fabry-Pérot cavity. The fiber-optic sensor uses a quadrature detection scheme based on the wavelength modulation of a DFB laser. This enables measuring position changes over a range of 5 m for velocities up to 2 m/s. The sensor is well suited to work in harsh environmental conditions such as ultrahigh vacuum, cryogenic temperatures, or high magnetic fields and supports multichannel applications. The interferometer achieves a repeatability of 0.11 nm ( $2\sigma$ ) at a working distance of 77 mm, a resolution of 1 pm, a measurement bandwidth of 10 MHz, and an accuracy of 1 nm.

**A-45****Design of a Miniature Dynamic Mirror Bender with Lamina Flexure Bending Mechanism for X-ray Microfocusing**

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<sup>3</sup> University of Illinois at Chicago, Chicago, IL 60607

Recently, collaboration between Argonne National Laboratory and Shanghai Institute of Applied Physics, as a part of the Argonne Strategic Partnership Project (SPP), has produced designs of a novel miniature dynamic mirror bender using Argonne's lamina nanopositioning flexure technique [1] for the beamline upgrade project at the Shanghai Synchrotron Radiation Facility. The motivation of the novel design is to develop a compact, cost-effective flexure mirror bender with high stability, especially in cases for x-ray focusing optics coated with multilayers in a K-B configuration. As the final focusing elements immediately upstream of the sample, the dynamic mirror benders provide high precision figuring to allow the mirror figure to be tuned to optimize the focusing at different incidence angles to cover a wide energy range [2].

The flexure bending mechanism module is constructed with stacks of thin metal weak-link sheets which are manufactured using photochemical machining processes with lithography techniques [3]. The module is a solid lamina bonded complex structure designed for ultrahigh positioning resolution and stability performance. The mechanical design and finite element analyses of the miniature dynamic mirror bender as well as the initial test results are described in this poster.

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[1] D. Shu, T.S. Toellner, and E.E. Alp (2003). U.S. Patent granted No. 6,607,840.

[2] R. Barrett, J. Härtwig, and C. Morawe, et al. (2010). *Synchrotron Radiation News* **23**(1): 36–42.

[3] D. Shu, T.S. Toellner, and E.E. Alp (2006). U.S. Patent granted No. 6,984,335.

**A-46****VIPIC: A Novel Detector for X-ray Photo-correlation Spectroscopy (XPCS)**

**John Weizeorick<sup>1</sup>, Rebecca Bradford<sup>1</sup>, Gregory Deptuch<sup>2</sup>, Eric Dufresne<sup>1</sup>, Piotr Grybos<sup>3</sup>, Scott Holm<sup>2</sup>, Anthony Kuczewski<sup>4</sup>, Timothy Madden<sup>1</sup>, Piotr Maj<sup>3</sup>, Joseph Mead<sup>4</sup>, Suresh Narayanan<sup>1</sup>, Abdul Rumaiz<sup>4</sup>, Kyung-Wook Shin<sup>1</sup>, and Peter Siddons<sup>4</sup>**

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VIPIC (Vertically Integrated Photon Imaging Chip) is a hybrid pixel detector currently being developed for coherent speckle experiments. VIPIC will use a unique multi-layer readout chip allowing more logic to be embedded in the ASIC. Most importantly, only those pixels hit by an x-ray during the exposure window will be read out. The reduced readout for sparse images increases the frame rate and makes this detector ideal for x-ray photon-correlation spectroscopy (XPCS) or other time resolved-techniques with low signal levels. Currently under development, the collaboration is working to produce a 1 Mega-pixel detector within the next few years.

This poster will give an overview of the detector and present recent highlights from the development effort, including beam testing of detector prototypes.

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**A-47****Electrochemistry Support Laboratory: Enabling Users' Battery Studies at the Advanced Photon Source**

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Since February 2015, the electrochemical support laboratory at the Advanced Photon Source (e-chem lab) has been open to users' community. The e-chem lab is equipped with an Ar-atmosphere glovebox fitted with a fridge/freezer unit, supplied with Li and Na metals, standard electrolytes, coin cell-crimpling tool and accessories needed for assembling battery cells. The lab is also equipped with three portable 8-channel MACCOR® battery cyclers, a single-channel CH Instruments® potentiostat, a vacuum oven, balances, bench space and standard laboratory consumables.

A local electrochemistry laboratory on the experimental floor is essential to the studies of electrochemical energy storage. A 24/7 access to a professionally supported laboratory during the beamtime and access to the facilities prior to scheduled measurements vastly increases the success rates of the experiments and opens avenues to *operando* studies otherwise unattainable (e.g., investigations of more advanced stages of battery cycling). Additionally, a well-equipped e-chem lab eliminates the need for shipping of the assembled battery cells fitted with "homemade" x-ray transparent windows, transport of which is regulated by U.S. Department of Transportation.

*This facility uses resources provided by:*

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- NECCES, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0012583.

**A-48****Diffraction Nanofocusing Optics Characterization Using Ptychography at 1-BM-B**

Michael Wojcik and Albert Macrander

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The Advanced Photon Source Upgrade (APS-U) will provide an x-ray beam with dramatically increased brightness compared with the current source. One of the advantages of the new source will be greatly improved potential for beamlines to focus x-rays to nanometer spot

sizes. High quality nanofocusing optics will be needed by beamlines to realize the potential of the source. Zone plates and multilayer Laue lenses (MLLs) are diffractive nanofocusing optics similar to gratings but with changing period as a function of zone number, and two options for nanofocusing optics. Characterizing the nanofocus for both types of optics has generally been measured by scanning a knife edge through the focus and measuring a scattered, fluoresced, or transmitted signal to create a histogram. But knife edge measurements are the convolution of the focus and the knife edge, to measure only the focus the object must be known and taken out of the signal. Ptychography is a method of taking a series of scattered images from scanning an x-ray beam across an object then reconstructing the object and probe images, separating the information of the focus from the object. The resulting probe can be analyzed with a free space propagation code to find the best focus and determine focus size [1,2]. We will present results from ptychography experiments performed at 1-BM-B of the APS, measuring both the focus from several zone plates and MLLs. We have measured a 1-D focus down to 25 nm with a MLL using ptychography, much smaller than was measured via knife-edge scan. We will also discuss challenges, opportunities, and the next steps for ptychography measurements for nanofocusing optics characterization.

*We thank Raymond Conley and Natalie Bouet for fabricating the MLL. We thank Jorg Maser, Junjing Deng, and Ross Harder for their help with ptychography. Finally, we thank Jessie Clark and David Vine for developing the ptychography codes. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.*

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**Materials Science****A-49****Synthesis and Characterization of Novel Strongly Coupled Type-I Multiferroics Oxide Materials**Kamal Chapagain<sup>1</sup>, Omar Chmaissem<sup>1,2</sup>, Stanislaw Kolesnik<sup>1</sup>, Denis Brown<sup>1</sup>, and Bogdan Dabrowski<sup>1</sup><sup>1</sup> Department of Physics, Northern Illinois University, DeKalb, IL 60115<sup>2</sup> Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

In this poster presentation, I will discuss the synthesis and characterization of promising multiferroics materials from the phase diagrams (Ba, Sr)(Mn, Ti)O<sub>3</sub>, Ba(Mn, Fe)O<sub>3</sub>, and



(Ba, Sr)MnO<sub>3</sub>. Neutron and x-ray diffraction experiments are needed to study the magnetic and crystal structures, and correlate them to the coupled ferroelectric and magnetic properties. These materials are exceptional because of their unusual properties in which magnetic and ferroelectric properties coexist. Typically Type I multiferroics exhibit weak coupling between the robust order parameters, and the commonly investigated Type II multiferroics exhibit strong magnetic-ferroelectric coupling but the ferroelectric order parameter is quite small. Our compounds show large ferroelectric distortions that are similar in arrangement and size to the prototypical nonmagnetic BaTiO<sub>3</sub>, for which ferroelectricity originates from the hybridization of the occupied oxygen p orbitals to the empty Ti d orbitals. However, our compounds are also magnetic due to the presence of the magnetic Mn<sup>4+</sup> ions with partially filled d orbitals.

In our Laboratory for Materials Design at Northern Illinois University, I have synthesized various metastable perovskites ABO<sub>3-δ</sub> by specially developed synthesis methods to put bonds between transition metal and oxygen under internal tension through a proper selection of the sizes and charges of the A and B ions. Our compounds containing A = Sr, Ba and La and B = Mn, Fe and Ti exhibit complicated phase diagrams. These materials are potential candidates for technological devices such as multi-functional devices, spintronic, memory devices, and magnetic random-access memories.

### A-50 Manipulating Oxygen Vacancies in Complex Oxides

Say Young Cook<sup>1</sup>, Tassie Andersen<sup>1</sup>, Richard Rosenberg<sup>2</sup>, Hawoong Hong<sup>2</sup>, Laurence Marks<sup>1</sup>, and Dillon Fong<sup>3</sup>

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The physical properties of complex oxides are highly sensitive to the oxygen coordination environment of the transition metal. Here we present our work on manipulating oxygen vacancies in two complex oxide systems using epitaxial synthesis and electric field and their characterization with synchrotron x-ray techniques. The first part is concerned with the reconstruction of oxygen sublattice in cobaltite-titanate epitaxial thin films. We compare the distribution of oxygen vacancies in epitaxial thin films of (SrCoO<sub>x</sub>)<sub>n</sub>:(SrTiO<sub>3</sub>)<sub>1</sub> (*n* = 1, 2) superlattices, in which single SrTiO<sub>3</sub> layers are injected within the unit cell of the brownmillerite SrCoO<sub>2.5</sub>, with that in a 50:50 random alloy Sr(Co,Ti)O<sub>x</sub>. Soft x-ray spectroscopy reveals

persistent Ti<sup>4+</sup>O<sub>6</sub> octahedra in the cobaltite-titanate thin films and variable Co valence that depends on the layered versus random Co/Ti arrangement and the superlattice periodicity. Surface x-ray diffraction measurements also reveal a relaxation of the *n* = 2 superlattice towards the brownmillerite SrCoO<sub>2.5</sub>, distinct from the *n* = 1 superlattice and the 50:50 alloy.

The second part is concerned with characterization of the electronic structure along an oxygen vacancy gradient in a single crystal SrTiO<sub>3-δ</sub> prepared using an *in situ* DC resistive heating setup. X-ray excited luminescence spectroscopy and lifetime measurements are used to track the evolution of blue luminescence arising from in-gap defect states along the oxygen vacancy gradient, as well as quantify the bulk oxygen vacancy distribution in terms of the doped electron concentration. The defect concentrations are then correlated with x-ray photoelectron and absorption spectra to obtain the evolution of the occupied and unoccupied density of states as a function of the oxygen vacancy concentration.

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### A-51 Stabilization of High-capacity, Mn-Rich Cathodes for Lithium-ion Batteries

Arturo Gutierrez, Meinan He, Eungje Lee, Jason R. Croy, and Micheal M. Thackeray

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Lithium-ion batteries (LIBs) are ubiquitous in our lives. The next-generation of LIBs is based on lithium- and manganese-rich “layered-layered” (LL) oxides due to delivering high reversible capacities (250–300 mAh g<sup>-1</sup>) that are a substantial improvement from other competing LIB cathodes (i.e., LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, Li<sub>1+x</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>Co<sub>c</sub>O<sub>2</sub> (NMC) and LiFePO<sub>4</sub>) that deliver capacities <180 mAh g<sup>-1</sup>. It is now well understood that the LL composite materials undergo voltage fade and hysteresis upon extended cycling that ultimately lowers the output energy of the system [1]. These structural deficiencies, accompanied by poor electrical conductivity and a low first cycle efficiency, have left the research community in search of an approach to arrest the structural degradation observed for LL composite cathode materials. One promising approach has been the incorporation of a spinel component forming a layered-layered-spinel (LLS) composite [2–4]. This poster will highlight our teams current strategies focused on: i.) structural (i.e., bulk) stabilization through selective cation-doping in LL and LLS composites and ii.) surface treatments of LLS powders intended to protect particle surfaces during high voltage cycling.

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## A-52

### MAUI: Modeling, Analysis, and Ultrafast Imaging at Argonne National Laboratory

Ross Harder<sup>1</sup>, Mathew Cherukara<sup>1</sup>, Kiran Sasikumar<sup>2</sup>, Tom Peterka<sup>3</sup>, Ian McNulty<sup>2</sup>, Nicola Ferrier<sup>3</sup>, Todd Munson<sup>3</sup>, Sven Leyffer<sup>3</sup>, Subramanian Sankaranarayanan<sup>2</sup>, Andrew Ulvestad<sup>4</sup>, and Haidan Wen<sup>1</sup>

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Coherent x-ray diffractive imaging (CXDI) can now reach down to sub ten nanometer structural imaging of materials [1]. When done in the Bragg geometry one can also image distortions of the lattice with  $10^{-5}$  sensitivity [2, 3]. Bragg CDI is also highly compatible with *in situ* and operando studies of materials owing to the relatively large free space around the sample.

Recently we have conducted imaging experiments with both catalytic systems and ultrafast laser pump—x-ray probe of energy transport by phonons in nanomaterials [4,5]. To quantify the response seen in the materials there is an increased requirement for image

analysis to understand the physical processes occurring.

Advanced image analysis and molecular dynamics (MD) simulations are now scaling in the opposite direction of CXDI. These computational methods are reaching UP to the length/time scales achieved in the imaging experiments. Image meshing techniques can be used to create models of the actual samples in an experiment, which can then feed into multi-million atom MD and finite element simulations over hundreds of picoseconds [5].

Building a complete workflow to understand nanoscale phenomena with atomistic origins is the goal the MAUI (Modeling, Analysis and Ultrafast Imaging) project at Argonne National Laboratory. Specialists in coherent imaging, ultrafast laser science, 4D image analysis, math and computer science have teamed up with molecular dynamics simulations experts to develop these tools.

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## A-53

### Trends on Thin Film X-ray Optics and Pinholes for Synchrotron Beamlines

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Different kinds of x-ray mirrors are required for beam alignment, guidance or monochromator applications. Therefore various types of optics with coatings for energy ranges between 100 eV and 80 keV have been investigated.

We will show stripe multilayer coatings which are often used as Double Crystal Multilayer Monochromators (DCMM) for example in tomography beamlines. The optics consists of up to 5 different coating stripes, optimized for each energy range.

In this contribution we will also present results of a 50 cm laterally graded multilayer optics, developed for special mini-synchrotrons with a deviation to a specified film shape of less than 0.2%.

We will present new developments of Montel Optics for synchrotron applications. Different types of these two-dimensional optics are used at DLS, NSLS and APS, for example in an analyzer system for inelastic scattering.

Parasitic aperture scattering causes loss in data quality

especially in SAXS and GISAXS applications. Various measurement results will be presented showing the improvement of data quality with Incoatec's scatterless pinholes called SCATEX. These pinholes are either made of Germanium for energies <11.2 keV or of Tantalum for energies >11.2 keV and are available with diameters from 2 mm down to 20  $\mu\text{m}$  and below.

## A-54

### Helium Implantation Effect on Spherical Nano-indentation in Tungsten: A Micro-beam Laue Diffraction Study

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Nuclear fusion promises to be the ultimate sustainable energy source: clean, virtually inexhaustible and intrinsically safe. A major hurdle for the development of commercial fusion reactors is a lack of sufficiently resilient materials. Tungsten-based alloys and composites are key candidates for armor components that will experience the harshest conditions. During service they will be exposed to high temperatures, intense neutron flux and ion bombardment. Here we use helium-ion-implantation to study the interaction of injected helium with displacement damage. Our experiments, using spherical nano-indentation, show that helium-induced defects substantially modify the mechanical properties of tungsten. We observe extensive hardening and a dramatic change in pileup behavior. Using micro-beam Laue diffraction we are able to examine the lattice rotations and residual strains near specific indents with 3D sub-micron spatial resolution. Our results show much smaller distortions at indents in the helium-implanted material than in an unimplanted reference crystal. This surprising result suggests a more compact plastic zone in the implanted material and sheds new light on the complex changes in deformation behavior brought about by helium-implantation-induced defects.

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## A-55

### Crystal Structure of a Large Unit Cell Icosahedral Approximant Determined by Charge Flipping

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The crystal structure of the  $\text{Al}_{12.8}(\text{Fe},\text{V})_3\text{Si}_{10.3}$  h-phase (P6/mmm,  $a=2.522$  nm,  $c=1.256$  nm) in the Al alloy RS8009 was determined *ab initio* from powder diffraction on a two-phase powder of the h-phase and the  $\text{Al}_{13}(\text{Fe},\text{V})_3\text{Si}$   $\alpha$ -phase (Im-3,  $a=1.251$  nm) using charge flipping with histogram matching. The h-phase is the most complicated intermetallic crystal structure solved *ab initio* from powder diffraction by far. Although complex crystal structures have been solved from powder diffraction before [1], they possessed significant differences from the crystal structures of intermetallics. For zeolites, one of the features that made their structure solvable from powder diffraction was the presence of local bonding geometries known beforehand. Complex intermetallics do not have this property, which complicates the structure determination process.

It is demonstrated that even without knowledge of bonding geometries, well-defined crystal structures can be determined for intermetallics using powder diffraction. Powder diffraction allows for accurate models of complex metastable intermetallics to be developed, which is useful when determining how to select for specific intermetallic phases during alloying.

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## A-56

### Studies of Diamond Endurance to Irradiation with X-ray Beams of Multi kW/mm<sup>2</sup> Power Densities for XFEL Application

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Recent advances in x-ray science have been considerably shaped by the advent of modern bright and powerful x-ray sources: 3<sup>rd</sup> generation synchrotron radiation storage rings, and x-ray free electron lasers (XFEL). XFELs in the oscillator configuration (XFELo) are possible future new sources, in

which x-ray beams generated by the undulator circulate in an optical x-ray cavity comprised of high-reflectance (close to 100%) diamond crystal mirrors working in Bragg backscattering [1,2]. XFELs will produce stable, fully coherent hard x-rays of ultra-high (meV) spectral purity. The average power density of the x-ray beams in the XFEL cavity is however predicted to be unprecedentedly high, on the order of  $\approx 4$  kW/mm<sup>2</sup>. Therefore, the XFEL feasibility relies on the ability of diamond to withstand such a high radiation load and preserve its high reflectivity.

We are reporting on endurance studies of the highest-quality practically flawless synthetic diamond crystals [3] to irradiation with multi-kW/mm<sup>2</sup> power density beams. Most important, we are studying whether the extremely high Bragg reflectivity of meV-monochromatic x-rays from the diamond crystals in backscattering is conserved after the irradiation.

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## A-57

### Directing the Lithium-sulfur Reaction Pathway via Sparingly Solvating Electrolytes for High Energy Density Batteries

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DOE's energy storage hub (JCESR) is exploring "beyond lithium-ion" solutions that can attain important metrics (pack level energy density of 400 WhL<sup>-1</sup> and cost of \$100 per kWh) relevant to transportation applications [1,2]. Lithium-ion batteries have been widely applied in consumer electronics successfully for over two decades but further development of next-generation battery systems is an inevitable task for researchers to satisfy the demand for efficient energy storage. Lithium sulfur (Li-S) is one such transformation chemistry that has been explored for decades with only modest success. While current Li-S cells are lighter than Li-ion (350 vs. 250 Wh kg<sup>-1</sup>), they have lower energy density and significantly poorer cycle life. Techno-economic modelling of Li-S suggests that

promising materials-only fundamentals can translate to long-term goals at the systems level, assuming progress is made in reducing excess material burdens [2]. Under lean electrolyte conditions, the dissolved LiPSs rapidly reach saturation limits, likely leading to the deposition of insulating products on the electrode surface. The precipitates can then lead to large cell polarization and adversely affect sulfur utilization. Controlling the precipitation process in such a way that the electrode conductivity is not compromised is undoubtedly a key aspect for the success of this approach. To meet such challenges in designing lean electrolyte systems, new information on sulfur speciation is required. To this end, we have performed electrochemical and x-ray spectroscopic measurements on Li-S cells with a sparingly soluble electrolyte reported by Cuisinier et al [3]. The results of this study will be presented in the meeting.

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## A-58

### Hydration and Ion Adsorption at Yttria-stabilized Zirconia-water Interfaces

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Zirconia has numerous applications (e.g., gas sensors, solid oxide fuel cell electrolytes, bio-medical materials, etc.) and plays a key role in protecting zirconium alloys in highly corrosive environments like nuclear power plants, pressurized water reactors. Its degradation is primarily

caused by the surface interaction with water. Here we report the detailed interfacial hydration structures at 8 mol% yttria-stabilized zirconia (8YSZ) surfaces, (100), (110), and (111) planes, respectively, with high-resolution x-ray reflectivity. We could identify common features among these probed surfaces as well as the differences intrinsic from surface chemistry. All three surfaces terminate with significant number of point defects presumable caused by the metal depletion and intrinsic oxygen vacancies. Water molecules fill those vacancies, forming highly ordered and layered structure near the top surfaces. Above the termination planes, two additional adsorbed layers are commonly formed in the interfacial hydration structures. The first adsorbed layers likely include metal species as indicated by the promoted electron density, whereas the second layers seem to consist of pure water. We also studied the effect of zinc adsorption on the interfacial hydration structures, which show obvious changes in the hydration structure at (100) and (111) surfaces, but minor changes at (110) surface. We further confirmed the detailed element specific adsorption profile of  $Zn^{2+}$  ions at YSZ (110) and (111)-water interfaces with resonant anomalous x-ray reflectivity measurements. With the adsorbed zinc species, the (100) and (110) surfaces qualitatively maintain the original features in the water layers, while the interfacial hydration at (111) surface is completely altered by the zinc adsorption.

### A-59

#### Curved Diamond-crystal Spectrographs for X-ray Free-electron Laser Noninvasive Diagnostics

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The development of x-ray free electron lasers (XFEL) addresses needs for more intense and coherent beams required to study new emerging scientific problems. XFELs generate extremely bright x-ray beams with a high degree of coherence based on the self-amplified spontaneous emission (SASE) phenomenon, which is stochastic in nature and gives rise to shot-to-shot fluctuations in most of the beam characteristics. Self-seeding XFELs, on the contrary, produce x-rays with a much narrower and more well-defined spectrum. Development of noninvasive and nondestructive methods for beam diagnostics is, therefore, necessary for the proper XFEL operation and experimental data interpretation.

We report on the successful design, manufacturing, and x-ray performance tests of the single crystalline diamond bent spectrographs for noninvasive diagnostics of the x-ray spectra of the synchrotron and FEL sources. The whole assembly is made of diamond components. The ultra-thin diamond plate in the (110) orientation is bent in a controlled fashion and ensures safe operation in intense x-ray beams. The experiment conducted at the APS bending magnet beamline shows that the spectrograph performance is very close to the design parameters in terms of the spectral window of imaging and the linear dispersion rate.

### A-60

#### X-ray Studies of the Diamond Crystals for the Split-and-delay Line

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X-rays generated by the synchrotron storage rings and free electron lasers can be used for observation of a matter dynamics on a molecular level (e.g., by x-ray photocorrelation spectroscopy). One of the approaches to this problem is the split-pulse technique, in which each x-ray pulse is split into reference and delayed pulse of equal intensity, and after scattering from the sample they are collected into the area detector. The split-and-delay experiment requires specific arrangement of crystal optics.

We report on the design and manufacturing of the highest quality diamond single crystals of various orientations and thicknesses for the split-and-delay line. Further processing of the crystals, polishing and annealing is crucial to obtain required surface quality and to remove the strain. Double crystal topography reveals that they exhibit highly uniform properties of the x-ray diffractive properties in large sections.

### A-61

#### Adaptive Feedback Control Methods for X-ray Imaging

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In this work, we explore the use of adaptive iterative feedback techniques from control theory to reduce the number of measurements required for sample reconstructions in x-ray diffraction imaging. Preliminary results will be presented.

**A-62****Synthesis and Characterization of Low Symmetry Ortho-fluoroazobenzene Metal Organic Framework Linkers**

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Photo-responsive metal organic frameworks (MOFs) are an appealing class of materials for a wide variety of applications including separations, advanced sensors, drug delivery, and data storage. By incorporating light-responsive molecular switches into the MOF structure, one can afford external control over the physical properties of the system. This presentation will describe recent efforts to integrate light sensitive ortho-fluoroazobenzenes into MOF linkers with reduced symmetry. In general, azobenzenes undergo a large structural change when isomerized from the thermodynamically stable *trans* form to the metastable *cis* form. The isomerization of suitably positioned chromophores can affect the ability of the MOF to retain and/or exchange guests from the pores. Ortho-fluoroazobenzenes are particularly attractive photo-active groups as they contain electron withdrawing substituents that alter the excitation energies resulting in a favorable separation of the absorption bands in the visible light region. This enables the selective excitation of either the *cis* or *trans* isomers. Previous studies have also demonstrated the lifetime of the *cis* isomer is longer for ortho-fluoroazobenzenes when compared to their non-fluorinated counterparts.

Despite the crystalline nature of these materials, the photo-active portions of the structures often lack a high degree of structural organization which prevents the structural characterization of these groups using diffraction methods. To improve the likelihood of producing materials with crystallographically resolvable photo-active groups, we have designed and synthesized a variety of low symmetry linkers which should reduce or eliminate common motifs that lead to high symmetry MOF structures.

**A-63****Synthesis of High-temperature Materials from Amorphous Precursors at Ambient Conditions**Michael L. Whittaker<sup>1</sup>, Wenhao Sun<sup>2</sup>, Gerbrand Ceder<sup>2</sup>, and Derk Joester<sup>1</sup><sup>1</sup> Northwestern University, Department of Materials Science and Engineering, Evanston, IL 60208<sup>2</sup> Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Solid solution strengthening is a classical method for enhancing the mechanical properties of materials through lattice distortion from disparate ionic radii. This mechanism is also active in carbonate minerals, out of which many

organisms form their skeletons, teeth, and/or shells. Unlike most engineering materials, however, organisms are able to achieve enhanced properties by synthesizing and maintaining highly metastable compositions under ambient conditions. In this study, I demonstrate a bioinspired method for generating a highly metastable  $\text{Ca}_{1-x}\text{Ba}_x\text{CO}_3$  structure with hardness equivalent to that found in biogenic calcite. Barium-substituted disordered calcite (balcrite) contained up to 50× more barium than the solubility limit of barium in calcite [1], and is thermodynamically stable only above 525°C, yet was formed under ambient conditions using amorphous precursors. Its structure was confirmed for the first time from high-resolution powder x-ray diffraction. Local structure in the amorphous precursor, investigated with vibrational spectroscopy, x-ray absorption spectroscopy, pair distance distribution function analysis, and a combined molecular dynamics/density functional theory approach, resembled that of balcrite. Using microfluidically produced water-in-oil drops as microreactors, this structural similarity was shown to selectively reduce the barrier to balcrite formation through a non-classical crystallization mechanism. This synthesis pathway improves our understanding of biomineral synthesis, which often proceeds through metastable, amorphous intermediates and introduces new mechanisms to generate persistent non-equilibrium compounds.

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**A-64****In operando EDXRD of Graphite and Silicon-graphite Anodes in Lithium Ion Batteries**Koffi P. Yao<sup>1</sup>, Kaushik Kalaga<sup>1</sup>, John S. Okasinski<sup>2</sup>, Jonathan D. Almer<sup>2</sup>, and Daniel P. Abraham<sup>1</sup><sup>1</sup> Chemical Sciences and Engineering, Argonne National Laboratory, Argonne, IL 60439<sup>2</sup> Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Improvements in the energy density of lithium-ion batteries (LIBs), through the adoption of novel high-capacity anodes as alternatives to graphite, are being widely pursued. Silicon, with a theoretical capacity of 3579 mAh g<sup>-1</sup>, lithiation-voltage comparable to that of graphite, and high-abundance, is considered the most appropriate

alternative. The advantages of high energy density are countered by severe capacity fade, limiting the cycle life of Si-containing cells. Fundamental mechanistic understanding of lithiation and de-lithiation processes in Si-electrodes is essential to identify causes of capacity loss. Several *in situ* and *ex situ* techniques such as SEM, TEM, XRD, AES, etc. have provided knowledge on structural, chemical and morphological changes of electrodes at specific states of charge or stages of cycle life ageing.

We adopted *in operando* energy dispersive x-ray diffraction (EDXRD) to track structural changes in all components of pure Graphite- (Gr) and Silicon/Graphite- (Si/Gr = 15/73 w/w) based lithium-ion cells. Beamline 6 A-B at the Argonne Photon Source (APS), equipped with a fixed 3° angle single element Ge detector and incident white x-ray beam was used to obtain *in operando* EDXRD spectra from CR2032-type coin cells. The coin cells were assembled with a Li-metal counter electrode, and 1.2 M LiPF<sub>6</sub> in EC/EMC (3:7 w/w) + 10 wt% FEC as the electrolyte, and underwent electrochemical cycling at a ~C/8 rate. Lattice parameters corresponding to the spectral peaks were derived from the energy of the diffracted x-rays. Variations in the average Gr layers-spacing during lithiation of the pure Gr half-cell was used to calibrate an “average layer spacing vs. state of lithiation” in the Gr-component. The lattice parameters of different phases formed upon lithiation and de-lithiation of Si and graphite were estimated which can, thus, be used to obtain the extent of lithiation in Si and in graphite quantitatively at every state-of-charge. Future work will extend our approach to full cells with graphite and Si/Gr as anodes and quantitatively estimate the discrepancies in amount of Li<sup>+</sup> lost from cathodes to amount of Li<sup>+</sup> actually inserted into the anodes. The fraction of Li<sup>+</sup> trapped in the interfacial layers can provide a better understanding of the nature of the solid electrolyte interphase (SEI) on the negative electrode and the origin of capacity loss.

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## Nanoscience and Nanotechnology

### A-65

#### Three-dimensional Bicontinuous Nanostructured Porous Metals

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Nanomaterials generally and nanoporous metals specifically have fascinated scientists due to their exotic and promising chemical and physical properties over nanoparticles and bulk counterparts. Although nature is rich in porous materials, nanoporous metals are exception. They mainly come from synthetic routes and their fabrication is challenging due to the surface energy constraints. The finite-size effect and metallic nature of the nanoporous metals placed them at the forefront as potential platforms for many technological applications (e.g., sensing, catalysis, environmental remediation, biotechnology, filtration, protective coatings, energy related devices, etc.). As a result, a number of fabrication techniques have been developed to prepare these interesting nanostructures [1–5]. To date, the fabrication of 3D bicontinuous nanoporous metal structures still represents a real challenge.

Herein, we present a well-established strategy for the preparation of multifunctional nanostructured 3D porous metals based on the combination of inorganic-chemistry and electrochemistry. Through the application of the developed strategy a variety of 3D bicontinuous nanoporous metal structures were successfully fabricated and their potential applications in sensing, catalysis, energy storage, accelerator components, and next-generation x-ray optics are currently undergoing.

*AF thanks the Advanced Photon Source, Argonne National Laboratory for providing the fund to attend the meeting.*

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## A-66

### Small Particles and Even Bigger Data Problems in Bragg Coherent Diffractive Imaging

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Advances at third generation synchrotron sources and free electron lasers as well as developments of reconstruction algorithms open up exciting opportunities for Bragg Coherent Diffractive Imaging (BCDI). By mapping the reciprocal space in the vicinity of a given reciprocal lattice point, three-dimensional projections of the deformation field and even functional properties such as the electric dipole inside a nanocrystal can be reconstructed with the aid of iterative phase retrieval algorithms.

One of the critical challenges during BCDI experiments is the search for an isolated and stable nanocrystal within an ensemble of differently oriented neighbors. User-operated experiment suffers from loss of speed due to the nature of control and feedback requiring operator to search in the reciprocal space "blindly" leading to the accumulation of large and unwarranted datasets over a long period of time.

A traditional solution around this problem is to design ideal test samples with close to perfect roughness profile and well-defined separation of the nanocrystals in real space. While always being a good idea for technique development, this approach puts limitations on studying *in operando* devices or mesoscale features. A more reliable solution is the *Big Data* based approach where instead of collecting excessive amounts of data and analyzing post-experimental, one can implement search-reject-and-map algorithms to increase information-to-quality ratio while decreasing the time of experiment.

We shall discuss criteria and potential implementation of automated workflow to address current challenges for faster-and-smarter data collection at BCDI dedicated beamlines.

## A-67

### X-ray Scattering for Nanoscale Dimensional Metrology in the Semiconductor Industry

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The semiconductor industry continues to scale integrated circuits to ever small dimensions and more complex nanostructures. Current integrated circuits contain minimum feature sizes on order of 10 nm with spacings less than 40 nm. Each microprocessor contains billions of transistors that all must work to function properly. The semiconductor industry depends on in-line metrology for process control to enable high product yields. Current metrology methods use scattering from broadband visible light to probe the nanostructures and are reaching fundamental limits. The industry is looking towards smaller wavelengths, and in particular x-rays, for next generation metrology. NIST has been working closely with the semiconductor industry to develop critical dimension small angle x-ray scattering (CDSAXS) as a potential solution. CDSAXS is a variable angle, transmission small angle scattering measurement where single crystal diffraction is done on a periodic nanostructure. The nanostructure is the "atom" and the periodic grating is the "lattice". The average shape of the nanostructure is inversely solved from the scattering pattern. We will report on the latest results with CDSAXS.

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A-68

### Nanoscale Structure of a Protein-DNA Conjugate with Its Surrounding Counterion Distribution

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Quantification of the structure of the ionic environment around biomolecules is crucial to understanding their functions and interactions with other solution bound species [1]. In this study we elucidate the structure of the ionic atmosphere surrounding a novel class of biomaterials composed of a protein core densely functionalized with DNA. These bio-constructs couple the cell transfection capabilities of a dense DNA architecture with the enzymatic activity of a protein core thereby resulting in a potentially powerful therapeutic with a dual functionality [2]. Since the diffuse counterion cloud surrounding these protein-DNA (Prot-DNA) conjugates is not amenable to traditional x-ray characterization techniques, we employ Anomalous small-angle x-ray scattering (ASAXS) to probe the distribution of Rb<sup>+</sup> ions surrounding the Prot-DNA. A combined analysis of SAXS profiles collected at several x-ray energies below the Rb K-edge (15.2 keV) when coupled with classical density functional theory (DFT) calculations yields the Rb<sup>+</sup> ion distribution profile around Prot-DNA with nanometer resolution. This combined ASAXS-DFT approach also enables a determination of the sub-molecular features of these bio-constructs which are inaccessible through other techniques.

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A-69

### Sequential ALD Nanolaminate Devices for X-ray Optics

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Atomic layer deposition (ALD) can be used to deposit sequences of films of two or more materials, with controllable thickness in the range from few to tens of nm ("nanolaminates"). Deposition with ALD is highly conformal and isotropic, generating layers of decreasing roughness or roughness saturation at low levels in the nm range. Here we report on the onset of a study to fabricate Fresnel zone plates and other diffractive devices for x-rays (e.g., diffraction gratings and multilayer Laue lenses-MLLs) using ALD deposition of sequences of low-Z – high-Z materials as a bottom-up fabrication approach. Examples of films are BN, Al<sub>2</sub>O<sub>3</sub> for low-Z materials, and W, Pt, Ir for high-Z materials. The thickness of the ALD films in the sequence can be varied to satisfy relations such as imposed by device rules (e.g., a thickness variation proportional to the square root of the order number in the sequence) by simply counting the ALD cycles during the deposition. The present approach uses sequential ALD around Si pillars or within cylindrical holes etched into Si wafers using a Bosch process, after a smoothing procedure is applied. The resulting structures are batch-processed to form membranes containing the micro-optics devices. Zone plates with smallest zones of 5–20 nm are possible, with practically no limits in absorber/phase shifter material thickness, making them fit for ultra-high focusing resolution in high energy x-rays. Moreover, by using sequences of 3 or more layers with different atomic numbers and densities, one can approach graded index kinoforms, with very high focusing efficiencies. Composite zone plates and zone plate with integrated beam stops are also possible with this approach.

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## Other

### A-70

#### Ambient Vibration Measurement in APS Sector 29

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Prior to the installation of the intermediate energy x-ray beamline in Sector 29 of the Advanced Photon Source (APS) a survey of the ambient vibrational noise present in the sector was conducted. Beamline 29-ID-C,D specializes in angle-resolved photoemission spectroscopy (ARPES) and resonant soft x-ray scattering (RSXS). Ambient vibration levels caused by building and floor dynamics, air and water handling systems, and electro-mechanical equipment in this sector are important for scientists and engineers in the design of beamline equipment. Ambient vibration noise levels in Sector 29 were measured in the vertical and horizontal directions.

This poster summarizes the results of this survey, which were originally published in the APS Light Source Notes [1]. The vibration levels in Sector 29 are compared to standard vibration criteria [2]. The pre-installation vibration measurements are compared to more recent measurements on the constructed beamline. Finally, the vibration levels measured in Sector 29 are compared to vibration levels measured in other sectors of the APS.

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### A-71

#### Diverse Sample Environments for a Diverse User Community at 11-ID-B

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In order to collect high quality data at a high-energy x-ray beamline, many factors go into designing the experiment. Sample preparation and detector selection are obviously important, but choosing/creating the correct sample environment is essential. 11-ID-B, the world's first

dedicated PDF beamline, offers a broad spectrum of sample environments for measurements involving vast temperature and pressure ranges, reactive gas chemistry, electrochemistry, and has multi-probe capabilities with the Combined PDF/IR cell.

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

### A-72

#### Deploying GSAS-II for Automated Area-detector Powder Diffraction and Pair Distribution Function Data Reduction

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The general purpose crystallographic package GSAS-II [1] has been deployed at beamlines 17-BM, 11-ID-B and 11-ID-C in a collaboration between the Structural Sciences (SRS) group and Computational X-ray Science (CXs) group. Code has been added to stream diffraction images directly to GSAS-II for immediate correction and integration and optionally determine the pair distribution function. This automation of the data processing greatly reduces the time between data acquisition and analysis. Due to the advanced visualization capabilities of GSAS-II, users can better follow the course of their experiments. They can judge easily the success of their experiment and intervene, if needed. This new computational feature reduces significantly effort needed from beamline staff, while obtaining nearly instantaneous results significantly improve users' likelihood to perform successful experiments.

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

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**A-73*****In situ* Spectroscopy of Highly Active and Stable Fe-based Nano-structured ORR Fuel Cell Catalysts**

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Fuel cells (FCs) are a clean and efficient technology and have the potential to revolutionize energy production and transportation. Their wide scale implementation will reduce greenhouse gas emissions and dependence on oil and, if coupled to renewable hydrogen, will eliminate greenhouse gas emissions. The major factor preventing widespread use of commercial PEMFCs is the heavy use of precious metals like platinum (Pt) in the catalysts. In particular, the oxygen reduction reaction (ORR) catalyst must use a heavy loading of Pt due to the slow kinetics of the ORR.

However, non-precious metal (NPM) ORR catalysts holds great promise to replace expensive Pt with much cheaper and Earth abundant elements like iron or cobalt. We achieved a significant breakthrough discovering the new method of preparation of Fe-based ORR which produces catalysts inferior to Pt controls only by 20 mV. According to preliminary spectroscopic results samples represent a carbon wrapped iron carbide nanoparticles. Similar materials were already noted to be a new, highly promising class of ORR catalysts with performance approaching that of commercially available Pt catalysts. Our produced materials are highly stable in acidic environments required for PEM FCs.

Our next step will be to explore the synthesis parameters for new materials, effect of nano-structuring using different surfactants, calcination temperatures and environments, effect of dopants (Co, Mn, P) will be investigated. In depth characterization of the active sites will be achieved using a variety of highly sensitive techniques *ex situ* and *in situ* under catalytic conditions.

*Synthesis and spectroscopic studies were supported by CRDF Global under the 2015 U.S.-Russian University Research Competition (OISE-16-62146-0).*

**A-74****Vibration Noise and Isolation of the Experiment Floor at the Advanced Photon Source**

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The Advanced Photon Source (APS) plans to upgrade to a higher brilliance x-ray source. Because of the APS upgrade, many synchrotron instruments will have higher spatial resolution, and therefore be more sensitive to vibration noise. To prepare for the upgrade, we started to survey the current state of vibration noise and isolation of the experiment floor at the APS. The survey includes measurement of ambient vibrations of the experiment floor at each beamline, and the effectiveness of vibration isolation by the isolation joint between the APS walkway floor and experiment floor. We assessed the magnitude of ambient vibrations by comparing them to the Institute of Environmental Sciences and Technology (IEST) vibration criteria standards, the VC curves [1]. For a standard, we used the VC-G curve, which designates an extremely quiet facility. In comparison to VC-G, the mean horizontal vibration magnitudes, in the 5–100 Hz spectrum, were less than VC-G, however for the vertical direction only the ranges 5–15 Hz, 35–55 Hz and 70–100 Hz were less than VC-G [2]. For the isolation joint, the mean transmissibility for the horizontal direction was less than 50% for the majority of the 1-100 Hz spectrum, and for the vertical direction was less than 20% for the entire 1–100 Hz spectrum. However, the magnitudes of ambient vibrations on either side of the isolation joint were similar, which suggests that flanking vibrations or local noise sources are present on the experiment floor. Future surveys will attempt to locate vibration noise sources and flanking paths.

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**A-75****SAS2018—International Meeting on Small Angle Scattering**

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SAS2018 will be hosted by the Advanced Photon Source at the Grand Traverse Resort in Traverse City, Michigan on October 7–12, 2018. The conference will be centered on three themes addressing the critical needs of society in energy, environment and health. Sessions under energy can include: energy storage and production, renewable energy and catalysis. There will be environmental area sessions on transport in porous media, surface properties and nanogeoscience. Complex nucleoproteins, soft-matter self-assembly and cellular machines are included in the health theme. There are a number of areas to be covered, which are important in all of the themes such as: combined *in situ* techniques, dynamics, kinetics, time resolved, and advances in modeling and data analysis. Educating the community especially for SAS teachers is a common goal. The organizing committee will entertain suggestions for addition topics.

SAS2018 will serve to showcase the progress of small-angle scattering research in North America, including the many instruments at user facilities across the continent and the rich variety of research taking place. We expect that high-level researchers from around the world involved in all aspects of small-angle scattering research will attend and draw even greater participation in this conference by U.S. researchers. The conference will also help to raise the visibility of the importance of small-angle scattering investigations in research and industry. We chose this venue to promote strong interactions among the conference participants and to return this conference to a more intimate setting, in the style of a Gordon Research Conference.

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

**A-76****The APS Upgrade: Building the World's Leading High-brightness Hard X-ray Synchrotron Facility**

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The APS is undergoing a major upgrade in aim to build the world's leading high-brightness hard x-ray synchrotron facility. This paper overviews the goal and the upgrade

project scope; introduces our current developments on beam dynamics; hardware design and testing results. Many innovation technologies and ideas have been developed.

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**Polymers****A-77****Enabling Thinner, Radio-opaque Bioresorbable Vascular Scaffolds Using Biocompatible Nanocomposites of Poly (L-lactide) and Tungsten Disulfide**Tiziana Di Luccio<sup>1,2</sup>, Karthik Ramachandran<sup>2</sup>, Carmela Borriello<sup>1</sup>, Francesca Di Benedetto<sup>3</sup>, Fausta Loffredo<sup>1</sup>, Tara L. Schiller<sup>4</sup>, Loredana Tammaro<sup>1</sup>, Fulvia Villani<sup>1</sup>, and Julia A. Kornfield<sup>2</sup>

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Bioresorbable Vascular Scaffolds (BVSs) are a promising new treatment for Coronary Heart Disease (CHD). In contrast to permanent metal stents, BVSs are transient implants that are completely resorbed by the body in ~2–3 years, leaving behind an artery capable of vasomotion with no incidence of fatal side effects such as Late Stent Thrombosis [1–3]. BVSs are made from the semicrystalline, biocompatible polymer poly L-lactide (PLLA), which hydrolyzes in the body to form L-lactic acid, a metabolic product processed by the body [4]. Despite PLLA's excellent biocompatibility, it is notorious for being a brittle material (fracture strain <10%) and suffers from poor radio-opacity (nearly transparent to x-rays). As a result, BVSs are nearly 2 times thicker (~150  $\mu\text{m}$ ) than metal stents (~80  $\mu\text{m}$ ) and are difficult to implant or image under x-ray guidance. The promising clinical success of the current generation of BVSs provides an impetus to make them thinner and radio-opaque, allowing a greater patient population to benefit from BVSs.

This report investigates nanocomposites of PLA and Tungsten Disulfide ( $\text{WS}_2$ ) nanotubes in enabling the next generation of thinner, radio-opaque BVSs.  $\text{WS}_2$  nanoparticles were selected due to their promising biocompatibility and excellent radio-opacity. In agreement with the literature [5,6], cytotoxicity studies performed in our group indicate that  $\text{WS}_2$  is well tolerated *in vitro* (HUVEC and HASMC cell lines). The high atomic mass of

WS<sub>2</sub> confers radio-opacity similar to that of platinum, the current standard for radio-opaque markers. The impact of WS<sub>2</sub> nanotubes (0.05 wt%) on PLLA's semicrystalline morphology was investigated using *in situ* synchrotron x-ray diffraction (APS Beamline 5-ID-D, Argonne National Labs). Solvent-cast films of PLA and PLA-WS<sub>2</sub> (~100 μm thick) were stretched at 90°C (Instron 8500 series) to 100% strain at three different extension rates (5 mm/min, 100 mm/min and 500 mm/min) with simultaneous acquisition of WAXS data. The stretching phase was followed by a 15 min annealing step to enhance crystallization. In the data set, we observe little difference in morphology between the PLA and PLA-WS<sub>2</sub> films, possibly due to the relative low concentration of WS<sub>2</sub> (0.05 wt%), but we do observe a dramatic change in morphology with extension-rate. The (110)/(200) Bragg peaks of PLA appear as isotropic rings at 5 mm/min but as highly oriented peaks at 500 mm/min. Furthermore, at higher strain rates the films were mainly amorphous during the stretching phase but they became rapidly crystalline showing intense diffraction peaks during the annealing process, with a post-stretching induction time <10s at 500 mm/min, ~60s at 100 mm/min and >100s at 5 mm/min. These data provided useful insights on the evolution of structure of PLA and PLA-WS<sub>2</sub> and helped defining the strain rate and post-stretching conditions for the next experiments, when nanocomposites with a higher concentration of nanotubes will be investigated.

Steven Weigand (beamline scientist at 5ID-D beamline at APS) is kindly acknowledged for his support during the synchrotron experiments.

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## Technique

### A-78

#### XDesign: A Sandbox for Tomographic Experiments

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Designing an experiment with x-ray computed tomography may be difficult because many techniques exist which have unique advantages and disadvantages which may fit one application better than another. Comparisons between techniques tends to be qualitative, and there may not be sufficient knowledge about materials, data acquisition methods, and object reconstruction to know which method is best. XDesign is a new Python based experiment simulator under development at the APS that can be used to plan experiments or develop new data collection and processing methods. XDesign is unique because it combines custom imaging phantoms with quantitative quality metrics so that scientists can directly compare x-ray imaging and reconstruction methods on models that represent their own unique materials.

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### A-79

#### TomoBank: A Tomographic Data Bank for Computational X-ray Science

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There is a widening gap between the fast advancement of computational methods for tomographic reconstruction and their successful implementation in production software at various synchrotron facilities. This is due in part to the lack of instrument datasets and phantoms representative of physical properties readily available to computational scientists for validation and comparison of new numerical methods.

Recent advancements in detector technology made sub-second and multi-energy tomographic data collection possible, but also increased the demand to develop new reconstruction methods able to handle *in situ* and dynamic systems that can be quickly incorporated in beamline production software.

The x-ray Tomography Data Bank or tomoBank, provides a repository of experimental and simulated datasets with the aim to foster collaboration among computational scientists, beamline scientists, and experimentalists, to help accelerate the development of tomographic reconstruction methods and their implementation in the synchrotron facility production software by providing easy access to challenging datasets and their descriptors.

At few months after its creation tomoBank already hosts over 100 data sets collected at different synchrotron facilities around the world.

## A-80

### **NXcanSAS: Standard to Store Reduced SAS Data of any Dimension**

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The communication of experimental results is common to scientific investigation. The method of presentation varies widely across investigation technique, and may stymie fundamental scientific goals such as sharing of results and replication of experiments. Even within a limited community, such as small-angle scattering, the choice of how to organize stored information is fragmented, with the result that often, the data are deposited in ad hoc form. To increase access to data produced from publicly-funded research, funding agencies are now requiring that proposals describe how data will be made available. With the increases in data volume due to higher-efficiency collection, increased experimental complexity, and larger and faster detectors, the plethora of ad hoc formats is a burden to the scientific community. Reliance on a few, well-considered standards facilitates automated processes for analysis and correlation of scientific data. Furthermore, it leads to development of common tools for data visualization and analysis, and data catalogues for access, reference, and data mining.

NXcanSAS [1] is a standard to store reduced small-angle scattering data of any dimension. It is sufficiently general that it may be used for any form of reduced SAS data in different scientific applications. The hierarchical structure of the canSAS [2] standard has been designed within the NeXus [3] data format.

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

[1] NXcanSAS: <http://download.nexusformat.org/doc/html/classes/applications/NXcanSAS.html>

[2] canSAS, <http://www.cansas.org>

[3] NeXus, <http://www.nexusformat.org>

## A-81

### **The Development of the X-ray Fluorescence Tomography at the Microprobe 2-ID-E Beamline**

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The x-ray fluorescence microscopy provides a non-destructive method to study the sample element distribution. It is widely used to measure the projective element maps of mostly thin-sliced biological and medical samples. In the past decade, with the development of the third generation synchrotron storage ring, the increase in x-ray flux enables us to examine bulk samples with the computerized tomography approach [1]. Projective element maps are measured at a collection of angles, so that 3D element distribution can be retrieved by tomographic reconstruction [2,3]. Due to the nature of the x-ray fluorescence tomography, there are two major limitations: (a) the emitted fluorescence photons tend to be absorbed/attenuated by the sample material on the way to the fluorescence detector, which is the notorious self-absorption issue and (b) the data acquisition is time consuming. In this work, we will demonstrate with a wood cell sample, the experimental optimization of the x-ray fluorescence tomography [4].

*The authors would like to thank Xiaogang Yang and Young Pyo Hong for many discussions, and Joseph Jakes for the sample supply. The experiment was performed at the 2-ID-E beamline at the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.*

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# DRIVING DISCOVERY

2017 APS/CNM USERS MEETING

CNM POSTER ABSTRACTS



## Chemistry

### C-1

#### Surface Sensitivity of Fluoroethylene Carbonate Breakdown on $\text{Li}_{15}\text{Si}_4$ Surfaces

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Silicon anodes are a promising material for lithium ion batteries due to their large theoretical capacity for storing lithium. The anode works by allowing lithium ions to intercalate into the silicon where the lithium ions are reduced. In addition to the lithium ions being reduced, unwanted side reduction reactions of the electrolyte also occur. When the electrolyte reductively decomposes at the anode surface, a solid-electrolyte interphase (SEI) is formed. Fluoroethylene carbonate (FEC) is added to the electrolyte to make a more robust SEI which prevents further electrolyte decomposition. Other researchers have determined the FEC reduction products to be  $\text{CO}_2$ ,  $\text{CH}_2\text{CHO}$ , and  $\text{F}^-$  [1]. Although the decomposition products have been discovered, the initial mechanism for the breakdown of FEC into those products is still unknown. Here FEC and its reduction products are being studied on different facets of the crystalline  $\text{Li}_{15}\text{Si}_4$  phase using density functional theory. The facets under consideration are the (100), (110), and (111) facets. Initial work has been done to determine the binding energies of FEC on the lithium silicide surface facets. Future work will determine the binding energies of the FEC reduction products. From the binding energies of the reactants and products, FEC dissociation reaction energies can then be calculated to determine on which facet SEI formation begins on the  $\text{Li}_{15}\text{Si}_4$  lithiated silicon anode.

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## Condensed Matter Physics

### C-2

#### Temperature Dependent Resonant Raman Scattering in $\text{Cu}_x\text{TiSe}_2$ Single Crystals

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$\text{TiSe}_2$  is a member of the transition metal dichalcogenide class of materials which are being extensively studied for use in next generation nanotechnology applications.  $\text{TiSe}_2$  in particular is home to many exotic correlated electron phases, such as the excitonic insulator condensate, chiral charge density wave (CDW), and superconducting state. The evolution of these many-body correlations with temperature and doping is important for understanding the mechanism of CDW and superconductivity.

We report resonant Raman spectroscopy of the shearing and breathing phonon modes in layered  $\text{TiSe}_2$  and  $\text{Cu}_x\text{TiSe}_2$  single crystals. The semi-metallic character of intrinsic  $\text{TiSe}_2$  allows for selective phonon excitation with different optical excitation wavelengths. As the temperature is decreased,  $\text{TiSe}_2$  undergoes a phase transition from normal semi-metallic state into CDW state at around 210K. We find that the in-plane shearing  $E_g$  phonon splits upon entering the CDW phase, with a softened branch being activated by 514nm and 633nm excitations and a hardened branch being active under the 785nm excitation. Raman spectra show signatures of fluctuations of the CDW amplitude mode that extend up to 100K above the thermodynamic phase transition, which is also shown to follow the suppression of  $T_{\text{CDW}}$  with Cu doping in a manner reminiscent of similar observations made in high  $T_c$  superconducting pnictides [1] and in  $\text{NbSe}_2$  [2]. We also show that Cu intercalation responsible for superconductivity in  $\text{Cu}_x\text{TiSe}_2$  causes a splitting of the out of plane breathing mode and drastically reduces its amplitude.

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## C-3

**Terahertz Emission from Ultrafast Spin and Charge Current at a Rashba Interface**

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Ultrafast broadband terahertz (THz) radiation is highly desired in various fields from fundamental research in condensed matter physics to bio-chemical detection. Conventional ultrafast THz sources rely on either nonlinear optical effects or ultrafast charge currents in semiconductors. Recently, however, it was realized that ultrabroad-band THz radiation can be produced highly effectively by novel spintronics-based emitters that also make use of the electron's spin degree of freedom [1]. Those THz-emitters convert a spin current flow into a terahertz electromagnetic pulse via the inverse spin-Hall effect. In contrast to this bulk conversion process, we demonstrate here that a femtosecond spin current pulse launched from a CoFeB layer can also generate terahertz transients efficiently at a two-dimensional Rashba interface between two non-magnetic materials (i.e., Ag/Bi). Those interfaces have been proven to be efficient means for spin- and charge current interconversion [2,3].

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## Instrumentation

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## C-4

**Development of Thick Electroplated Bismuth Absorbers for TES X-ray Detectors**

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Through their high energy resolution, cryogenic micro-calorimeters offer new scientific opportunities at synchrotron facilities. Possible applications include fluorescence microscopy and improved XAFS. We are

developing transition edge sensor (TES) detectors for energy ranges up to ~20 keV. Because TES energy resolution scales inversely with the square root of heat capacity, it is important to have an x-ray absorber with both a small heat capacity and a large x-ray stopping power. Electroplated bismuth (Bi) absorbers meet these criteria. We examine the impact of plating current density, agitation, film thickness, and seed layer thickness on the grain size, residual resistance ratio, and uniformity of Bi absorbers. Additionally, we show the result of plating Bi absorbers on a full TES device and discuss processing considerations important for successful electroplating.

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## C-5

**Simulations and Fabrication of Hard X-ray Zone Plates with High Aspect Ratios**

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Metal-assisted chemical etching (MACE) [1] combined with zone doubling [2] has been shown to be a promising method for the fabrication of zone plates with very high aspect ratio. We have used a multi-step process which first involves high resolution e-beam lithography, metal deposition and lift-off to produce the metal precursor pattern for MACE. We then followed this process with deep reactive ion etching in order to thin the wafer substrate under the zone plate region to about 10–20  $\mu\text{m}$  prior to atomic layer deposition for zone doubling. With this process, we have fabricated zone plate with 16 nm outermost zone width and 2  $\mu\text{m}$  thickness, thus achieving a very high aspect ratio up to 120. The optical performance of thick zone plates and multilayer Laue lenses is usually calculated by using coupled wave theory for a fixed grating period, extrapolating the results to the range of grating periods present in an actual optic [3]. In order to understand arbitrary optical structures, we have explored the use of multislice propagation. We show that the multislice method is able to reproduce the results of coupled wave theory for regular structures, and describe its application to optics with irregular flaws such as the actual fabrication errors that can be present in thick zone plates [4].

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

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## C-6

### X-ray Coded Aperture Masks for Edge Illumination Phase Contrast Imaging

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X-ray phase-contrast imaging (XPCi) is a promising approach for improving soft-tissue contrast and lowering radiation dose in biomedical applications. A novel x-ray phase contrast imaging technique which uses coded apertures to implement the edge illumination principle was developed at the University College London, which enables XPCi with conventional x-ray sources at low radiation dose levels acceptable for live imaging. This XPCi method removes the limitations of other phase contrast approaches, providing high resolution, high speed, low dose, and laboratory x-ray imaging capability with image quality similar to that obtained using synchrotron radiation. The method is based on two sets of gold coded aperture x-ray masks placed on either side of the imaged object.

We report on the fabrication of the gold coded aperture x-ray masks for new high-speed, quantitative x-ray phase contrast imaging system for high resolution imaging of tumors. The fabrication method is based on UV-lithography using rigid graphite as a substrate for SU-8 resist, followed by gold electroforming.

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## Materials Science

### C-7

#### The Effects of Thermal Annealing on Domain Structure in Quasicrystal Artificial Spin Ices

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Artificial spin ices (ASIs) have recently emerged as a model system for studying magnetic frustration. While most work to date has focused on periodic ASI lattices, we have focused on quasicrystal ASIs that lack translational symmetry. We used FIB milling to pattern Permalloy thin films into a P2 Penrose tiling. We used Lorentz transmission electron microscopy (LTEM) to study the quasicrystal ASIs in the as-fabricated state, after demagnetizing, and after thermal annealing [1]. The magnetic induction was mapped using the transport-of-intensity equation reconstruction from the LTEM images. From these reconstructions, we determined the magnetic configuration of each vertex in the lattice and we used OOMMF micromagnetic simulations to calculate the energy for each vertex configuration. We then calculated the total energy of the ASI by summing the vertex energies. Demagnetization in a rotating AC field produced the state with the lowest net energy and magnetization.

After annealing the quasicrystal ASI we observed the presence of domain walls within the magnetic bars, and to explore this further we performed an *in situ* TEM heating experiment in which quasicrystalline ASIs were heated gradually to ~500°C. We analyzed two different sizes of quasicrystalline ASIs in order to explore the effects of edges. Interestingly we found that the domain walls originally present in the smaller ASIs after heating had disappeared, likely due to relaxation to lower energy, and after heating a second time, significantly fewer domain walls were seen. The larger lattices, however contained a number of domain walls after thermal annealing. We will discuss the implications of these findings in detail.

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## C-8

**Halide Perovskites Doped Electrochemically by Lithium and Its Application in Ion Battery, Electrochromism and Electroluminescence**Qinglong Jiang<sup>1</sup>, Mingming Chen<sup>1</sup>, Junqiang Li<sup>1</sup>, Qiangfeng Xiao<sup>1</sup>, Xiaoqiao Zeng<sup>2</sup>, Jun Lu<sup>2</sup>, and Zhibin Yu<sup>1</sup><sup>1</sup> Department of Industrial and Manufacturing Engineering, High Performance Materials Institute, Florida State University, Tallahassee, FL 32310<sup>2</sup> Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439.

Doping is critical for junction formation in semiconducting thin-film electronics to direct the flow of charge carriers and improve their transport properties. The dopants in a form of electron donor or acceptor are typically added during deposition of the semiconductor thin films or introduced through a subsequent diffusion or implantation process. Doping can also be achieved using an electrochemical approach. We explored for the first time electrochemical doping of cesium lead tribromide (CsPbBr<sub>3</sub>). Lithium was intercalated into the reduced perovskite, resulting in *n*-type doping of the perovskite. The perovskite after the doping exhibited an improved conductivity and evolved into a dark color with an over 40% transmittance decrease from 450 to 850 nm wavelength. The doped perovskite could be used as an ETL to enhance electron injection efficiency into the perovskite crystals, resulting in bright LEDs at a low operation voltage.

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## C-9

**Electron Counting Model, Surface Reconstructions, and Surface States of Heusler Compounds**Jason Kawasaki<sup>1</sup>, Anderson Janotti,<sup>2</sup> and Chris Palmstrom<sup>3</sup><sup>1</sup> University of Wisconsin, Madison, Madison, WI 53706<sup>2</sup> University of Delaware, Newark, DE 19716<sup>3</sup> University of California, Santa Barbara, Santa Barbara, CA 93106

Gapped half Heusler compounds show great promise for the development of earth abundant thermoelectrics, half metallic ferromagnets for spin injection, and topological heterostructures. However, due to the lack of momentum resolved electronic structure measurements, the origins of the bulk bandgap in these materials remain unclear. Moreover, the surfaces and interfaces, which are critical to heterostructures, are poorly understood. Here, using the canonical 18 electron half Heusler CoTiSb, we demonstrate the existence of a bulk bandgap and dispersions in quantitative agreement with density functional theory calculations, but also metallic surface states. Using a combination of molecular beam epitaxy, angle resolved and core level photoemission, scanning tunneling microscopy, and density functional theory, we show that

surface states are formed by a surface reconstruction in CoTiSb that compensates for surface charge via creation of Ti vacancies, and minimizes Sb dangling bonds through dimer formation. Our studies, which are the first momentum resolved measurements for any finite gapped Heusler, place design constraints on Heusler heterostructures, in which parasitic conduction through trivial metallic surface states needs to be minimized.

## C-10

**Determining *Operando* Surface Structure by Combining First Principles Theory with Experimental Data**Kendra Letchworth-Weaver<sup>1,2</sup>, Alex P. Gaiduk<sup>2</sup>, I-Cheng Tung<sup>3</sup>, Dillon Fong<sup>4</sup>, Giulia Galli<sup>2,4</sup>, Paul Fenter<sup>5</sup>, and Maria K.Y. Chan<sup>1</sup><sup>1</sup> Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439<sup>2</sup> Institute for Molecular Engineering, University of Chicago, Chicago, IL 60637<sup>3</sup> Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439<sup>4</sup> Materials Science Division, Argonne National Laboratory, Argonne, IL 60439<sup>5</sup> Division of Chemical Sciences and Engineering, Argonne National Laboratory, Argonne, IL 60439

Recent advances in experimental techniques, such as *in situ* x-ray reflectivity, allow researchers to probe the structure of surfaces and thin films during growth and under electrochemical conditions. However, uniquely determining the positions of the individual atoms can be challenging because commonly employed multi-parameter fitting procedures often depend on the initial assumptions about the surface structure. This challenge is compounded because surfaces under applied bias and in contact with liquid often vary significantly from the bulk structure. First principles calculations provide a quantum-mechanical description of both the energetics and atomic structure of interfaces, allowing direct computation of x-ray reflectivity signals for comparison to experimental data. Furthermore, incorporating theory-based constraints during fitting and analysis of x-ray reflectivity data [1] determines surface structure under realistic conditions and simultaneously ensures that the so-obtained structure is energetically favorable. We present examples of this combined theoretical and experimental approach for investigation of the Al<sub>2</sub>O<sub>3</sub>-water interface as well as the (001) surface of SrTiO<sub>3</sub> during homoepitaxial growth. Future studies employing this approach will facilitate more precise engineering of devices for energy storage and conversion and beyond.

Use of 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, under Contract No. DE-AC02-06CH11357.

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## C-11

### First-principles Studies of Structural Evolution and Core-level Spectra of Li-rich Cathode Material

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In the pursuit of novel cathode materials with high Li capacities, the Li-rich oxides with Li/TM (transition metal) ratio larger than 1 have recently gained increased interest. For instance, the active role of oxygen ions in the charge compensation has been reported in layered rocksalt  $\text{Li}_2\text{IrO}_3$  [1], which serve as a model system to understand the structural response of Li-rich cathodes to Li extraction, as well the role of oxygen in compensating  $\text{Li}^+$  loss.

First-principles techniques have been well recognized for being an effective tool in elucidating the structural and chemical properties of battery materials. In this study, we employ first-principles density functional theory (DFT) to study the phase transitions of  $\text{Li}_2\text{IrO}_3$  induced by Li extraction, based on a structure enumeration scheme. The core-level spectra of  $\text{Li}_2\text{IrO}_3$  at various delithiation stages are also simulated within the first-principles theoretical framework. Both the predicted delithiation structures and core-level spectra show excellent agreement with *in situ/ex situ* experimental characterizations, such as x-ray diffraction (XRD) and x-ray absorption near-edge spectroscopy (XANES). We demonstrate in this study that first-principles approaches not only facilitate the interpretation of experimental observations, but also provide valuable insights into predicting the structural and electronic properties, which efficiently assists in the experiment design and implementation.

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## C-12

### Tribology in Full View of Graphitic Materials

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Graphitic materials are of substantial interest for tribological applications, both applications involving graphene as well as multilayer graphene (graphite). The details of how they deform at the nanoscale are not well understood because of the buried interface problem; one cannot observe with most techniques how the material is changing during sliding, only indirect consequences. A relatively new approach is to directly observe sliding within a transmission electron microscope, which allows one to see how the material deforms both plastically and elastically. This presentation will describe recent results on *in situ* experiments on graphitic materials.

## C-13

### Integrated Imaging and Multiscale Simulation to Investigate Lattice Deformations in Externally Stimulated Nanocrystals

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Despite the increasing role of nanomaterials in technology, their mechanical and dynamical properties under external stimulation are not well understood. One such problem is the pulsed laser excitation of a diverse class of nanomaterials, such as ZnO nanorods,  $\text{WSe}_2$  nanopillars, and Au-Al core-shell bimetallic nanocrystals. Another class of problems is the investigation of lattice deformations in nanostructured catalysts during multi-electron transfer processes. These constitute an important class of materials systems for catalysis, biomedical and energy applications. Understanding the temporal behavior of such nanomaterials under conditions of external stimulation is, thus, crucially important for energy research. In addition, characterizing lattice distortions can provide key insights into the behavior of nanomaterials and nanoscale interfaces.

Recently, experimental techniques have evolved to conduct time-dependent lattice dynamics measurements in nanomaterials. In particular, Bragg Coherent Diffraction Imaging (BCDI) has been used to directly

image ultrafast lattice distortions in laser-heated nanocrystals. BCDI measurements have also been successfully used to observe reversible lattice distortions in metallic nanocrystals facilitating chemical reactions at low-coordination corner and edge sites. Suitable simulation models prove to be an ideal foil to explore the underlying mechanisms behind the observed lattice deformations. With the convergence of time and length scales accessible by both experiments and simulations, we are now able to integrate experimental observations with classical molecular dynamics (MD) simulations and continuum finite element calculations to enhance the fundamental understanding of materials behavior under external stimulation.

Here, we demonstrate the machine learning and data driven approaches to integrate BCDI measurements with large-scale atomistic molecular dynamics simulations and finite element models to investigate lattice dynamics in externally stimulated nanocrystals. We will demonstrate the suitability of the workflow(s) as applied to a diverse class of materials systems and external stimulus. We show that direct comparisons between experiments and simulations are possible by using the appropriate level of theory or a combination of simulation techniques. In addition, the integrated experiment-informed simulation approach yields new insight into deformation mechanisms of nanomaterials that cannot be obtained and validated by either approach alone.

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### C-14 First-principles Modeling of Lattice Anharmonicity and Thermal Conductivity

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PbTe is an excellent thermoelectric material because of high power factor and low lattice thermal conductivity. Recent studies by Kanatzidis et al. showed significant enhancement in the ZT of PbTe doped with Na, Mg and Sr. However, fundamental understanding of the contribution of various mechanisms to the enhancement of ZT is far from satisfactory. We used recently developed compressive sensing lattice dynamics (CSLD) to investigate lattice heat transport in doped PbTe. The lattice thermal conductivity of pristine MTe (M=Mg, Ca, Sr, Ba and Pb) is calculated. Comparison between pristine and doped phases is made. The results from this study show the importance of scattering of optical phonons due to mass disorder,

and provide a quantitative explanation of lattice thermal conductivity reduction in moderately doped PbTe.

With a primary focus on properly treating extremely anharmonic systems with imaginary modes, we developed an iterative renormalization scheme with which we are able to obtain temperature-dependent interatomic force constants by taking into account temperature-dependent atomic displacements. Efficient and accurate renormalization of harmonic phonon dispersion and lattice thermal conductivity will be demonstrated for SrTiO<sub>3</sub> and Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub> thermoelectrics.

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## Nanoscience and Nanotechnology

### C-15 Detailed Characterization and Fabrication of 3D Printed Graphene/Polymer Structures for Heterojunction-devices with MoS<sub>2</sub> and Other 2D Nanomaterials

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It is known that the 2D nanomaterials (2DN) can be interfaced with another to realize heterostructures with controlled and/or expanded properties, which can be applied to achieve functional devices. Currently, such structures have been produced at nano- to micro-scale dimensions. Here we show that 3D printing of graphene/polymer composite can allow device fabrication with 2DN-heterostructures produced at larger and accessible scale, while leveraging their unique properties. For example, fusing graphene, a zero bandgap 2DN and MoS<sub>2</sub>, a semiconductor 2DN, together can produce ultrafast optoelectronic switches because of the mismatched Fermi level. As a first step towards this goal, graphene/polymer-MoS<sub>2</sub>-graphene/polymer junctions were produced via 3D printing and experiments were conducted to measure



the carrier transport characteristics. The results from carrier-transport studied at cryogenic temperatures (25 K) to room temperature were analyzed to determine transport barriers, carrier concentrations, Coulomb blockade, inter-particle capacitance, conduction mechanism and opto-electronic response. Furthermore, the effects of the mechanical strain in the 3D-printed heterostructure was investigated. We envision that these 3D printed structures with 2DNs will lead to an evolution of next-generation optoelectronic, electronics and electromechanical devices, which would be printed on-demand.

### C-16

#### All CVD Direct Growth of Large-scale Graphene and Hexagonal Boron Nitride Heterostructures

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Transfer-free and direct growth of large-scale graphene/hexagonal boron nitride (h-BN) heterostructures will be an important advancement in the development of high performance nano and optoelectronic devices. Atomically flat surface and lack of charged impurities enable h-BN an ideal substrate platform for complex 2D heterostructured circuits. However, current techniques mostly rely on the transfer (mechanical or chemical) of both h-BN and graphene to build the 2D heterostructures, which ultimately degrade their structure and properties, implying underperformance of the final devices. Here we report the direct growth of large-scale graphene/h-BN heterostructures via chemical vapor deposition (CVD). First, h-BN is directly synthesized on SiO<sub>2</sub>/Si substrates via chemical-interaction guided mechanism [1,2] followed by the deposition of a thin metal film (Cu) on h-BN/SiO<sub>2</sub>/Si substrates. Then graphene is grown via a process, which relies on the diffusion of catalytically produced carbon radicals through Cu grain-boundaries and their crystallization at the interface of Cu and h-BN/SiO<sub>2</sub>/Si dielectrics. Finally, removing the top graphene and Cu, produces the graphene/h-BN heterostructures with a sharp defect-free interface. The directly-grown, van der Waals bound graphene/h-BN heterostructures are characterized by scanning Raman spectroscopy, x-ray photoelectron spectroscopy, and transmission electron microscopy. Futuristically, this all-CVD direct growth strategy will be a transformative approach for scalable production of complex 2D van der Waals heterostructures.

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### C-17

#### Retained Carrier-mobility and Enhanced Plasmonic-photovoltaics of Graphene via Ring-centered $\eta^6$ Functionalization and Nano-interfacing

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Binding graphene with auxiliary nanoparticles for plasmonics, photovoltaics, and/or optoelectronics, while retaining the trigonal-planar bonding of sp<sup>2</sup> hybridized carbons to maintain its carrier-mobility has remained a challenge. The conventional nanoparticle-incorporation route for graphene is to create nucleation/attachment sites via "carbon-centered" covalent functionalization, which changes the local hybridization of carbon atoms from trigonal-planar sp<sup>2</sup> to tetrahedral sp<sup>3</sup>. This disrupts the lattice planarity of graphene, thus dramatically deteriorating its mobility and innate superior properties. Here, we show large-area, vapor-phase, "ring-centered" hexahapto ( $\eta^6$ ) functionalization of graphene to create nucleation-sites for silver nanoparticles (AgNPs) without disrupting its sp<sup>2</sup> character. This is achieved by the grafting of chromium tricarbonyl [Cr(CO)<sub>3</sub>] with all six carbon atoms (sigma-bonding) in the benzenoid ring on graphene to form an ( $\eta^6$ -graphene)Cr(CO)<sub>3</sub> complex. This non-destructive functionalization preserves the lattice continuum with a retention in charge carrier mobility (9% increase at 10 K); and with AgNPs attached on graphene/n-Si solar cells, we report an ~11-fold plasmonic-enhancement in the power conversion efficiency (1.24%).

**C-18****Metal Oxide Protected Lithium Anode Enabled by Atomic Layer Deposition towards Practical Applications**

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Lithium metal is considered to be the “holy grail” of battery anodes due to its ultrahigh theoretical capacity (3,860 mAh/g), low potential (-3.04 V versus standard hydrogen electrode), and very low density (0.534 g/cm<sup>3</sup>). However, dendrite growth during cycling and low Coulombic efficiency, resulting in safety hazards and fast battery fading, are significant technical hurdles that prevent the commercialization of lithium metal anodes. In this work, we used atomic layer deposition to grow conformal, ultrathin Al<sub>2</sub>O<sub>3</sub> films on lithium metal in an effort to mitigate these technical problems. We employed *in situ* QCM, for the first time, to study the growth mechanism of Al<sub>2</sub>O<sub>3</sub> on lithium and found larger growth than expected during the initial cycles followed by steady growth at the expected rate. We discovered that both carbonate and ester electrolytes show enhanced wettability on Li with ALD coatings, leading to more uniform and dense SEI formation as well as enabling stable battery operation with smaller electrolyte volumes compared to the uncoated Li. Moreover, XPS investigations and *in situ* TEM demonstrate excellent Li dendrite prevention with the robust ALD Al<sub>2</sub>O<sub>3</sub> films. As a result, ALD protected Li provides several times longer cycling life with stable Coulombic efficiency and voltage profiles than bare Li at a practical current density of 1 mA/cm<sup>2</sup>.

**C-19****Improved Performance of Graphene-silicon Solar Cells with Deposition of WS<sub>2</sub> Layers**

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Interfacing two-dimensional (2D) semimetal graphene with 2D semiconducting transition metal dichalcogenides leads to van der Waals bound structures with unique electrical and optical properties. In this work, we have designed two different atomically thin solar cell devices by (i) transferring single-layer graphene sheet onto n-type silicon (Gr-Si) and (ii) depositing few-layers of tungsten disulphide (WS<sub>2</sub>) on the Gr-Si substrate (WS<sub>2</sub>-Gr-Si) *via* chemical vapor deposition. The two devices exhibited non-linear current density-voltage (J-V) characteristics with ideality factors of 2.78 and 20.6 for the Gr-Si and WS<sub>2</sub>-Gr-Si device, respectively. The deposition of few-layers of WS<sub>2</sub> on Gr-Si resulted in a 4-fold increase in short-circuit current density

(J<sub>sc</sub>: 0.52 to 2.28 mA/cm<sup>2</sup>) and a 40% increase in the open-circuit voltage (V<sub>oc</sub>: 130 to 184 mV) for the WS<sub>2</sub>-Gr-Si device in contrast to the Gr-Si solar cell device, which lead to a 10-fold increase in the solar cell power conversion efficiency. Futuristically, this approach will be an important step towards realizing high efficiency graphene-silicon heterojunction solar cells.

**C-20****Combined Experimental-computational Approach to Determining Nanoscale Structures**Spencer T. Hills<sup>1</sup>, Alper Kinaci<sup>2</sup>, Fatih G. Sen<sup>1</sup>, and Maria K.Y. Chan<sup>1</sup><sup>1</sup>Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439<sup>2</sup>High Performance Computing Center, Northwestern University, Evanston, IL 60208

The structures of nanoparticles are difficult to determine due to their reduced symmetry compared to bulk crystal structures [1]. As such, new techniques are required to determine their structures. Various experimental and computational techniques have been proposed, but each comes with its own limitations. Computational predictions of the lowest energy structure require approximations to be made in the energy calculation and sampling of incredibly large parameter space (i.e., every possible configuration of the atomic arrangements). Although the energy calculations can be benchmarked with known energy values, and the possible structures can be efficiently sampled using heuristic global optimizers, some doubts remain in the accuracy of the computational predictions. In some cases the computationally predicted lowest energy state is actually the lowest energy state, in others it is not. Experimental characterization also presents difficulties. For example, the pair distribution function (PDF) provides information on the specific structure of a nanocluster, but is difficult to extract that data.

It has been proposed that combining multiple data types into one computational framework can reduce or eliminate these difficulties [2]. In this work, we will develop one such computational framework that uses single-objective basin-hopping to optimize energy calculated by classical force-fields (FF) using LAMMPS and the PDF residual from DiffPy. We benchmark this framework on two Au<sub>14</sub> nanoclusters (globular and planar), and compare them to a structural determination that uses one data type (i.e., using FF or PDF only). We find that the combined approach accurately determines the target structure and distinguishes between the lowest energy globular structure and a slightly higher energy planar structure, when the single data type optimization fails to do so.

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## C-21

### 2D Micro-Raman Mapping of Cell Interfaced with Graphene to Determine Surface Potential and Cellular Activity: An Ultrasensitive Biosensor for Non-invasive Cancer Diagnosis

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Success in cancer treatment is critically dependent on the diagnostic accuracy of tissue samples and the ability to monitor response and recurrence of tumor cells. On the basis of doping induced modification of phonon vibrations on graphene, we present an ultrasensitive graphene-based Raman biosensor capable of differentiating cancerous (Glioblastoma Multiforme, GBM) from normal cells (Astrocytes) at single cell resolution. Examining the effects of different cells interfaced with graphene via Raman Spectroscopy, we observed sensitive responses exhibited by GBM cells (highly p doped with a large 2D peak shift of approximately  $6.3 \text{ cm}^{-1}$ ) and Astrocytes (p doped with 2D peak shift of approximately  $2.2 \text{ cm}^{-1}$ ). This is attributed to the heightened acidic nature and the increased surface electronegativity of cancer cells. This work can be applied to other cancer cell types, particularly metastatic tumors that circulate through the blood stream and potentially be utilized as a pathological assessment tool. The high sensitivity of the device can be leveraged to characterize different grades of cancer, as in the case of brain tumors, based on their malignancy and aggressive nature.

## C-22

### Zinc Oxide Infiltration of Two-photon Polymerized Polymer Structures

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The properties of zinc oxide (ZnO) have various applications in gas sensing, semiconductors, and optics. Recently, it has been shown that poly(methyl methacrylate) (PMMA) can be infused by ZnO through the process of sequential infiltration synthesis (SiS), allowing for lithographically patterned ZnO/PMMA structures [1]. In this work, we investigate SiS of two-photon polymerized (2PP) polymers with ZnO. Energy dispersive x-ray spectroscopy (EDS) indicates an infiltration depth of approximately 1 μm in IP-L 780 photoresist thin films. Three dimensional (3D) structures infiltrated with ZnO were readily amenable to electron microscopy without the need of conductive coating with higher infiltration rates than those seen in thin films.

Use of 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, under Contract No. DE-AC02-06CH11357.

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## C-23

### Application of Ring Resonators in Astronomy

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Many important astrophysics topics, such as the study of distant supernovae and galaxies, and the lowest mass stars, rely on the observations at near-infrared (NIR) wavelengths. However, observations in the NIR are difficult due to hundreds of sky-background emission lines from atmospheric OH molecules [1,2]. Using optical ring resonators, implemented as notch-filter sets, provides a versatile and cost-effective way to solve this problem. Specifically, a series of ring resonators are needed with large free spectral range and suitable quality factor, and designed or tuned to the OH emission wavelengths. Therefore, the ability to determine the suitable design and design parameters is crucial. In our work, we use finite difference time domain (FDTD) simulations to guide designs, and fabricate devices at the Center for Nanoscale Materials, and test the devices in the ANL High Energy Physics division, as well as by collaborators in Australia. We will present the current status of ring resonator designs and test results.

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## C-24

### 3D Printing of Graphene-on-silicon Heterostructure for Energy Harvesting

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Graphene's high electrical conductivity and optical transmittance makes it attractive for integration in photovoltaic devices as an active layer and as a transparent current spreading electrode. Graphene-on-silicon Schottky junction solar cell has recently garnered enormous attention due to its potential to achieve high efficiency conversion. However, current methods to produce this heterostructure involve complicated processes including transfer of graphene onto silicon (Si) surfaces. Here we develop a method using a low-cost FDM printer to deposit a reduced graphene oxide (rGO) and polylactic acid polymer composite in controlled structures on p-Si wafers. Annealing the composite under vacuum removes the polymer and leaves an rGO-on-Si heterostructure as confirmed by Raman spectroscopy and optical microscopy. Further, we assessed the rGO-on-Si solar cell by depositing an Ohmic metal contact to Si and characterized the dark and light photovoltaic characteristics under AM 1.5G illumination. Considering the dual role of rGO as an active solar cell layer and transparent current spreading electrode, the printed solar cell device construct is expected to be cost-effective and efficient. We envision that further optimization via controlled printing of the rGO/p-Si interface geometry, transmittance-to-sheet resistance of rGO layer, and subsequent annealing process will enhance the device performance.

## C-25

### Fabrication of Power Delivery Substrate for MEMS Electrostatic Microactuators

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In the past two decades, the Micro-Electro Mechanical Systems (MEMS) have been used in applications ranging from gyroscopes and accelerometers in cell phones to autonomous self-driving cars. Stress-engineering

in MEMS is a method for inducing curvature in initially planar micromachined actuators. That can be achieved by deposition of a stressor metal (i.e., Cr layer). The Cr layer is patterned to precisely define deflection and hence motion of the stress-engineered microstructures (MicroStressBots) during electrostatic actuation [1]. The amount of metal deposited on the steering arm of these MicroStressBots [2] dictates its tip deflection and varies the pull-down and release voltages during actuation.

The operating environment or the power delivery substrate of these electrostatic microactuators consists of parallel set of interdigitated metal electrodes with a high-k dielectric layer deposited on top. The metal electrodes consist of Cr/Au/Cr (10/50/10 nm) layers of 2  $\mu\text{m}$  spacing patterned with JEOL E-Beam Lithography System. Sputtered Yttria-stabilized zirconium oxide (YSZ) of 500  $\mu\text{m}$  thickness with a dielectric constant between 20 and 27 is used as the dielectric layer. Application of a voltage waveform [2] between the two parallel set of electrodes results in coupling of capacitive force to the microrobot chassis, thus supplying power to both the Untethered Scratch Drive Actuator (USDA) for translation and the steering arm for rotation.

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## C-26

### Highly Sensitive VOCs Sensor Based on Atomic Layer Deposition of TiO<sub>2</sub> on Carbon Nanotubes

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Volatile organic compounds (VOCs) are largely used in industries as reaction intermediates for the synthesis of chemicals and in research laboratories as solvents. The probability of over-exposure to such toxic agents is very high; therefore, the development of gas sensors for early detection of toxic VOCs is necessary. So far, attempts have been focused on the development of thin-film n-type semiconducting metal oxide-based gas sensors, such as SnO<sub>2</sub>, ZnO, TiO<sub>2</sub> [1].

Our approach targets the fabrication of low-cost low-power chemi-resistive sensors based on multiwalled carbon nanotubes (MWCNTs) functionalized by atomic layer deposition (ALD) with metal-oxide (MOX). Specifically, we report the design and synthesis of high-surface-area TiO<sub>2</sub> functionalized MWCNT based sensors. Prior to ALD TiO<sub>2</sub> deposition on MWCNTs surface, we performed site-specific O<sub>2</sub>-plasma activation on the MWCNTs surface. The creation of physical active sites is an effective way to enhance and spatially control the growth of TiO<sub>2</sub>. By varying the deposition temperature during the ALD process, the morphology and crystallinity of the TiO<sub>2</sub> varies. At 175°C, the TiO<sub>2</sub> layer on the MWCNT is continuous and amorphous, while at 200°C it is crystalline.

The TiO<sub>2</sub>/MWCNT heterostructure chemi-resistive sensor arrays for the selective detection of low concentrations of different VOCs at room-temperature (RT) have been tested. The resulting TiO<sub>2</sub> (at 200°C)/MWCNT sensors operate at RT and show fast and reliable responses to benzene (C<sub>6</sub>H<sub>6</sub>) and to toluene (C<sub>6</sub>H<sub>5</sub>-CH<sub>3</sub>) while TiO<sub>2</sub> (at 175°C)/MWCNT sensors show no response. Our aim is to elucidate the mechanism by which the ALD coating increases sensitivity to the final composite materials, thus paving a way toward the fabrication of chemi-resistive sensors with high selectivity, lifetime, and reliability toward specific VOCs.

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## C-27

### Spectroscopic Imaging of NIR to Visible Upconversion from NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> Nanoparticles on Au Nano-cavity Arrays

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We use spectroscopic imaging to assess the spatial variations in upconversion luminescence from NaYF<sub>4</sub>:Er<sup>3+</sup>,Yb<sup>3+</sup> nanoparticles embedded in PMMA on Au nano-cavity arrays over a wide range of excitation intensities. The nano-cavity arrays support a surface plasmon (SP) resonance at 980nm, coincident with the peak absorption of the Yb<sup>3+</sup> sensitizer. Spatially-resolved

upconversion spectra show a 30X to 3X luminescence intensity enhancement on the nano-cavity array compared to the nearby smooth Au surface, corresponding to varying excitation intensities from 1 W/cm<sup>2</sup> to 300kW/cm<sup>2</sup>, spanning the non-linear and saturation power dependence regimes. Our analysis shows the power dependent enhancement in upconversion luminescence can be almost entirely accounted for by a constant shift in the effective excitation intensity, which is maintained over five orders of magnitude variation in excitation intensity. The variations in upconversion luminescence enhancement with power are modeled by a 3-level-system near the saturation limit, and by simultaneous solution of a system of coupled nonlinear differential equations, both analyses agree well with the experimental observations. The amplification of the excitation field is independent of the emission wavelength, suggesting the enhancement in upconversion emission is due to entirely to increased absorption by the Yb<sup>3+</sup> sensitizer. Analysis of the statistical distribution of emission intensities in the spectroscopic images on and off the nano-cavity arrays provides an estimate of the average enhancement factor independent of fluctuations in nano-particle density. As an extension of this work, to gain a microscopic view of the plasmonic upconversion enhancement, preliminary experiments using collection mode near-field microscopy were performed at the CNM in collaboration with the Nanophotonics group. We observed and spatially-resolved upconversion luminescence from individual upconverting NaYF<sub>4</sub>:Er<sup>3+</sup>,Yb<sup>3+</sup> nano-particles in single Au nano-cavities supporting a surface plasmon polariton near coincident with the Yb<sup>3+</sup> absorption.

## C-28

### Ultrafast Dynamics of Lattice Plasmon Nanocavities

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One important criteria for designing plasmonic lasers is whether the gain can overcome the loss in the system. However, quantifying the losses of plasmonic nanocavities is not straightforward, because metallic materials are absorptive and the definition of mode volume is inadequate for the unconventional cavity modes. Lattice plasmon nanocavities sustain lasing at room temperature and provide directional and spectral control of lasing signals. In this work, we have characterized the intrinsic losses of lattice plasmon nanocavities and the ultrafast dynamics of plasmonic lasing action by time

correlated single photon counting method. In contrast with femtosecond lifetime of surface plasmons, lattice plasmons exhibited a picosecond photon lifetime, dramatically slowing down the group velocity of light and providing optical feedback for lasing action. Furthermore, we identified amplified spontaneous emission (ASE) as an energy transfer channel that competes with lasing action at high pump power. The picosecond lifetime of lattice plasmons indicated the extremely low loss in the cavities, which is promising to enhance light-matter interactions on nanoscale.

### C-29

#### Optical Properties of Monolayer MoS<sub>2</sub> Nanoribbons

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Single atomic layers of transition metal dichalcogenide such as monolayer MoS<sub>2</sub> are direct bandgap semiconductors with distinct optical and electronic properties. Like in graphene, nanoribbon structures provide a lateral degree of freedom for tailoring the material's optical and electronic properties. MoS<sub>2</sub> nanoribbons are predicted to have interesting edge dependent electronic properties useful for spintronic applications, however experimental on these features work is limited. We use nanolithography techniques to create monolayer MoS<sub>2</sub> nanoribbons that exhibit size-tunable photoluminescence and anisotropic Raman scattering. Our process also allows characterization of transport properties of the nanoribbons. This approach demonstrates how dimensionality influences monolayer semiconductors, which could impact charge and valley dynamics relevant to nano-scale opto-electronic devices.

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### C-30

#### Photovoltaic and Spectral Response of Monolayer WS<sub>2</sub>/Silicon Heterojunctions

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Transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS<sub>2</sub>) and tungsten disulfide (WS<sub>2</sub>) are attractive because of their ultrathin structure and inimitable electronic band structures with unique functionalities including: indirect-to-direct bandgap transition, semiconductor-to-metal phase engineering, and the large excitonic effect. Further, the TMDs with thickness-dependent tunable optical bandgaps in the near-infrared to visible spectral range can exhibit extremely strong light-matter interactions suitable for energy harvesting devices such as solar cells. Currently, the WS<sub>2</sub>-based solar cells are realized *via* micromechanical exfoliation or transfer of two-dimensional (2D) WS<sub>2</sub> layers onto conventional 3D bulk semiconductors. Here, we report the photovoltaic response of WS<sub>2</sub>/Si heterojunction solar cells developed *via* chemical vapor deposition (CVD). The photoresponse and quantum efficiency of the WS<sub>2</sub>/Si-based solar cell devices are also investigated in order to further understand the junction characteristics (trap states and recombination mechanisms). The present study opens avenues for the direct integration of CVD-grown monolayer WS<sub>2</sub> with Si-based heterojunctions for efficient optoelectronic devices.

### C-31

#### Scanning Tunneling Microscopy Study of Cu<sub>2</sub>O Surface Facets

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Cuprous ions and defects on Cu<sub>2</sub>O surface facets play important roles in the catalytic reactions, such as CO oxidation and methanol synthesis. Unfortunately, accurate reaction pathways, especially the active sites for the chemical reactions on the surface, are still unclear due to the lack of knowledge on the chemisorption and dissociation of reactant molecules on Cu<sub>2</sub>O surfaces. Studies mainly focused on defining the surface structures and adsorption of molecules have been performed by first principles density functional theory (DFT) calculations, low-energy electron diffraction (LEED) [1–3],

and ultrahigh-vacuum scanning tunneling microscopy (STM) [4,5]. However, apart from the  $\text{Cu}_2\text{O}(100)$  surface [5], other crystalline surfaces, such as (111) and (110), which have been suggested as more chemically active for catalysis [6,7], have been scarcely investigated. Herein we discuss a combined STM-DFT study of  $\text{Cu}_2\text{O}(111)$  and (110) surfaces to determine the stable structure under either oxygen-poor or oxygen-rich condition. The combined approach allows us to also determine the structure of surface defects.

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# DRIVING DISCOVERY

## 2017 APS/CNM USERS MEETING

ESRP POSTER ABSTRACTS



**ESRP-1****The Self-assembly and Chirality of Histidine on a Copper (111) Substrate**C. Turner<sup>1</sup>, S. Roberts<sup>1</sup>, A. Carani<sup>1</sup>, D. Covelli<sup>1</sup>, D. Crossland<sup>1</sup>, J. Cuthbert<sup>1</sup>, K. Beardsley<sup>1</sup>, and N. Guisinger<sup>2</sup><sup>1</sup> Glenbard East High School, Lombard, IL 60148<sup>2</sup> Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

The exploration of molecular self-assembly of biological molecules can provide insight into an array of biological processes that occur throughout nature. Amino acids are chiral molecules, which, in nature, are only present in the left-handed orientation (L enantiomer). It is hoped that increasing the understanding of amino acid molecular self assembly L and D (right-handed orientation) enantiomers can lead to advancements in pharmaceuticals, medical nanoscale diagnostics, and even the understanding of the origins of life on Earth. This study investigated the molecular self assembly of the amino acid histidine on Cu(111). Using Scanning Tunneling Microscopy (STM), necessary for its capability to image at atomic resolution, we sought to determine if there were similarities between previously characterized amino acid superstructure assemblies to that of histidine on Cu(111). We found that, like many other amino acids, histidine formed chiral superstructures.

**ESRP-2****Using X-ray Diffraction to Determine the Crystal Structure of an Unknown Crystal**Zornitsa Aleksieva<sup>1</sup>, Harpreet Auby<sup>1</sup>, Jill Prigge<sup>1</sup>, Miraj Shah<sup>1</sup>, Matt Vlasaty<sup>1</sup>, Rudolph Webster<sup>1</sup>, Wayne Oras<sup>1</sup>, Yu-Sheng Chen<sup>2</sup>, Sean Griesemer<sup>2</sup>, Binhua Lin<sup>2</sup>, Grass Wang<sup>2</sup>, and Tiejian Chang<sup>2</sup><sup>1</sup> Hoffman Estates High School, Hoffman Estates, IL 60169<sup>2</sup> ChemMatCARS, University of Chicago, Chicago, IL 60637

Some of the most important materials in our world are comprised of crystal structures. Crystallography is a well-established research tool in chemistry, biology, and material science. Over the last century, improvements in x-ray crystallography have provided 3-dimensional structures of molecules at atomic resolution, which is necessary for understanding chemical and biological systems and their resultant mechanisms. For example, structure and function are intertwined in biology, and changing one often has great effects on the other. Crystals in biology are involved with determining protein structures. In biochemistry, this is important as it leads to the development of drugs that can inhibit or promote enzymes. In the field of microelectronics, determining crystal structure allows for the advancement of technology in integrated circuits. Determining crystal structures also allows us to differentiate between allotropes. One example

of this is looking at the differences in the arrangement of carbon atoms in graphite and diamonds to understand the causes of their respective properties. X-ray crystallography can be used to determine many crystal properties from resultant electron density maps, such as bond length and particle spacing. Quantitative information derived from the experiment can give way to various chemical, physical, and biological properties. Through this, the interactions between the respective particles in the crystals can be determined and a function of the crystal can be cataloged.

**ESRP-3****Continued Observations from X-ray Elemental Analysis of Ash Tree Species Related to the Growth of Emerald Ash Borer Populations**R. Winarski<sup>1</sup>, Q. Jin<sup>1</sup>, J. Jakes<sup>1</sup>, O. Antipova<sup>1</sup>, C. Cannon<sup>2</sup>, and E. Horan<sup>3</sup><sup>1</sup> Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439<sup>2</sup> Morton Arboretum, Lisle, IL 60532<sup>3</sup> Lemont High School, Lemont, IL 60439

For the last couple of summers, a pest devastated our area and killed millions of trees in America—the Emerald Ash Borer (EAB). This small beetle traveled here in wooden packing crates from Asia and has been destroying the ash tree populations across the country for over 10 years. The larvae of the invasive Emerald Ash Borer live in and feed off of the ash trees' vascular cambium region, making them unable to transport water and nutrients up and down the trunk. Some species of ash are more susceptible to the beetle, while others do not attract it.

The purpose of this study is to analyze cells from different types of ash trees—some borer-resistant and some not—and to determine the concentration of different elements throughout the layers of bark. The findings in this experiment may help researchers understand why some species are more resistant to the EAB than others. This information may help scientists protect non-resistant ash trees from future invasions.

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**ESRP-4****X-ray Crystallography of Hen Egg-white Lysozyme with and without Ligands**

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The structure of proteins can be affected by binding different ligands to them. Chicken egg white lysozyme is an important protein in protecting the egg from bacterial infections. N-Acetylmuramic acid (NAM) and N-Acetyl-D-glucosamine (NAG) are known amino sugars they are commonly found in bacterial cell walls. They are typically arranged in a regular, alternating pattern. NAM and NAG are present in both gram-positive and gram-negative cell walls, but are much more prominent in gram-positive cell walls. This research solved for the structure of chicken egg white lysozyme with and without NAM or NAG sugars.

**ESRP-5****Secrets of the Pyramids: Analyzing Paint Samples of a Mummy Cartonnage to Reveal Socio-economic Status**

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Ancient Egyptians are credited with creating the world's first synthetic paint, Egyptian Blue Frit, which is cuprorivaite ( $\text{CaCuSi}_4\text{O}_{10}$ ) based. This was a relatively inexpensive blue paint. During that same era, one of the only natural blue pigments available was derived from lapis lazuli, which primarily contains the mineral lazulite ( $(\text{Na,Ca})_8(\text{AlSiO}_4)_6(\text{S},\text{SO}_4,\text{Cl})_{1-2}$ ), which resulted in a very soft and expensive paint. In Egyptian culture, blue represented fertility, the Nile River, and wealth. Due to its important symbolism, blue paint was often used in tombs for wall decorations and mummy cartonnages in order to represent the importance of the deceased.

Naperville Central High School has its own Egyptian mummy, dating from the Ptolemaic period (55–30 BCE). Its cartonnage is elaborately decorated, with traces of blue paint. Our objective was to utilize the Advanced Photon Source so that we could determine whether this blue paint was Frit or lapis-based. We can evaluate this by examining the APS analysis for presence or absence of copper, sodium, aluminum, and sulfur, elements unique

to the two pigment bases. If there are high concentrations of copper but not of the other three, then it will be likely that Frit was the main component of the paint used to decorate the cartonnage; if we find a higher prevalence of sodium, aluminum, and sulfur then it will be more likely that a lapis-based paint was used for the decoration. Analysis of the results is ongoing; however, we observed very rich fluorescence spectra with highly localized trace element concentrations. Based on what the results reveal we will gain better insight on the status of the mummy's family and possibly region of origin.

**ESRP-6****Micronutrient and Porosity Study of Monoculture and Undisturbed Soil**

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The focus of the research was to determine differences in the elemental composition and physical structure of mono cultured and untampered soils using EXAFS (extended absorption fine structure) and XANES (x-ray absorption near-edge structure) spectroscopy techniques.

**ESRP-7****Comparing and Contrasting Surgical Meshes in Various Specimens Using Synchrotron X-ray Tomography**

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The goal of the experiment was to evaluate the differences between various sizes and shapes of surgical meshes, using synchrotron x-ray tomography. The propagation phase contrast-based x-ray synchrotron imaging techniques provided detailed 3D images that allowed the group to virtually dissect the surgical mesh and observe its structure in detail. A comparison between the different sizes and shapes of surgical meshes allowed the lab team to analyze the underlying reason for the differences in the healing processes, enabling the lab team to fully discover the relationship between the structure and function of the mesh samples. The samples were scanned using a medium resolution setup to study the general morphology of the specimens. Areas of interest were further scanned at a high resolution. Each medium resolution scan takes from 15 to 30 minutes, depending on the sample horizontal size, and each high resolution scan takes approximately

40 minutes. The use of the synchrotron at the Advanced Photon Source enabled visualization of enhanced detail not achievable through conventional methods.

### ESRP-8

#### Threonine: An Amino Acid Autonomous Molecular Assembly

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Our project is to utilize scanning tunneling microscopy to study the molecular self-assembly of chiral amino acids, specifically aspartic acid, on metal surfaces. The study of molecular self-assembly is a key component to nature and a phenomenon that is utilized by nanoscale research. Chiral molecular assemblies are of interest for drug development, catalysis, and sensing. Amino acids are chiral molecules that are the building block of proteins. One of the unsolved mysteries in physics, chemistry and biology is why life has chosen to only use one chirality of amino acids in the synthesis of proteins. The goal of this study is to further our understanding of chiral molecular assembly on single crystal metal surfaces. In particular, we explored the hypothesis that racemic mixtures will lead to selective chiral assemblies. We utilized the scanning tunneling microscope to characterize these molecular assemblies at the atomic-scale. This proposal combines fundamental elements of physics, chemistry, and biology.

### ESRP-9

#### Soil Mineral Composition and Its Effect on Biological Mineral Composition

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With the recent community concerns in Chicago Public Schools and other cities like Flint, MI regarding high lead levels in the water, students are concerned about possible toxins that may be present in the green spaces located near their homes and schools. We investigated the concentration of elements for life in several soil and leaf samples taken from local area parks. Our students participated in Argonne National Laboratory's Exemplary Student Research Program from Schurz High School in the 2016–2017 school year. They collected soil and grass samples from area parks and green spaces from various city locations. The students used x-ray fluorescence

microscopy at beamline 2-ID-D at the APS to study the elemental components and concentrations of these samples. Our team worked under the guidance of our Argonne mentor, Robert Winarski from the x-ray Microscopy Group at the Center for Nanoscale Materials, and receiving assistance in sample preparation and data analysis from Olga Antipova, the 2-ID-D beam line operator. We examined five soil and leaf samples and evaluated the elemental content and concentrations in each.

### ESRP-10

#### Observing the Effects of Diets High in Sugar on the Concentration of Trace Elements in Teeth

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“Diseases of Civilization” is a term used to describe various non-contagious and non-genetic illnesses that can occur due to a mismatch between our anciently-derived human genome, which has been little changed over the past 200,000 years or so, and diets and lifestyles commonly associated with cultural industrialization. One particularly well-known problem is the high sugar content of diets in the industrialized world. Diets high in sugar have been linked to a number of different human illnesses, such as obesity, type 2 diabetes, and tooth decay.

In this experiment, we will use synchrotron radiation to determine the effect of a diet high in sugar on the concentration of trace elements in rat teeth. The concentration of various trace elements in teeth has been linked to environmental or dietary exposure, and can have an effect on the physical and chemical properties of teeth. There is a well-established causal link between a diet high in sugar and tooth decay, and some evidence to show that dental caries (tooth decay) has an impact on the chemical composition of teeth, but to our knowledge no research that studies the effect of a high sugar diet on the chemical composition of teeth.