



# 2018 APS/CNM USERS MEETING

## POSTER ABSTRACTS

A# = Advanced Photon Source abstracts

C# = Center for Nanoscale Materials abstracts

ESRP# = Exemplary Student Research Program abstracts





2018 APS/CNM  
**USERS MEETING**

APS POSTER ABSTRACTS



## Chemistry

### A1

#### Internal Atomic-scale Structure, Band Alignment, and Charge Transfer Dynamics of ZnTe/CdSe Core/Shell Quantum Dots

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Heterostructured nanomaterials (i.e., core/shell quantum dots, quantum dot-metal oxides, heterostructured rods) are ideal high efficiency solar energy chromophores because of the broad absorption spectra, excellent photostability of quantum dots, as well as their promising potential to increase the conversion efficiency above the Shockley-Queisser limit. The aim of this project is to unravel the internal atomic-scale structure, band alignment and charge transfer dynamics of Type II ZnTe/CdSe core/shell quantum dots (CSQDs). To achieve this goal, a multitude of static and ultrafast characterization tools, including femtosecond-resolved laser spectroscopy and picosecond resolved x-ray absorption spectroscopy are used.

Our static EXAFS results at the Zn and Se K-edges confirm the presence of pure zinc blende (ZB) ZnTe and CdSe phases in the core-shell quantum dots. On the other hand, EXAFS at the Cd and Te K-edges indicate the presence of an intermediate CdTe layer at the core-shell interface. Such interface layer was suggested in the literature, but unambiguous element-specific analysis was lacking so far. Initial ps-resolved XAS results show clear transient features at both the Se and Zn K-edges. When compared to a static difference spectrum, it is evident that the transient cannot be explained by a simple shift of the ionization edge. A first qualitative analysis indicates contributions from photoinduced charge transfer and band filling/depletion to the transient XANES spectrum, as well as structural rearrangements affecting the higher-energy transient XANES/EXAFS spectra. We are currently performing FEFF calculations to disentangle the various processes and obtain a more quantitative picture of charge transfer dynamics. Laser induced heating of the sample may contribute to the apparent red shift observed at both edges. For the laser fluences employed we expect temperature increases of the nanoparticle between on the order of ~100–300 K. Heat diffusion calculations are underway to estimate the nanoparticle cooling times. Heat controlled static XAS experiments will be conducted to

estimate the magnitude of this effect. Further ultrafast XAS studies on the Cd and Te edges and fs optical transient absorption studies will provide a full picture of the charge separated state in ZnTe/CdSe CSQDs.

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### A2

#### Mapping the Electrochemical Double Layer at the Graphene-water Interface with Resonant Anomalous X-ray Reflectivity

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Electrochemical energy storage is driven by the formation of a capacitive electrochemical double layer (EDL) at the electrode-electrolyte interface. A complete understanding of the atomic-scale structure of the EDL would enhance the ability to optimize energy storage in capacitive devices. Gouy-Chapman theory for the EDL predicts a diffuse ion profile near electrode surfaces under dilute electrolyte conditions. This theory is often assumed in the analysis of many electrochemical studies, but the diffuse nature of the EDL has not been confirmed by experimental observation. We aim to determine the applicability and limits of Gouy-Chapman theory to the EDL by probing the element-specific adsorbed ion structure as a function of electrode potential and electrolyte concentration using resonant anomalous x-ray reflectivity. Here, we present preliminary *in situ* electrochemical studies of Rb<sup>+</sup> ion adsorption at the graphene-water interface. The results show a deviation from the ideal diffuse profile predicted by Gouy-Chapman. We explore the complexity of the observed EDL and implications of these findings.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Midwest Integrated Center for Computational Materials (MICCoM), the U.S. Department of Defense through the NDSEG program, and the Ryan Fellowship from the Northwestern International Institute for Nanotechnology. X-ray reflectivity measurements were performed at the Advanced Photon Source at ANL. The Advanced Photon Source is supported by the U.S. DOE/BES.

### A3

## X-ray Spectroscopy of Iron-based Catalysts for Oxygen Reduction

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While it has been reported that fuel cells can have 50–55% efficiency versus their 15–25% gasoline internal combustion engine counterparts, they also face several challenges that prevent wide scale integration into the energy sector. One of the largest challenges is the use of platinum. This precious metal is used in both the anode, where hydrogen fuel gets oxidized, and at the cathode, where oxygen gets reduced. Our work focuses on replacing the platinum in the cathode, which has up to 10x higher loading of platinum, with an iron-based catalyst. Fe-based catalysts were prepared starting from the readily available Fe<sup>2+</sup> salt and were shown to produce upon (900–1000°C) calcination Fe-carbide and Fe metallic nanoparticles coated with graphene sheets. This material has high stability in both acidic and alkaline environments compared to the nitrogen coordinated iron systems previously reported [1]. XAS analysis demonstrated that Fe centers are mostly in oxidation state Fe<sup>0</sup> which is in agreement with Fe-carbide and Fe metal nano-particles composition. *In situ* XAS showed change in the oxidation state of Fe centers at the catalytic conditions with oxygen present and applied reducing potential. Fe K $\beta$  XES was used to assess the spin state via main peak and coordination environment of Fe via cross-over transition. Carbon coordination typical for Fe-carbide was noted. While nitrogen containing aromatics was used in samples preparation we did not detect the presence of FeNx species implicated in catalytic activity of other Fe-based oxygen reduction systems. Obtained spectroscopic data will be used for further optimization of the catalytic performance of this system.

[1] Y. Hu, L. Zhong, J.O. Jensen, and Q. Li (2016). "Graphene layer encapsulated metal nanoparticles as a new type of non-precious metal catalysts for oxygen reduction." *Asia-Pacific Journal of Chemical Engineering* **11**: 382.

### A4

## High-capacity Sodium Peroxide Based Na–O<sub>2</sub> Batteries with Low Charge Overpotential via a Nanostructured Catalytic Cathode

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Rechargeable metal–air batteries, especially the nonaqueous Li–O<sub>2</sub> batteries, are recognized as one of the most promising techniques for next-generation energy storage owing to their high theoretical specific energy. However, one of the biggest challenges facing the Li–O<sub>2</sub> battery is the large charge overpotential, which results in low round-trip efficiency and poor cycle life. Therefore, an efficient oxygen evolution reaction (OER) catalyst is required to reduce the charge overpotential in the Li–O<sub>2</sub> system. Alternatively, via substitution of lithium by sodium, Hartmann et al. reported a rechargeable Na–O<sub>2</sub> battery with a very low charge overpotential of 0.2 V, even without any catalyst employed on the cathode support. Such low overpotential is mainly due to the relatively high conductivity of the discharge product, sodium superoxide (NaO<sub>2</sub>). In contrast, the formation of LiO<sub>2</sub> in a Li–O<sub>2</sub> cell is very difficult because of its unfavorable thermodynamics. The formation of NaO<sub>2</sub> is accomplished in a one-electron transfer reaction:



From an energy density point of view, the one-electron transfer process (forming superoxide) has a theoretic specific energy (1108 Wh kg<sup>-1</sup>) that is drastically lower than that of a cell with peroxide as discharge product via a two-electron process (1605 Wh kg<sup>-1</sup>):



With almost equal Gibbs free energy of formation shown in reactions 1 and 2, NaO<sub>2</sub> and Na<sub>2</sub>O<sub>2</sub> are both thermodynamically possible discharge products in a Na–O<sub>2</sub> cell, with Na<sub>2</sub>O<sub>2</sub> being slightly more favorable at standard conditions. In fact, sodium peroxide (mostly as hydrates) based Na–O<sub>2</sub> batteries have been reported. However, the results are ambiguous and the overpotentials are large (~1.6 V). Here, we have applied Pd nanoparticles as catalysts to promote the formation–decomposition of the sodium peroxide and substantially reduced the charge overpotential of such Na<sub>2</sub>O<sub>2</sub> based cells to ~0.5 V.

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## A5

## Understanding the Structural Dynamics of Bismuth-based Cathodes in Solutions of Alkyl-imidazolium Ionic Liquids, under Conditions for Electrochemical CO<sub>2</sub> Reduction

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Bismuth-based cathodes deliver high efficiency and selectivity for CO<sub>2</sub> reduction to CO, when used in organic solutions containing alkylimidazolium-based ([Im]<sup>+</sup>) ionic liquids such as those having 1-butyl-3-methylimidazolium ([BMIM]<sup>+</sup>) or 1-ethyl-3-methylimidazolium ([EMIM]<sup>+</sup>) as their cation. The reduction of CO<sub>2</sub> to CO is an energetically uphill process that requires the transfer of two electrons (2e<sup>-</sup>) and two protons (2H<sup>+</sup>) into the thermodynamically stable CO<sub>2</sub> molecule. Mechanistic studies have shown that [Im]<sup>+</sup> cations such as [BMIM]<sup>+</sup> can act as both proton donors and catalytic promoters during CO<sub>2</sub> reduction at the Bi-electrolyte solution interface. Likewise, it has been demonstrated that Bi itself is critical to this catalytic process. However, only recently it was discovered that Bi electrodes undergo significant structural transformations in [Im]<sup>+</sup>-containing solutions, under conditions of potential that favor the reduction of CO<sub>2</sub>. *In operando* x-ray reflectivity measurements conducted at the APS, using well-ordered Bi (001) thin films (~6 nm-thick) in acetonitrile solutions containing [BMIM]OTf (100 mM), showed that by scanning the potential negatively from open circuit conditions (~ -0.3 V vs Ag/AgCl) native bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>) gets reduced to metallic Bi<sup>0</sup>. At increasingly negative potentials, right before the onset potential for CO<sub>2</sub> activation (i.e., near -1.5 V) the Bi (001) Bragg peak reflectivity unexpectedly begins to drop, and a ~60% decrease is seen as the potential reaches -1.9 V. This loss of Bi (001) reflectivity is the result of changes in both coverage (i.e., lateral domain size of Bi (001) crystallites drops by ~40%) and film thickness (i.e., 4–10% decrease); these changes are driven by the strong binding of [BMIM]<sup>+</sup> cations to the negatively charged Bi surface which leads to the formation of Bi•••[BMIM]<sup>+</sup> species that migrate from the electrode surface, according to the results of ReaxFF

and DFT simulations. Remarkably, the decrease in Bi (001) Bragg peak reflectivity is reversed almost entirely during a subsequent anodic scan (voltammetry scan rate = 10 mV/s). This work addresses the possible implications that this structural evolution and ‘cathodic corrosion’ of Bi electrodes may have on the mechanism of CO<sub>2</sub> activation at the Bi-[Im]<sup>+</sup> interface.

## A6

## Diarylmaleimide-based Crystalline Solids

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Photo-responsive metal crystalline solids are an appealing class of materials for a wide variety of applications including separations, advanced sensors, drug delivery, data storage. By incorporating light-responsive molecular switches into solid crystalline structures, such as metal organic frameworks (MOFs) and co-crystals, one can afford external control over the physical properties of the system. This presentation will describe recent efforts to integrate light sensitive diarylmaleimides (DAMs) into MOF linkers and co-crystals. In general, DAMs, similar to diarylethenes, can undergo a reversible ring-closing isomerization in both solution and solid state. Previous studies have also demonstrated that hydrogen bonding with the oxygen on the maleimide based backbone can disrupt conjugation, effectively turning off the photochrome. Since co-crystals are synthesized by non-covalent interaction of two different molecules, certain synthon interactions with the maleimide backbone can potentially permanently deactivate the crystalline solid. Unlike co-crystals, MOFs are organic linkers coordinated to metal centers creating empty voids which can be filled with guest molecules. However, we believe a similar deactivation of the DAM can potentially be seen in MOFs when the guest molecules interact with the malimide in the pore. This creates an exciting material where the photoactive form can indicate whether the pore is free from guest molecules. Therefore, we propose the importance of designing both co-crystals and MOFs that contain DAMs due to the potential of changing the overall photo reactivity of the crystalline material due to secondary molecules.

## A7

**Focused MHz Pink Beam for X-ray Emission Spectroscopy**

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X-ray emission spectroscopy (XES) involves the excitation of a core electron into the continuum and the measurement of the spectrum of the fluorescence emitted in the relaxation process to fill the core hole. Among the XES spectra,  $K\alpha$  (1s2p) and  $K\beta$  (1s3p) spectra are highly sensitive to the spin states while the valence to core (vtc) spectra offer direct information of occupied valence orbitals and emerge as a powerful tool for the ligand identification, bond length, and structural characterization in coordination compounds. However, the vtc feature is typically two orders of magnitude weaker than  $K\alpha$  emission lines, making it hard to collect, especially for transient species.

To overcome the difficulty, a pink beam capability was achieved recently at sector 7 of the APS synchrotron at Argonne National Laboratory. A water-cooled flat mirror is used to reject higher harmonics, and beryllium compound refractive lenses (CRLs) are utilized to focus the reflected fundamental beam (pink beam) to an around  $40\mu\text{m} \times 10\mu\text{m}$  elliptical spot at sample target that matches the laser spot size used for photoexcitation. With a flux around  $10^{15}$  photons per second, non-resonant XES spectra were taken on Iron(II) Ferrocyanide and on photoexcited iron(II) tris(2,2'-bipyridine). We could reproduce previous measurements with only a fraction of the acquisition time, demonstrating the ability to measure high quality spectra of low concentration species.

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## A8

**Probing Adsorption Interactions in High Valence Metal-organic Frameworks by *in situ* Single Crystal X-ray Diffraction**

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The crystallographic characterization of framework–guest interactions in metal–organic frameworks enables the location of guest binding sites and provides meaningful information on the nature of these interactions, allowing the correlation of structure with adsorption behavior. Herein, techniques developed for *in situ* single-crystal x-ray diffraction experiments on porous crystals have enabled the direct observation of CO<sub>2</sub> adsorption in the open metal site of Fe<sub>3-x</sub>M<sub>x</sub>O clusters (X=0, 1, 2) in PCN-250. PCN-250 is a metal–organic framework that can possess trivalent and bivalent metals in the cluster [1]. The single crystal samples were characterized before and after activation in N<sub>2</sub> at 423 K and after CO<sub>2</sub> adsorption. Interestingly, the CO<sub>2</sub> binding is stronger to the bivalent metals than to the trivalent metals, indicating orbital interaction plays a bigger role in the gas-open metal site interaction than the static electric force. To the best of our knowledge, this work is the first single-crystal structure determination of a trivalent metal–CO<sub>2</sub> interaction and the first crystallographically characterized open metal site for trivalent metals.

*We acknowledge the support from the Advanced Photo Source on beamline 15ID-B of ChemMatCARS Sector 12.*

[1] D. Feng, K. Wang, Z. Wei, Y.P. Chen, C.M. Simon, R.K. Arvapally, R.L. Martin, M. Bosch, T.F. Liu, S. Fordham, D. Yuan, M.A. Omary, M. Haranczyk, B. Smit, and H.C. Zhou (2014). *Nature Communications* **5**: 5723.

## Condensed Matter Physics

### A9

#### Structural Comparison of the Metallic and Insulating Interface at the $\text{LaCrO}_3/\text{SrTiO}_3$ Heterojunction

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We investigated the properties of the  $\text{LaCrO}_3/\text{SrTiO}_3$  (LCO/STO) interface grown by molecular beam epitaxy (MBE). We find that by varying the growth temperature, the formation of a quasi-two-dimensional gas (q2DEG) can be controlled. Using surface x-ray diffraction data obtained at the Advanced Photon Source, we compare the structure of both insulating and metallic samples. We find that the structure of both is remarkably similar, suggesting that mechanism for the formation of the q2DEG is not structurally dependent.

### A10

#### GISAXS Studies of Self-assembled Gold Nanoparticles at the Liquid-vapor Interface

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Grazing incidence x-ray small-angle scattering (GISAXS) and *in situ* x-ray reflectivity (XRR) were used to study: (1) unfunctionalized (bare) Au nanoparticles (AuNPs), (2) DNA-functionalized Au nanoparticles (DNA-AuNPs), and (3) polyethylene-glycol-grafted Au nanoparticles (PEG-AuNPs) at the air-liquid interface. Both bare AuNPs and DNA-AuNPs adsorb to a Langmuir monolayer of DPTAP (1,2-dihexadecanoyl-3-trimethylammonium-propane) but bare AuNPs display higher degree of the in-plane order. The presence of salts, such as KCl, NaCl or  $\text{K}_2\text{CO}_3$  in the aqueous subphase leads to formation of the crystalline PEG-AuNPs monolayers at the air-liquid interface, and the degree of in-plane ordering depends as well as the hexagonal lattice spacing depend on the salt concentration.  $\text{MgCl}_2$  or  $\text{CaCl}_2$  salts, on the other hand, induce formation and 2D ordering of the DNA-AuNPs monolayers.

### A11

#### A Nanoscale View of Assisted Ion Transport across the Liquid-liquid Interface

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The extractant-assisted transport of ions from aqueous to organic bulk phases is investigated by thermally arresting the extraction process, then characterizing ion-extractant complexes at the interface with x-ray measurements. X-ray measurements reveal that trivalent ions Y and Er are promptly transported to the organic side of the interface and positioned within a condensed inverted bilayer phase of ion-extractant complexes. Divalent Sr remains temporarily on the water side of the interface. Chemical analysis shows that both divalent and trivalent ions are extracted from the aqueous to the organic phase, though trivalent Y and Er ions are extracted with greater efficiency than divalent Sr. The extraction mechanism for divalent Sr must include a second step in the mechanism that has not yet been observed experimentally. This second step may be line tension driven interfacial budding. A simple theory for budding of reverse micelles at the interface has both quantitative and qualitative correspondence with values and trends in the solvent extraction literature.

**A12**

**Suppression of the Magnetic Order in CeFeAsO: Non-equivalence of Chemical and Hydrostatic Pressure**

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We studied the suppression of the magnetic order in CeFeAsO due to the application of chemical and hydrostatic pressure by means of energy- and time-domain Mössbauer spectroscopy as well as x-ray diffraction experiments. We found a similar change in the crystallographic features for both pressures but qualitatively different magnetic behaviour.

We obtained a linear suppression of the magnetic hyperfine field to zero between 0 and 40% As by P-substitution level while the magnetic hyperfine field is reduced by ~25% between 0 and 4.5 GPa followed by a subsequent suppression to 0 at 5.2 GPa.

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**A13**

**X-ray Diffraction to Probe Orthorhombic Domain Detwinning and Elastoresistance on Single Crystal Ba(Fe<sub>0.975</sub>Co<sub>0.025</sub>)<sub>2</sub>As<sub>2</sub> under *in situ* Tunable Uniaxial Stress**

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Underdoped BaFe<sub>2</sub>As<sub>2</sub> exhibits both a nematic and antiferromagnetic transition which result in orthorhombic twin domains and an in-plane electronic anisotropy. In the orthorhombic state, uniaxial stress can be used to detwin the system and induce additional lattice distortion. Here we present x-ray diffraction data on a single crystal sample under *in situ* tunable uniaxial stress, where we demonstrate the ability of our stress apparatus to change the domain state and lattice constants of the sample while simultaneously measuring resistivity. This allows for the first measurement of elastoresistivity coefficients in orthorhombic phase, which cannot be determined without the microscopic structural information obtained by x-ray diffraction measurements.

**Environmental Science and Geology**

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**A14**

**Anthropogenic Aerosol Microparticulates Measured Middle East**

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Environmental aerosols are one of the most ubiquitous hazards to human health in the world today. Aerosols present a global risk to human respiratory health and are not restricted to geographic or state boundaries [1]. Monitoring of aerosol concentrations is an important metric for determining air quality for areas of high and low population density and areas of minimal to extreme pollution. Without the high flux and broad energy range of beamline devices the low surface density of aerosol samples is invisible to spectroscopic measurements. Additionally the inherent characteristics of x-ray atomic fluorescence provide a rigorous and linear calibration for standard comparison to determine sample concentrations. These devices have proven reliable measures of particulate concentrations from 10 um to sub-micron particle size distributions [2]. Synchrotron x-ray sources are vital to the continued advancement of environmental aerosol science both for public health and monitoring

of pollution sources. We present environmental aerosol concentrations for deployed samplers to the Middle East, with a focus on anthropogenic lead and other heavy metal particulate concentrations.

*The authors would like to acknowledge the efforts and invaluable assistance of Albert Macrander and Michael Wojcik with beamline support.*

- [1] Cahill, C.F. (2003). "Asian aerosol transport to Alaska during ACE-Asia." *Journal of Geophysical Research: Atmospheres* **108**(D23).
- [2] Barberie, S.R., Iceman, C.R., Cahill, C.F., and Cahill, T.M. (2014). "Evaluation of different synchrotron beamline configurations for x-ray fluorescence analysis of environmental samples." *Analytical Chemistry* **86**(16): 8253–8260.

## High Pressure

### A15

#### Studies of Magnetism in Dysprosium under Extreme Pressures

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The magnetic and valence state of dysprosium have been investigated under high pressure up to 1.4 Mbar using synchrotron Mössbauer spectroscopy, x-ray magnetic circular dichroism and x-ray absorption techniques. With applying pressure, Dy's magnetic ordering temperature changes drastically while remaining tetravalent. At 10 K the hyperfine magnetic field of Dy remains almost constant with increasing pressure up to 141 GPa, showing the robustness of the magnetism. With applying pressure, the magnetic ordering temperature changes drastically. At pressures of 120 GPa, magnetic ordering temperature rises to almost room temperature.

### A16

#### An Integrated Portable Online Sample Observation, Ruby Fluorescence and X-ray Absorption Measurement System

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Synchrotron x-ray techniques are important for high-pressure research. However, there are only few beamlines truly optimized for high-pressure experiments. One mission of COMPRES at Argonne has been building preferred access to existing, primarily non-high-pressure beamlines, where high pressure experiments can be performed, but specialized infrastructure is lacking. The sample chambers used for high-pressure diamond anvil cell (DAC) experiments are in general smaller than 500  $\mu\text{m}$ . Therefore, accurate measurements with focused synchrotron beam typically require on-axis high-resolution video microscope for sample viewing, and online pressure measurement system, which are often not available at non-high-pressure synchrotron beamlines. A long working-distance lens system with large magnification is necessary for viewing and positioning such small samples. Due to the limited space near sample stage, the viewing system must be moved out from the x-ray path when collecting data. In addition, an online ruby fluorescence spectrometer is essential in every experiment in which data is acquired at more than one pressure. A Rigaku xPin Detector is attached to the optical system to collect 2D x-ray image. Here, we report on the status of development of portable spectroscopy system for DAC experiments at the non-high-pressure APS beamlines. The system is capable of viewing DAC samples and measuring ruby fluorescence spectrum utilizing modular Navitar microscope components and OceanOptics spectrometer, with the emphasis on portability and ease of alignment. With this system, based on class II laser which does not require enclosure or interlock, we are able to easily view the samples with adjustable magnification controlled by motor (max 60x zoom) and accurately measure (0.39 nm spectral resolution) ruby fluorescence signal in a DAC with 1 s data collection time for 10 micrometer ruby sphere.

### A17

#### X-ray Emission Spectroscopy at High-pressure, High-temperature Conditions

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The spin-state of iron in Earth-forming iron bearing phases is important for understanding processes in the deep Earth. Many high-pressure studies of the spin state of iron in iron-bearing oxides have been conducted in recent

decades, some involving x-ray emission spectroscopy (XES) [1–4], whereas others employed Mössbauer spectroscopy [3,5,6]. However, only a few studies have been performed at high-temperature conditions [7,8] due to the technical difficulties.

Here we report our recent success in further developing the capability to perform XES at high-pressure and high-temperature conditions, using a combination of a diamond anvil cell and double-sided laser-heating. The technical details of the system, including beamline configuration, detectors, shielding, background reduction, software development, and sample preparation will be discussed.

An example of XES data collected at pressures above 1 Mbar, and temperatures up to 2500 K will be shown.

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- [4] Ozawa et al. (2011). *Phys. Rev. B* **84**.
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## A18

### 16-ID-D: High Pressure Spectroscopy Beamline at HPCAT

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The structural, electronic and magnetic properties of materials under high pressure are of fundamental interest in physics, chemistry, materials science, and earth sciences. The 16-ID-D beamline of the High Pressure Collaborative Access Team (HPCAT) at the Advanced Photon Source (APS) is dedicated to high pressure research using x-ray spectroscopy techniques typically integrated with diamond anvil cells. The beamline provides x-rays of 4.5–37 keV, and current available techniques include x-ray emission spectroscopy, inelastic x-ray scattering and nuclear resonant scattering [1,2].

Firstly, we discuss on the particular requirements and instrumentations for x-ray spectroscopic methods under high pressure. We then present several examples to illustrate the recent progress in high pressure XES, NRS and IXS studies at HPCAT, followed by a discussion on recent developments include XRS spectrometer with a polycapillary full lens, cryostats for low temperature and high pressure XRS and NRIXS.

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

## A19

### Recent Developments at the Partnership for Extreme Xtallography Program

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The Partnership for eXtreme Xtallography (PX<sup>2</sup>) program is a research initiative focusing on high-pressure diamond anvil cell research, supported by the Consortium for Materials Properties Research in Earth Sciences (COMPRES). PX<sup>2</sup> is a collaboration between the University of Hawaii at Manoa and GeoSoilEnviroCARS (GSECARS), located at the Advanced Photon Source (APS) experimental station 13-BM-C. This beamline provides focused x-rays at 29 keV energy, and a unique 6-circle heavy duty diffractometer, optimized for a variety of advanced crystallography experiments including interface studies, powder and single crystal structure determination, equation of state studies and thermal diffuse scattering. Multiple auxiliary experimental capabilities, including online ruby fluorescence pressure determination, Raman spectroscopy, and remotely-controlled resistive heating, are available for high-pressure research. Diffraction studies at P-T conditions of more than 150 GPa and 2000 K have been carried out at PX<sup>2</sup>, and several materials of interest to Earth's deep interior have been studied. These new capabilities are available to all researchers interested in studying deep earth materials through the APS general user proposal system.

*PX<sup>2</sup> was supported by COMPRES under NSF Cooperative Agreement EAR-1606856 and by GeoSoilEnviroCARS through NSF grant EAR-1634415 and DOE grant DE-FG02-94ER14466. 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.*

## Instrumentation

### A20

#### Fabrication and Performance of Diamond Refractive Lenses for Hard X-ray Applications

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The next generation light sources such as diffraction limited storage rings and high repetition rate free electron lasers (FELs) will generate x-ray beams with significantly increased peak and average brilliance. These future facilities will require x-ray optical components capable of handling large instantaneous and average power densities while tailoring the properties of the x-ray beams for a variety of scientific experiments. In this paper we report on research and development of a single crystal diamond compound refractive lens. Diamond lenses presented here are fabricated by femtosecond-laser cutting and subsequent polishing. Grating interferometry measurement data of these lenses had been performed at the Advanced Photon Source (Argonne). We also report on diamond lens packaging and alignment of the CRL stack.

### A21

#### Real-time *in situ* Metrology of an X-ray Adaptive Mirror Using an Array of Interferometric Absolute Position Sensors

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The demand for higher resolution x-ray imaging in scientific applications is driving the need for smaller and more stable focal spot sizes in x-ray beamlines for the next generation of brighter and more coherent x-ray sources (e.g., LCLS-II, ALS-U, NSLS-II, APS-U, ESRF and SIRIUS). These stringent requirements can be met by the use of adaptive/active optics to compensate the continuous changes of the mirror shape due to heat loads from the x-ray beam, environmental changes, actuator hysteresis, material micro-creep, mounting distortion and other disturbances. Currently, these adaptive mirrors are operated open-loop (i.e., without direct *in situ* feedback). The mirror shape is measured *ex situ* to determine the actuator influence functions and then fine-tuned in the beamlines using the actual x-ray focal spot size as a feedback loop or by using a dedicated invasive wavefront sensor. These feedback options are typically no longer available once the beam diagnostics have been replaced by the experimental

sample in the beamline, leaving the beamline blind to any subsequent changes in mirror shape.

We propose and demonstrate a real-time *in situ* metrology system using an array of absolute interferometric fiber sensors with sub-nm precision and noise performance (ZYGO's new ZPS™ system) [1,2] which can enable the real-time closed loop control of such mirrors in the beamline, thereby enabling the real-time control of focal spot size and location. We use an 18" Fizeau to measure and optimize the shape of a 500 mm long piezo-drive bimorph mirror and compare these measurements to simultaneous direct measurements of the *reflecting surface* of the mirror by the sensor array. The sensors are mounted in a stable independent metrology frame which holds two parallel linear arrays of 19 sensors each with a sensor spacing of ~23 mm. These two arrays straddle a ~16 mm wide central rectangular aperture in the metrology frame which provides access to the mirror surface for a simultaneous Fizeau measurement. We present details of the sensor system, the measurement setup and the results of the comparison.

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[2] <https://www.zygo.com/?/met/absolutepositionmeasurement/zps.htm>

### A22

#### Full-field *in situ* Nano-tomography Activity at the Advanced Photon Source

V. De Andrade, A. Deriy, M. Wojcik, D. Shu, D. Gürsoy, S. Bean, T. Bicer, M. Wolfman, A. Glowacki, T. Mooney, K. Peterson, K. Fezzaa, C. Jacobsen, and F. De Carlo

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

A Transmission X-ray Microscope (TXM) [1] was developed and is performing for more than 4 years full-field nano-tomography at the Advanced Photon Source beamline 32-ID at the Argonne National Laboratory. This instrument, combining flexibility and performance, provides unique capabilities for *in situ* and *in operando* experiments for broad materials science applications. It benefits from the in-house development of cutting-edge high resolution and high efficiency grating x-ray optics, mechanical components and a suite of software including Tomopy and other based on machine learning to push the limit of 3D nano-imaging while reducing total x-ray dose. *In situ* heating and nanomechanical testing capabilities have also been developed. It operates either with a moderate spatial resolution (60 nm) and large field of view of (~60 μm) or at very high spatial resolution (16 nm) at a smaller field of view (~10 μm). The present poster will give an overview of the capabilities of the instrument and show some of the

most innovative applications that emerged from first years of operation. The fields of battery research, metallurgy, concrete industry and neurosciences will be covered, with a special emphasize on the 4D evolution of materials at the nano scale.

- [1] V. De Andrade, A. Deriy, M. Wojcik, D. Gürsoy, D. Shu, K. Fezzaa, and F. De Carlo. "A new Transmission X-ray Microscope for nano-scale 3D imaging at the Advanced Photon Source." SPIE Newsroom.

## A23

### Development of Fast-framing Hybridized X-ray Imaging Detector for "single shot" Experiments

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The capabilities of modern x-ray light sources have opened up new areas of research in the study of *in situ* fast processes. Irreversible processes or "single shot" experiments are challenging since they require detectors that can obtain a succession of x-ray images within the time frame of the process in question. This requires high sensitivity, wide dynamic range x-ray detection at frame rates approaching the bunch repetition rates of modern light sources. However, the capability to do such research is limited by the current state of detector technology.

Sydor Technologies, in collaboration with Cornell University is advancing the development of the Keck PAD, a novel fast framing hybridized x-ray imaging detector developed by the Cornell Detector Group [1]. The Keck-PAD detector is proven capable of acquiring up to 8 successive x-ray images at frame rates of  $\sim 7$  MHz with single x-ray (e.g., @10keV) sensitivity and with a dynamic range exceeding  $10^3$  x-rays/pixel/frame. These performance features have been demonstrated by experiments at CHESS [2]. The functionality of the detector system is being expanded by reengineering its hardware and software, and by investigating new sensor materials able to detect x-ray energies above 20 keV [3]. A general overview of the system development and test results will be presented.

Support provided by the U.S. DOE Office of Science, Office of Basic Energy Sciences under the SBIR/STTR award DE-SC0013234 and U.S. DOD Defense Threat Reduction Agency under Contract No. T152-002-0090.

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## A24

### Advanced High-resolution Integrated Optical System

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Raman and optical spectroscopy *in-situ* at extreme high pressure and temperature conditions relevant to the planets' deep interior is as a versatile tool for characterization of a wide range of properties of minerals essential for understanding the structure, composition, and evolution of terrestrial and giant planets. Here we show updated construction on a conceptually-new, user-friendly, integrated system for worldwide users at APS combining advanced Raman and optical spectroscopy tools adopted for studies of materials *in situ* at static and dynamic extreme P-T conditions in the diamond anvil cell and newly synthesized materials at ambient conditions with a high spatial resolution.

## A25

### Radio-frequency Scanning Tunneling Microscope (RF-STM): A Strong Resistant to External Current's Interference to the Conventional Tunneling Current

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When coupling an external advanced light source, such as x-ray, to an STM, the Induced electrons would strongly interfere with the tunneling current of an STM, which is typically used for the STM tip scanning feedback system. This interference presents difficulty for stable scanning in an environment where x-ray or an external electron beam is present. Here we present a new design of an STM, where the tunneling resistance becomes part of a predefined circuit system that forms a resonance

frequency around 800 MHz. With this predefined circuit system that incorporates the tunneling resistance, we demonstrate the detected power and phase of the particular resonance frequency is resistant to the external electron beam flux, which has the potential of replacing the conventional tunneling current for scanning feedback.

## A26

### ***In situ* Hard X-ray Characterization for Growth of Complex Metal Oxide Thin Films**

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The amorphous to crystalline structural transformation is the fundamental physical process that underpins thin film growth methods based on solid phase epitaxy (SPE) in complex oxide materials systems. The structural transformation includes the nucleation and growth of crystalline phases with crystallographic orientations that are templated by the substrate. SPE is a versatile thin film growth method in which materials systems with diverse compositions can be grown in the amorphous phase and post-annealed to form epitaxial films on a wide variety of substrates. We are developing new instrumentation to probe the atomic-level processes that drive the re-ordering of amorphous layers to a crystalline phase. A sputter deposition chamber with the built-in capability for *in situ* hard x-ray characterization of thin film surfaces will be installed at Station 12-ID-D of the Advanced Photon Source at Argonne National Laboratory. This instrumentation will incorporate a focused synchrotron x-ray beam that will enable studies of nucleation and growth phenomena at relevant length and time scales.

## A27

### **SoftGlueZynq: Custom Electronics for Beamlines**

**Tim Mooney and Kurt Goetze**

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SoftGlueZynq is the combination of a Linux processor running EPICS and an FPGA loaded with custom and user programmable electronics, with good communication between the two. We will show the general architecture, a sample of typical use, and some data-acquisition components including a histogramming scaler, an interferometer recorder, and a multichannel scaler.

*This work was supported by and 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.*

## A28

### **Xspress 3 Mini Digital Pulse Processor**

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Xspress 3 Mini is a fast digital pulse processor designed for use with solid state detectors. It utilises the same successful data processing algorithm as Xspress 3, but in a much smaller form factor. The analog front end has been significantly redesigned to allow users to switch the electronics easily between detectors. Recent software developments enable the user to calibrate onto any pulse-reset type detector via a graphical user interface in just 3 clicks. EPICS and TANGO drivers are available in the relevant software repositories.

Xspress 3 Mini has been used to read out both silicon drift diode (SDD) and germanium (Ge) detectors with dramatic improvements over the standard readout system. Data presented here shows Xspress 3 Mini is capable of output count rates of 4 MHz in SDD and almost 2 MHz in Ge.

## A29

### **Hard X-ray Transition-edge Sensor Spectrometer for the Advanced Photon Source**

**Orlando Quaranta<sup>1,2</sup>, Sunil Bean<sup>1</sup>, Lisa M. Gades<sup>1</sup>, Antonino Miceli<sup>1</sup>, Umeshkumar M. Patel<sup>1</sup>, Daikang Yan<sup>1,2</sup>, Douglas A. Bennett<sup>1</sup>, William B. Doriese<sup>1</sup>, Joseph W. Fowler<sup>1</sup>, Johnathon D. Gard<sup>1</sup>, John A.B. Mates<sup>1</sup>, Kelsey M. Morgan<sup>1</sup>, Daniel R. Schmidt<sup>1</sup>, Daniel S. Swetz<sup>1</sup>, and Joel N. Ullom<sup>1</sup>**

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We present the status of a hard x-ray (up to 20 keV) transition-edge sensor (TES) spectrometer being developed for the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). The spectrometer will consist of two interchangeable application-specific TES arrays fabricated at ANL, which will be read out with microwave-multiplied SQUIDs fabricated at NIST. Two TES arrays will target applications in hard x-ray emission spectroscopy (XES) and x-ray absorption fine structure (XAFS). High-resolution XES measurements of the  $K\alpha$  and  $K\beta$  emission lines can give precise information on the molecular orbitals and population of the electronic bands important in bonding, magnetism, and electronic properties

of the transition metals and other heavy elements. XAFS can provide detailed chemical and structural information about very dilute components of a sample when moderate energy resolution TES are combined with pre-filtering x-ray optics. The XES array will consist of ~100-pixels optimized for energy resolution at low count rate. The XAFS array will consist of ~100-pixels optimized for high-count rates at modest energy resolution. Details on the instrument, such as sensor design, readout electronics and cryogenic solutions, will be provided.

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### A30

#### Design and Development Progress at the Nanopositioning Support Lab for APS Operations and Upgrade Project

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Nanopositioning techniques present an important capability to support the state-of-the-art synchrotron radiation instrumentation for the APS operations. To facilitate the development of nanopositioning techniques, the APS has equipped laboratories for the assembly and characterization of nanopositioning devices. The APS Nanopositioning Support Lab is located at APS Building 401 L1119 and L1120. The mission of the Nanopositioning Support Lab is to provide engineering and technical support to enable the world class performance of nanopositioning instruments for APS operations and research as well as for APS Upgrade project. A brief summary of the recent design and development activities at the APS Nanopositioning Support Lab is presented in this poster [1–6].

*This work was supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02 06CH11357.*

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### A31

#### Development of a Miniature X-ray Emission Spectrometer (miniXES) for Simultaneous Multi-color Emission Studies of the Non-resonant X-ray Emission Spectroscopy (XES) and Sequential Resonant XES for Multiple Edges/Elements

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The miniXES style of x-ray emission spectrometer was designed to use flat crystals, in a pseudo-Johann or pseudo-von Hamos configuration, to get a spectrum in a single shot without having to scan an analyzer crystal [1]. *In situ* calibration and readily swappable crystals to change energy range are hallmarks of the design, but the design targeted individual samples of small size, and user demand for higher efficiency and larger sample clearance has increased since inception. In particular, for those who are studying *in situ* catalysis, high pressure and imaging, there is a need to upgrade to a system with improved clearance and improved collection efficiency.

In this talk, I will discuss ongoing developments in the design of the next generation of miniXES by using more crystals and larger pixel array area detector to improve the clearance and efficiency. In combination with the Advanced Photon Source Upgrade (APS\_U), we expect to improve the efficiency ~500x after APS\_U. Furthermore, I will discuss the methodology of using a miniXES-style spectrometer for simultaneous non-resonant XES for multiple emissions, and sequential resonant XES at multiple edges/elements. The experimental results of simultaneous non-resonant XES of Fe K $\beta$  and Cu K $\beta$ , and sequential resonant XES of Fe K $\beta$  and Cu K $\beta$  under the same experimental conditions will be presented. These developments open up the revenue for time-resolved non-resonant XES at multiple edges/elements simultaneously, and *in situ/operando* study of resonant XES at multiple edges/elements sequentially.

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**A32****Senis Hall Probe Speed Dependence Issues**

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An extensive test of a Senis 2-axis Hall probe was done at the Advanced Photon Source using the Undulator A device. Strong dependence of the measurement data on the speed of the sensor is observed. Discussion of the possible reason of such dependence is provided.

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**A33****Progress Towards Ultrafast Detectors for GHz Hard X-ray Imaging**Junqi Xie<sup>1</sup>, Robert Wagner<sup>1</sup>, Zhehui Wang<sup>2</sup>, Joshua Wright<sup>3</sup>, John Katsoudas<sup>3</sup>, Marcel Demarteau<sup>1</sup>, Chen Hu<sup>4</sup>, Xuan Li<sup>2</sup>, C.L. Morris<sup>2</sup>, L.P. Neukirch<sup>2</sup>, Carlo U. Segre<sup>3</sup>, Yanhua Shih<sup>5</sup>, Thomas A. Smith<sup>5</sup>, Lei Xia<sup>1</sup>, Liyuan Zhang<sup>4</sup>, and Renyuan Zhu<sup>4</sup><sup>1</sup> Argonne National Laboratory, Argonne, IL 60439<sup>2</sup> Los Alamos National Laboratory, Los Alamos, NM 87545<sup>3</sup> Illinois Institute of Technology, Chicago, IL 60616<sup>4</sup> California Institute of Technology, Pasadena, CA 91125<sup>5</sup> University of Maryland, Baltimore County, Baltimore, MD 21250

High-speed imaging is one of the most important techniques and sometimes the only option to examine material properties, structures, and their functions on micro- and nano- second timescales. Higher imaging frame rate requires higher x-ray pulse repetition rate. APS-U, with 88-MHz pulse repetition with a low beam emittance and more than  $10^5$  x-ray photons per pulse, is anticipated in the near future. Similar capability is available at the French ESRF facility and elsewhere. To take advantages of these new source capabilities and future facilities such as MaRIE, ultrafast hard x-ray imaging capabilities with a frame-rate no less than 100 MHz is desired, which will be at least  $10\times$  faster than the state-of-the art technologies (about 10 MHz frame-rate). We report the first successful time-resolved x-ray measurements at the Advanced Photon Source (APS) 10-ID-B beam line. An ultrafast x-ray detector concept was proposed using ultrafast crystals and detectors with picosecond timing resolution. Multiple crystal and sensor pairs (LYSO, BaF<sub>2</sub>, plastic scintillators, PMTs) as well as a standalone detector (diamond) have been tested to demonstrate the time-resolved measurements using hard x-rays at energies of 30 keV and above. The experimental results show that a number of choices exist for time-resolved high-energy x-ray beam measurement, paving the way towards ultrafast imaging technologies using hard x-rays for many applications.

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**Materials Science****A34****Cation Mixing in Li-rich Mn-Ni-Fe Oxide Cathodes and Its Impact on Voltage Fade**S. Aryal<sup>1</sup>, E.V. Timofeeva<sup>2</sup>, and C.U. Segre<sup>1</sup><sup>1</sup> Department of Physics and CSRRRI, Illinois Institute of Technology, Chicago, IL 60616<sup>2</sup> Department of Chemistry, Illinois Institute of Technology, Chicago, IL 60616

Li-rich oxides  $\text{Li}(\text{Li}_{0.2}\text{Mn}_a\text{Ni}_b\text{Fe}_c)\text{O}_2$  ( $a+b+c=0.8$ ) are promising high capacity, high voltage cathodes for Li-ion batteries. In such materials, monoclinic  $\text{Li}_2\text{MnO}_3$  and rhombohedral  $\text{LiMO}_2$  phases are integrated into a layered structure. Voltage fading (decrease in discharge voltage with cycling) is a known problem for these materials and in this work we investigate correlation between the voltage fade and cation mixing.

The hypothesis is that as the ionic radii of  $\text{Li}^+$  ion (0.69) and  $\text{Ni}^{2+}$  ion (0.76) are close, during synthesis some Ni ions occupy the Li sites and vice versa. Ni ions are critical for the formation of reversible layered structure and superior material capacity, however it is suggested that reduction of Ni content in the material will decrease the cation disorder and hence will stabilize the discharge voltage. The specific element sensitive, x-ray absorption spectroscopy of pristine and cycled cathodes to understand the local structural change of transition metal ions during battery cycling in addition to the detailed electrochemical study will be presented.

**A35****Evolution of Carbon Fiber Microstructure during High-temperature Graphitization Measured *in situ* Using Synchrotron Wide-angle X-ray Diffraction**Michael Behr<sup>1</sup>, James Rix<sup>2</sup>, Brian Landes<sup>1</sup>, Bryan Barton<sup>1</sup>, Eric Hukkanen<sup>1</sup>, Jasson Patton<sup>1</sup>, Steven Weigand<sup>2</sup>, and Denis Keane<sup>2</sup><sup>1</sup> Core Research and Development, The Dow Chemical Company, Midland, MI 48667<sup>2</sup> DND-CAT Synchrotron Research Center, Northwestern University, Argonne, IL 60439

Carbon fiber (CF) exhibits a unique combination of material properties, including high tensile strength and modulus, low weight, high temperature resistance, and low thermal expansion. The unique combined properties of this material are a direct consequence of

its constituent highly-oriented graphitic microstructure, which is typically obtained commercially through controlled pyrolysis of either polyacrylonitrile (PAN) or mesophase pitch-based fiber precursors. Current precursors and conversion processes are expensive, and limit the low cost potential of CF to \$10/lb, which has thus far precluded its wide-spread adoption in automotive and industrial markets. Polyethylene is a promising precursor to enable a high volume industrial grade CF as it is low-cost, melt-spinnable, and has a high carbon content. However, sulfonated polyethylene-derived carbon fibers (SPE-CFs) have thus far fallen short of the 200 GPa tensile modulus threshold for industrial applicability. Here we present a graphitization process catalyzed by the addition of boron that produces carbon fiber with > 400 GPa tensile modulus at 2400°C. To better understand the fundamental processes occurring during graphitization, and the structure-property-process relationships for these very different precursor materials, measurement of the characteristics of the graphitic microstructure, such as orientation, domain size, and interlayer spacing is critical.

This poster will describe the design and operation of a custom high-temperature tensile device that, when combined with synchrotron wide-angle x-ray diffraction (WAXD), enables us to observe *in situ* and in real time the microstructural transformation from carbon fiber precursor to high-modulus carbon fiber. Specifically, this tensile device heats fiber bundles from 25°C to greater than ~2300°C, while simultaneously applying tensile stress, and monitoring the resulting fiber strain. Synchrotron WAXD patterns obtained as a function of temperature reveal the conversion to graphitic microstructure, and provide key insights into the physical processes that occur during carbonization and high-temperature graphitization. Experiments conducted using PAN-, pitch-, and boron-doped PE-derived fiber precursors reveal stark differences in the carbonization and high-temperature graphitization behavior among these precursor types. Surprisingly, it was found that the presence of boron reduces the onset of graphitization by nearly 400°C, beginning at ~1200°C for SPE-CF precursors. The B-doped SPE-CFs herein attained 200 GPa tensile modulus and 2.4 GPa tensile strength at the practical carbonization temperature of 1800°C.

### A36

#### Advanced Characterization of Crystallinity-controllable Growth of Nanostructured Zinc Oxide via Atomic Layer Deposition

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A thorough study of crystallinity-controllable ZnO nanofilms deposited by ALD was investigated. Using synchrotron-based x-ray reflectivity (XRR) and diffraction (XRD) techniques at the beamline 12-ID-D at APS, we found that the planar ZnO films present different crystallinities and densities by varying ALD deposition temperatures. The beam Scientist at Argonne National Laboratory, Dr. Hua Zhou, supervised the measurements. Using scan electron microscope (SEM) and atomic force deposition at University of Arkansas, we could demonstrate the morphology and surface characteristics of ALD ZnO nanofilms. We believe that these findings are very favorable for our next step to investigate the effects of ZnO crystallinity on the electrochemical performance of ZnO in sodium-ion batteries. In addition, we further deposited the ALD ZnO films onto nitrogen-doped carbon nanotubes (N-CNT) and studied the resultant N-CNT@ZnO core-shell structures using transmission electron microscopy (TEM) at CNM. Dr. Yuzi Liu supervised the TEM analysis. The TEM characterization is consistent with the XRD data but provided more details on the ZnO films deposited at different temperatures. This ZnO investigation will further help investigate advanced sodium-ion batteries using both atomic/molecular layer deposition (i.e., ALD and MLD) in order to develop large-scale energy storage system for resolving global energy deficiency.

### A37

#### *In situ* EXAFS-derived Mechanism of Highly Reversible Tin Phosphide/Graphite Composite Anode for Li-ion Batteries

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Rapid growth applications of Lithium-ion batteries require significant improvement in their capacity, energy density and cycle life. Sn<sub>4</sub>P<sub>3</sub> is a promising conversion type anode material with a high initial capacity of 1255 mAhg<sup>-1</sup>, which suffers from rapid capacity and battery performance

degradation. A novel  $\text{Sn}_4\text{P}_3$ /graphite composite anode material with superior capacity of  $651 \text{ mAhg}^{-1}$  after 100 cycles is investigated by *in situ* x-ray absorption spectroscopy. EXAFS modeling and detailed analysis of local environment changes are correlated to the cell capacity and reveal the mechanism of lithiation/delithiation process. Results show that in the first two lithiation/delithiation cycles crystalline  $\text{Sn}_4\text{P}_3$  is fully converted to an amorphous  $\text{SnP}_x$  phase, which in further cycles participates in reversible conversion and alloying reactions. The superior reversibility of this material is attributed to the highly dispersed  $\text{SnP}_x$  in the graphite matrix, which provides enhanced electrical conductivity and prevents aggregation of Sn clusters during the lithiation/delithiation process. The gradual capacity fading in long-term cycling is attributed to the observed increase in the size and the amount of metallic Sn clusters in the delithiated state, correlated to the reduced recovery of the  $\text{SnP}_x$  phase. This study reveals the mechanism responsible for the highly reversible tin phosphides and provides insights for improving the capacity and cycle life of conversion and alloying materials.

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### A38 Synchrotron X-ray Microanalysis of Uranium Materials for Nuclear Forensics

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We have demonstrated the use of synchrotron radiation (SR) hard x-ray microanalysis to characterize nuclear forensic signatures in particle samples of nuclear fuel grade uranium oxide materials. Our work in this area has been motivated by an interest in characterizing materials at the single particle level, both as a capability for nuclear forensic trace evidence evaluation, and for the examination of different populations within heterogeneous nuclear materials. As the purity of materials increases further into the nuclear fuel cycle, impurity signatures become more dilute and speciation more consistent between different types of process (e.g., most nuclear fuel is produced as  $\text{UO}_2$ ). Therefore there is a need to develop and evaluate alternative signatures in these types of materials to

provide opportunities for forensic determination of sample provenance. We used spatially resolved synchrotron micro-XRF to evaluate the distribution and speciation of uranium and trace impurity elements that provide a valuable secondary signature that could be used to infer the source of the nuclear fuel cycle materials with greater confidence than possible using bulk analysis. The data from the hard x-ray microprobe facility at GSECARS Beamline 13-ID-E at the APS has the unique advantage over bulk techniques in that it permits separate evaluation of different impurity signatures (in our case Fe, Ce, Cu, and Zn) related to different sources in the sample, both intrinsic to the nuclear material and extrinsic contaminant particles. In addition, the high sensitivity of synchrotron microanalysis allows novel forensic signatures to be determined, such as apparent differences in oxide structure (stoichiometry), grain size or impurities.

### A39 An *in situ* Synchrotron X-ray Scattering Study of Microstructural Evolution in a Ni-based Alloy

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High performance Ni-based alloys are required for use in exhaust valve applications in the next generation, high efficiency automotive engines. These alloys are strengthened through the precipitation of coherent,  $\text{Ni}_3(\text{Al},\text{X})$  type  $\gamma'$  precipitates. Since these alloys are expected to operate at  $870^\circ\text{C}$  and above, microstructural stability of the  $\gamma'$  strengthening precipitates is critical to achieving the desirable performance characteristics of these alloys in this application. *In situ* USAXS/SAXS offers the ability to characterize particle size and particle size distributions in the aged condition and to monitor their evolution as a function of time at the typical exposure temperatures. This talk will present the results from an Ultra-small-angle (USAXS)/SAXS/WAXS study of  $\gamma'$  evolution in a model Ni-based alloy. Data obtained from room temperature measurements will be used to characterize the microstructure in the as-aged condition. Results from *in situ* high temperature ultra-small-angle (USAXS)/SAXS/WAXS measurements will be used to characterize precipitate coarsening behavior in the alloy.

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**A40****Studying Granular Micromechanics with Grain-resolved X-ray Computed Tomography and 3D X-ray Diffraction**Ryan C. Hurley<sup>1,2</sup>, Jonathan Lind<sup>2</sup>, Darren C. Pagan<sup>3</sup>, Minta C. Akin<sup>2</sup>, and Eric B. Herbold<sup>2</sup><sup>1</sup> Department of Mechanical Engineering, Johns Hopkins University, Baltimore, MD 21218<sup>2</sup> Lawrence Livermore National Laboratory, Livermore, CA 94550<sup>3</sup> Cornell High Energy Synchrotron Source, Ithaca, NY 14853

The macroscopic properties of granular materials are closely related to their micromechanics: inter-grain forces, grain kinematics, grain rotations, and pore space evolution. *In situ* x-ray computed tomography (XRCT) has traditionally been used to study grain kinematics and pore space evolution in granular materials but is unable to provide the information needed for determining inter-grain forces and grain rotations. To overcome this challenge, we have combined XRCT with 3D x-ray diffraction (3DXRD, also called far-field high energy diffraction microscopy). 3DXRD has provided grain strain tensors with  $10^{-4}$  resolution and grain crystal orientations with  $0.05^\circ$  resolution inside individual grains, permitting the calculation of inter-grain forces and grain rotations.

We will show examples of experiments performed at the Advanced Photon Source (APS) 1-ID and the Cornell High Energy Synchrotron Source (CHESS) F2 beamline that examine micromechanics in granular packings containing up to 1000 grains of various shapes. We will illustrate selected results, including: studies of stress and force heterogeneity; studies of the fracture mechanics of spherical, cubic, and angular grains; studies of grain kinematics and rotations in spherical and angular grains. We will illustrate the utility of these studies for assessing continuum descriptions of granular media and for calibrating numerical models. We will also discuss future work related to these measurements and additional measurement diagnostics.

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**A41****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>, Matthew Frith<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, APS, 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 everyday 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 five 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 APS general user program to world-wide user community at the APS sector 9ID (<http://usaxs.xray.aps.anl.gov>).

*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.*

**A42****Development of a Time-resolved Multimodal Imaging Platform**

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In the past decades, scanning probe microscopy (SPM) and scanning near-field optical microscopy (SNOM) have been developed to probe a broad spectrum of physical properties with unparalleled spatial and temporal resolutions. However, unlike scattering methods, SPM/SNOM rarely provide direct information about the structures underlying probed response. This has caused a number of unanswered questions for condensed matter systems, which are characteristic of mesoscopic heterogeneities in a spontaneous and/or excited nature.

Here at the Advanced Photon Source (APS), we have started an initiative to develop a platform that integrates SPM/SNOM with focused x-ray diffraction microscopy, which allows imaging of nonequilibrium states utilizing ultrafast lasers and picosecond-scale pulsed x-rays from the APS synchrotron. In this talk, I will briefly review the current development status, and discuss new technical leads and potential scientific applications. Finally, I will present a case study where we explored the structural mechanisms of mechanical switching in ferroelectric thin films. We observed enhanced diffuse scattering with well-defined spatial correlations in the pressure-scanned films and attributed it to Huang scattering due to defect redistributions, providing structural insights into mechanically induced ferroelectric switching.

### A43

#### **Understanding How the Halide Distribution Affects Charge Collection within Halide Perovskites Solar Cells Using *in situ* X-ray Nanoprobe Microscopy**

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The halide perovskites have rapidly become known for their excellent optoelectronic properties as well as their structural flexibility. This structural flexibility allows the substitution and mixing of different ions into hybrid halide perovskites to achieve finely-tuned optoelectronic properties such as bandgap and a continued search for greater environmental stability. The composition space has grown from the simple methylammonium lead iodide perovskite,  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , to complex quadruple cation A-sites and mixed halide chemistries to enhance both performance and optoelectronic properties. However, the microscopic effects of substitutions on charge-carrier transport and collection are not yet well understood. Using nanoprobe x-ray fluorescence (Nano-XRF) to examine films of increasing complexity from simple tri-halide phases to mixed A-site and mixed-halide perovskites, we find that the chemical flexibility in the perovskite phase results in a complicated heterogeneous elemental distribution in these films. *In situ* collection of spatially-resolved x-ray beam induced current (XBIC) provides a simultaneous nanoscale

measure of local quality for solar cell operation. The XBIC maps reveal large variations in local photocurrent collection within devices. The application of *in situ* XRF/XBIC technique allows us to precisely superimpose the halide distribution on the corresponding photocurrent response with resolution down to 200 nm. Combining the local elemental information from Nano-XRF and the local optoelectronic response from XBIC reveals the importance of nano-scale halide incorporation in electronic performance and opens new directions toward understanding the tuning of mixed-cation and mixed-halide perovskite systems toward optimal device efficiency.

### A44

#### **Resilient High Temperature UHV Sealing**

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Ultra-high Vacuum applications typically require all metal sealing due to outgassing and permeation concerns. Many of these systems are baked at a high temperature in order to reach the lowest base pressure and required cleanliness levels. However, high temperature bake outs can be problematic for traditional metals seals due to thermal expansion and the occasional need to have a shaped or non-circular configuration. Other critical sealing applications such as etching or thin film deposition also require a metal seal that has low outgassing and permeability—but must also be compatible with the process gasses or plasma.

This presentation will discuss a unique type of metal seal that utilizes a helical wound spring with layered metal jackets to address these issues. Presentation topics will include the metal-to-metal sealing concept along with design factors such as seating load, seal function, seal material selection, leak rate, and required seating load, groove configuration and finish.

### A45

#### **Direct Observation of Coherent and Anti-aligned Skyrmions in Co and Gd Layers in [Co/Gd/Pt]<sub>n</sub> Multilayers Using X-PEEM**

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Magnetic skyrmions, topologically distinct chiral spin textures, have attracted growing interest due to their potential applications in spintronics. Recent studies

confirmed the ability to stabilize sub-micron skyrmions in multilayers with broken inversion symmetry at room temperature. However, only a few experiments have investigated skyrmionic structures in multilayers with an antiferromagnetic exchange interaction. It is expected that antiferromagnetically coupled skyrmions show unusual topological effects. In particular, the skyrmion Hall effect, which causes a drift of skyrmions towards the device edge and their subsequent annihilation should be substantially suppressed for antiferromagnetically coupled skyrmions. We present the study of skyrmions stabilized in an artificially ferrimagnetic multilayer Ta (4 nm)/Pt (5 nm)/[Co (0.5 nm)/Gd (1 nm)/Pt (1 nm)]<sub>10</sub>/Al (2 nm). By using the synchrotron-based x-ray photoemission electron microscopy (X-PEEM) at beamline sector 4-ID-C of the Advanced Photon Source, we discovered that the magnetic skyrmions imaged at the Co L<sub>3</sub> edge have the exact same pattern but opposite magnetic contrast to the skyrmions imaged at the Gd M<sub>5</sub> edge, which indicates that the skyrmions in different layers of the multilayer films are coherent. More importantly, the magnetic structure of the skyrmions preserves ferrimagnetic alignment (i.e., the magnetization of Gd is opposite to that of Co). Furthermore, SQUID results show that, due to antiferromagnetic exchange coupling between Gd and Co, the magnetic moment of the Gd layers compensates that of the Co layers at around 100 K, which indicates that completely compensated antiferromagnetic skyrmions can be generated at this temperature. While above 100 K, the current driven motion of the skyrmion in [Co/Gd/Pt]<sub>n</sub> multilayers can be characterized by a reduced skyrmion Hall angle. Our experimental results directly demonstrate the coherence of skyrmions in coupled magnetic layers. This discovery opens a possibility for reducing possibly detrimental skyrmion Hall effect and generation of antiferromagnetic skyrmions by controlling the coupling in magnetic multilayers.

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#### A46

### ***In situ* Investigations of Catalysis and Batteries Using a Quick Scanning Monochromator at Beamline 9-BM**

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As a beamline dedicated to the x-ray absorption spectroscopy (XAS), 9-BM is capable to cover very wide

energy range (2145.5 eV P-K edge to 24350 eV Pd-K edge). In recent years more efforts have been devoted to the fields of catalysis and energy storage, focusing on catalysis for efficient conversion of energy resources into usable forms, and storage of such energy in efficient and safe capacitors. To understand and predict how catalysts and/or energy storage materials function, it's very important to characterize the materials under actual reaction conditions (*in situ* or *operando*). 9-BM has leveraged the advanced capabilities for *in situ* catalysis and electrochemistry, as well as the ability to collect high quality spectroscopy data at a rapid rate (Quick EXAFS). Scientists using 9-BM are able to gain unique insight to how chemical processes affect and are affected by the materials under investigation. We highlight these capabilities as well as a few examples of the science enabled by them.

*Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.*

#### A47

### **Analyzing the Accuracy Limits of Lattice Strain Extracted from Laue Microdiffraction Patterns Using Virtual Diffraction**

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The deviatoric lattice strain tensor within a subsurface voxel ( $\sim 1 \mu\text{m}^3$ ) can be extracted from the corresponding Laue microdiffraction pattern that was collected using differential aperture x-ray microscopy (DAXM). Due to the white beam radiation, the analytical solution for the strain tensor cannot be directly calculated, so an optimization based numerical method is necessary to estimate the lattice strain by iteratively minimizing the angular difference between the calculated and the measured scattering vectors for each voxel. The inherent accuracy limits of the recovered deviatoric lattice strain tensor using this type of method is systematically evaluated in this study. The results show that for a perfect diffractometer and detector, the optimization method can identify the deviatoric/full lattice distortion with an accuracy better than  $10^{-9}$  using a novel fitness function.

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A48

## Investigating Atomic Structures of Mesoscale and Highly Curved Two-dimensional Crystals by Surface X-ray Nanodiffraction

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Ever since the storming rise of graphene, the expanding list of 2D material family as predicted by theorists has been experimentally verified almost in every few months in the last years. Most fundamental properties of 2D atomic thin crystals, such as morphology/geometric profiles, electronic/magnetic transports and optoelectronic responses can be investigated by various optically excited and surface force sensitive techniques like Raman/IR spectroscopy and AFM/STM probes. However, determining atomic structures of versatile 2D crystal surfaces and interfaces in the burgeoning 2D heterostructure materials remains very challenging. So far, high-resolution cross-section TEM is still the most popular and viable method to map out surface/interface atomic structures of 2D crystal and other derivative materials although the delicate interface bonding can be undesirably vulnerable to electron-beam effects. Synchrotron-based surface x-ray diffraction, in particular crystal truncation rod (CTR) technique, can render a complete and precise atomic structure of single crystals and high quality epitaxial thin films/heterostructures in non-destructive manner. Nevertheless, the miniature lateral dimension (e.g., less than a few to tens of microns) of most 2D flakes and heterostructures makes conventional surface x-ray diffraction almost impractical to map out the complete Bragg rod so as to extract the complete atomic structures. Moreover, structural and electronic phases of some unique 2D crystals are strikingly controllable by strain applied by the underlying substrate or support when it has a large surface curvature, which for certain throws another big technical barrier for any surface-sensitive x-ray techniques.

High-brilliance, high flux synchrotron source and state-of-art focusing optics capable of routinely realizing nanobeam below 100 nm makes x-ray nanodiffraction, even surface x-ray nanodiffraction become practical and user-accessible. In this poster, we will present the feasibility of surface x-ray nanodiffraction measurements, and then demonstrate two most recent intriguing practices on investigating 2D atomic thin crystal and Lego-style 2D heterostructures. In one case, surface nanodiffraction helps to map out the complete specular CTR of a high quality

graphene-hexagon BN heterostructure. The resolved interfacial atomic structures suggest a subtle variation of interfacial van-der-waals bonding between exfoliated and CVD grown 2D thin crystals. In another example, surface nanodiffraction allowed for precise determining in-plane lattice expansion of miniature MoS<sub>2</sub> 2D flakes vapor grown on highly curved glass spheres, which provides an excitingly new approach to effectively manipulate electronic band valley structures. In summary, surface x-ray nanodiffraction brings about significant opportunities for us to explore new two-dimensional materials, unravel emergent phenomena, and develop novel functionalities.

## Nanoscience and Nanotechnology

A49

### Structure and Electrochemistry of Doped Li<sub>2</sub>FeSiO<sub>4</sub>/C Material as a Cathode for Li-ion Batteries

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Rechargeable lithium-ion batteries (LIBs), currently used in both electronic devices and in electric vehicles (EV) use expensive and toxic cathode materials such as layered lithium cobalt oxide (LiCoO<sub>2</sub>), lithium nickel manganese oxide (LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub>) mostly because of presence of Ni and Co elements [1,2]. Among other cathode materials, polyanion compounds (LiFePO<sub>4</sub>, LiVO<sub>3</sub>, etc.) have also been studied as the promising LIB cathode candidates due to safety, good stability and low cost [3]. Lithium iron orthosilicate (Li<sub>2</sub>FeSiO<sub>4</sub>, LFS) is a member of polyanion compound family [4], with theoretical capacity of 331 mAhg<sup>-1</sup> [5]. The drawback of this material is its low electronic conductivity, affecting electrochemical performance. The objective of this study is to improve the electrical conductivity of LFS material through doping with tri-valent cations in Fe and Si sites as well as reducing the particle size to nanoscale and coating with conductive carbon shells. Structural, morphological and phase analysis of the family of LFS materials correlated to their electrochemical performance will be discussed, including results from x-ray diffraction, scanning electron microscopy with energy dispersive x-ray analysis, thermogravimetric analysis, and electrochemical characterization (galvanostatic charge/discharge, cyclic voltammetry, impedance spectroscopy). Fe K-edge *in situ* x-ray absorption spectroscopy providing local environment of Fe atoms in pristine and doped LFS samples during cycling will also be presented.

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## A50

### Inter-polymer Complex Mediated Assembly of Gold Nanoparticles

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Using synchrotron small angle x-ray scattering, we demonstrate that nanoparticles can be crystallized into super-lattices with FCC symmetry, primarily driven by hydrogen bonding between two synthetic polymers, akin to programmable assembly using complementary DNA strands [1,2]. We functionalize gold nanoparticles (AuNPs) with poly(ethylene glycol)-thiol (PEG-SH) to form a AuNP-PEG core-shell nanoparticles and bridge neighboring nanoparticles via poly(acrylic acid) (PAA), taking advantage of the strong PAA/PEG hydrogen bonds [3]. We show the effect of polymer concentration, pH and length of PEG chains on the lattice constant and crystal quality. Molecular dynamics simulations and a theoretical model, OTM [4], predict a phase space that allows tuning lattice parameters and obtaining various crystal symmetries. Using simpler synthetic polymers instead of DNA allows easier processing and facile implementation of block copolymer based self-assembly techniques.

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## Other

### A51

#### Acoustic Levitation in X-ray Scattering Experiments

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We make direct structural measurements of the formation and evolution of pre-nucleation clusters in an extremely supersaturated  $\text{KH}_2\text{PO}_4$  (KDP) solution drop in a containerless environment. By performing in-situ small angle x-ray scattering (SAXS) measurements, we characterize distinctive cluster formation behaviors as a function of supersaturation. By achieving time-resolved SAXS measurements of the crystallizing sample, we show that nucleation does not take place directly from solutions (as predicted by classical nucleation theory), but instead requires intermediate steps, such as forming pre-nucleation clusters in the highly supersaturated solution.

### A52

#### Beamline Front Ends for CHESS-U

Alex Deyhim<sup>1</sup>, Eric Van Every<sup>1</sup>, Ernie Fonts<sup>2</sup>, Chris Conolly<sup>2</sup>, Aaron Lyndaker<sup>2</sup>, and Alan Pauling<sup>2</sup>

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The CHESS-U upgrade project entails the transition to a dedicated light source and enables the addition of three new x-ray beamlines with six new experimental stations with three new front ends fed by six insertion devices [1]. ADC is responsible for the Front Ends (FE), which are comprised of all components involved in safely transporting the x-ray beams from the storage ring (CESR) to the first optical enclosure (FOE) beyond the storage ring shielding wall. This includes all components related to personnel and equipment safety, beam position monitoring, collimators and shielding, water-cooled

apertures, and shutters. Novel designs and cutting-edge manufacturing techniques create components with reduced footprints and improved reliability. Accelerated installation of each FE is achieved with alignment and installation on a single massive steel I-Beam structure; taking after the alignment concepts seen at SPring-8 [2]. To accommodate a fast installation schedule, all equipment is aligned, tested, and baked-out at ADC and will be transported to CHESS under vacuum. All water, electrical and pneumatic utilities are run to an access panel to further facilitate installation. In this paper, ADC will discuss various unique design elements that minimize FE length and reduce installation time.

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### A53 Latest Development in X-ray Shielding Lead Encapsulated Enclosures

Alex Deyhim<sup>1</sup>, Eric Van Every<sup>1</sup>, Tim Shea<sup>1</sup>, Dana Richter<sup>2</sup>, Ernie Fonts<sup>2</sup>, and Chris Conolly<sup>2</sup>

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The transport of radiation through shielding materials is a major consideration in the safety design studies of Synchrotron Facilities around the world, and the design techniques used may be applied to many other types of scientific and technological facilities. As part of the Cornell High Energy Synchrotron Source Upgrade (CHESS-U), ADC has designed, fabricated and installed highly modular lead encapsulated enclosures (hutches). ADC will present the latest development in cutting-edge design and implementation of X-ray Shielding Lead Encapsulated Enclosures. ADC will discuss design features and critical calculations for; Modular lead shielded enclosures, White Beam and Monochromatic Hutches, Lead Shielded Transfer Pipes, and Interlocking lead brick enclosures. ADC used expert consultant offered by several facilities including engineers from Advanced Photon Source (APS) and Cornell High Energy Synchrotron Source (CHESS); with each facility providing guidance to assure that the design satisfies the rigorous radiation safety requirements. The highly modular shielding design allows for hutch installation over the course of days, dramatically reducing onsite downtime.

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### A54 LRL-CAT: An Automated X-ray Crystallography Synchrotron Beamline for Structure-based Drug Design

Anton J. Frommelt<sup>1</sup>, John W. Koss<sup>1</sup>, Laura M. Morisco<sup>1</sup>, David Clawson<sup>2</sup>, and Jordi Benach<sup>1</sup>

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Eli Lilly and Company operates its own fully automated x-ray macromolecular crystallography beamline, LRL-CAT, at the Advanced Photon Source (APS) of Argonne National Laboratory. LRL-CAT runs exclusively as a mail-in facility for protein crystallography and provides high quality, crystallographic data for Lilly, its corporate partners, and general users. The beamline is capable of running unattended from crystal mounting, loop centering, crystal screening, and diffraction scoring to determining optimal dataset parameters, data collection, data processing, and data transfer to the user. The full-time Lilly staff is devoted to maintaining the highest level of throughput and quality control at the beamline. In the past ten years, LRL-CAT has screened a total of 132,389 crystals and collected 38,901 datasets, including 36,863 crystals and 10,701 datasets screened and collected for general users/corporate partners, respectively. LRL-CAT remains one of the most efficient beamlines in the world with a median data turnaround of 23 hours from crystal harvest to screening images and a median of 27 hours from crystal harvest to processed data; this time includes the 16 hours of overnight courier shipping.

### A55 Quantitative Texture Analysis of Wet Clays during Thixotropic Hardening Using Synchrotron X-ray Diffraction

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Thixotropy describes an interesting phenomenon that the strength and stiffness of some materials increases with time even if the boundary conditions remain unchanged

(e.g., no change in pressure, temperature, or composition). Civil/geotechnical engineers have long observed the fact that the strength and stiffness of soft clay drop significantly when it is disturbed. Observations from macroscale laboratory experiments, including bender element testing and undrained shear strength testing, have shown that a completely remolded wet clay can recover its strength and stiffness with time, but the mechanisms remain unclear. For a closed, isothermal physical system (such as a wet clay without change in pressure, temperature, volume, or composition), any change in macroscopic mechanical properties with time (e.g., stiffness and strength) must stem from certain internal processes occurring within the system. The hypothesis is that the internal processes include (but are not limited to) microstructure evolution (e.g., clay particle rearrangement) as well as homogenization of microstructural flaws previously caused by disturbance.

Natural clays are composed of one or more clay minerals which have particle sizes smaller than 2  $\mu\text{m}$ . Owing to their tiny particle sizes, it is challenging to non-destructively quantify the clay texture evolution with time. Fortunately, advancement in two-dimensional synchrotron x-ray diffraction (2D-XRD) has provided a tangible approach to determine the clay particle orientation for such geomaterials as wet soils and shales. This study performed two-dimensional synchrotron x-ray diffraction on wet clay samples to reveal how the microstructure of clays, including clay texture or fabric, varies with time (e.g., rearrangement and reorientation of clay particles), and the corresponding influence on the thixotropic hardening behavior was also studied to characterize the thixotropy-governed microscale soil fabric evolution. Preliminary study was conducted on pure kaolinite (KGa-2) and it was scanned by 2D-XRD 6 days after the sample was remolded. Since the remolded clay was sheared when it was sucked into the kapton tube, clay particles were aligned along the axial direction of the tube and a preferred orientation at this direction was then able to be observed.

## A56

### Update from the APS/XSD Detectors Group Activities

Jonathan Baldwin<sup>1</sup>, Rebecca Bradford<sup>1</sup>, Lisa Gades<sup>1</sup>, Antonino Miceli<sup>1</sup>, Umeshkumar Patel<sup>1</sup>, Christopher Piatak<sup>1</sup>, Orlando Quaranta<sup>1</sup>, Russell Woods<sup>1</sup>, Kyung-Wook Shin<sup>1</sup>, John Weizeorick<sup>1</sup>, Russell Woods<sup>1</sup>, and Daikang Yan<sup>1,2</sup>

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The mission of the APS/XSD Detectors Group is to deliver cutting-edge x-ray detectors to APS beamlines. Our mission is accomplished in two ways. First, we introduce new commercial detectors to the APS community via the Detector Pool. Second, we are engaged in a number of detector R&D projects to meet the future needs of the APS. We focus our detector R&D efforts in three areas: pixel array detectors, high-energy sensors, and emission detection. We are involved in two collaborations on pixel array detectors. These include the VIPIC detector for ultra-fast XPCS with BNL and FNAL, and the MM-PAD detector with Cornell University. For high-energy sensors, we are collaborating with the BNL NSLS-2 Detector Group on germanium strip detectors for high-energy spectroscopic applications. Finally, for x-ray emission detection, we are collaborating with NIST and SLAC on transition-edge sensors (TES) for high-energy-resolution emission detection applications. We will present an update of our activities.

## A57

### Quantitative Texture Analysis of Wet Clays during Thixotropic Hardening Using Synchrotron X-ray Diffraction

Jing Peng, Shengmin Luo, Don J. DeGroot, and Guoping Zhang

Department of Civil and Environmental Engineering, University of Massachusetts Amherst, Amherst, MA 01003

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must stem from certain internal processes occurring within the system. The hypothesis is that the internal processes include (but are not limited to) microstructure evolution (e.g., clay particle rearrangement) as well as homogenization of microstructural flaws previously caused by disturbance.

Natural clays are composed of one or more clay minerals which have particle sizes smaller than 2  $\mu\text{m}$ . Owing to their tiny particle sizes, it is challenging to non-destructively quantify the clay texture evolution with time. Fortunately, advancement in two-dimensional synchrotron x-ray diffraction (2D-XRD) has provided a tangible approach to determine the clay particle orientation for such geomaterials as wet soils and shales. This study performed two-dimensional synchrotron x-ray diffraction on wet clay samples to reveal how the microstructure of clays, including clay texture or fabric, varies with time (e.g., rearrangement and reorientation of clay particles), and the corresponding influence on the thixotropic hardening behavior was also studied to characterize the thixotropy-governed microscale soil fabric evolution. Preliminary study was conducted on pure kaolinite (KGa-2) and it was scanned by 2D-XRD 6 days after the sample was remolded. Since the remolded clay was sheared when it was sucked into the kapton tube, clay particles were aligned along the axial direction of the tube and a preferred orientation at this direction was then able to be observed.

## A58

### Zone Plate Performance as a Function of Tilt Analyzed via Multislice Simulations

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Thanks to new nanofabrication processes for hard x-ray Fresnel zone plates [1,2], the finest zone width (required for high spatial resolution) has been decreasing while the thickness (required for diffraction efficiency) has been increasing. This leads to higher aspect ratios, with values as high as 500:1 having been demonstrated [2]. At these aspect ratios, one must consider carefully the effects of small tilt misalignments of a zone plate relative to the x-ray beam. Zone plates with very high aspect ratios, and finest zone widths that begin to approach a small

multiple of the x-ray wavelength cannot be described by simple models [3,4] as they begin to act as volume gratings [5], and these waveguide-like effects must be taken into account.

We have therefore used a multislice approach to consider the optical performance of high aspect ratio zone plates as a function of tilt. In the multislice approach [6], an object is conceptually “sliced up” in to thin slabs; one applies the refractive index effects of the slab on the wavefield, which is then propagated to the next slab position. This approach has been shown to reproduce coupled wave theory results for x-ray nanofocusing [7], provided one uses a weighted filling of voxels at boundaries between zone materials. For our calculations, we discretize a non-tilted zone plate, and consider incident beams at non-orthogonal angles. We observe that the performance of a zone plate versus tilt angle varies both as a function of number of zones and the thickness of a zone plate.

*This work is supported by NIH under grant U01 MH109100, and U.S. DOE Office of Science under Contract No. DE-AC02-06CH11357 to ANL. Code is available at: [https://github.com/s-sajid-ali/zone\\_plate\\_testing/releases/tag/0.1.0](https://github.com/s-sajid-ali/zone_plate_testing/releases/tag/0.1.0).*

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## A59

### Correlative Cryo Confocal Light Microscopy (C<sup>3</sup>LM) and X-ray Fluorescence

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Correlative microscopy has been growing in importance as a way to obtain more complete information about a specimen than any one type of microscopy can provide [1]. For example fluorescence microscopy allows specific localization of rare moleculars or events in a sample, while transmission techniques such as differential phase

contrast reveals subcellular structure at nanometer scale spatial resolution [2]. We present here the development of a system with unique characteristics: the ability to mount a frozen hydrated specimen once, on a robust sample-handling cartridge, and image it under cryogenic conditions using both confocal light microscopy and x-ray fluorescence microscopy.

The handling of thin, delicate biological specimens under liquid nitrogen is not straightforward. That is why we have chosen to use the same specimen cartridge as is used in the Bionanoprobe (BNP) [3], a scanning x-ray fluorescence microscope operated at the Advanced Photon Source (APS). Our Cryogenic Confocal Correlative Light Microscope (C<sup>3</sup>LM) design concept uses the same cartridges and transfer chamber as the BNP and makes significant use its cryogenically-cooled sample transfer robot components. With the BNP, one can obtain sub-20 nm resolution x-ray transmission images using ptychography, and sub-100 nm x-ray fluorescence images of trace element distribution [4]. The use of confocal fluorescence microscopy in the C<sup>3</sup>LM enables fluorescent element mapping in thicker biological specimens, and thus makes better use of one of the key advantages of x-ray microscopy over electron microscopy, namely the ability to image specimens tens of micrometers thick. Finally the C<sup>3</sup>LM being a separate microscope means it can be accessed independently of synchrotron beamtime scheduling. This allows one to evaluate specimen preparation protocols long before scheduled x-ray beamtime, and to identify the most interesting specimen regions far in advance making for more efficient use of x-ray beamtime.

*Progress towards the commissioning of our C<sup>3</sup>LM system will be reported at the XRM 2018 conference. This work is supported by the NIMH, NIH, under project R01 GM104530, as well as a LDRD project supported by Argonne. This research used resources of the APS, which is a U.S. Department of Energy (DOE) Office of Science User Facilities operated for the DOE Office of Science by Argonne under Contract No. DE-AC02-06CH11357. We thankfully acknowledge the advice of A. Petford-Long, G. Woloschak and T. Paunesku on system development.*

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## A60

### SAS2018 – International Meeting on Small Angle Scattering

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SAS2018 will be presented 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, materials science, magnetic materials 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, contrast variation, grazing incidence and advances in modeling and data analysis. Educating the community especially for SAS teachers is a common goal.

SAS2018 will serve to showcase the progress of small-angle scattering research in North America including the many instruments at user x-ray and neutron 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.*

## Polymers

A61

### Polymer-induced Structural Changes in Suspensions of Gold Nanorods

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Open, porous materials with controlled nanoscale structures can exhibit substantially improved mechanical and electrical properties while remaining lightweight. Production of these materials, however, is usually challenging and costly. Here, we use polymer-induced depletion interactions to assemble gold nanorods (AuNRs) in a bulk solution process into fractal structures with controllable interparticle spacing and fractal dimension. Depletion attractions arise in solutions because dissolved polymer chains are entropically excluded from a layer near the nanorod surface. To increase the free volume available to the polymer chains, the colloids aggregate to overlap their depletion layers. Although depletion forces are well understood for large spherical colloidal particles, how they drive the assembly of anisotropic particles in the “protein limit” where the particles are small in comparison to the polymer coils is poorly understood. Dispersing AuNRs grafted with polymer chains in solutions of high molecular weight poly(ethylene oxide) (PEO), we elucidate the physics underlying depletion interactions in the “protein limit” and exploit these physics to generate fractal structures with controlled nanoscale structures. Using small-angle x-ray scattering, we quantify the changes in aggregate morphology as a function of depletant size and concentration. The depletion force increases monotonically with PEO concentration to compress the grafted layers and drive the gold nanorods closer. Surprisingly, however, the fractal dimension and number of nearest neighbors in the aggregates change non-monotonically with PEO concentration, exhibiting maximums at intermediate PEO concentrations. These structural changes suggest that the aggregation process is reaction limited (RLA) at low PEO concentration and diffusion limited (DLA) at high PEO concentration. In contrast to the depletion-induced aggregation of large colloids, the transition between RLA and DLA for the AuNRs is independent of polymer molecular weight and bulk solution viscosity, which we attribute to the small size of the AuNRs. This independent control between aggregate morphology and solution properties as well as the bulk solution process opens the door to cheap, facile synthesis of materials with controlled and tunable nanoscale properties.

## Technique

A62

### Characterizing Photoinduced Excited States with ~10 ps Resolution Using Time Slicing X-ray Absorption Spectroscopy

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To date, time-resolved x-ray absorption spectroscopy is limited by the pulse duration of the x-ray pulse (~80 ps FWHM at APS in 24-bunch mode). However, recent improvements in optical pump and data acquisition schemes combined with the high average flux of synchrotron sources, as well as their exceptional stability, opens the door for performing spectroscopic measurements in a ‘time-slicing’ mode. By scanning finely, the time delay between the laser and x-ray pulses, one can effectively reconstruct the instantaneous transient signal by deconvolution of the temporal Instrument Response Function (IRF). As proof of principle, we studied Fe(II)CN<sub>6</sub> in water exciting a ligand dissociative state. From optical experiments, we expect two lifetimes to be present, a penta-coordinated state (Fe(II)CN<sub>5</sub>) and an aquated state Fe(II)CN<sub>5</sub>H<sub>2</sub>O, with 30 ps and 10s of μs lifetimes. By performing “Time slicing”, we managed to extract the clear 30 ps state XANES spectra, as well as the relaxation dynamics of this state feeding the long lived aquated state.

Our work will be a breakthrough for time-resolved x-ray spectroscopy measurements. It would open the door for the important time window from 10 to 100 ps in which many important photochemical processes take place and which is currently only accessible with free-electron laser sources. This work would help to expand the range of photoinduced molecular dynamics problems that can be studied at synchrotrons.

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### 3D Object Reconstruction beyond the Depth-of-focus Limit Using Automatic Differentiation

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When x-ray 3D imaging techniques are used to reach a spatial resolution approaching the diffraction limit, the depth-of-focus (DOF) of the imaging system shrinks greatly, and the pure-projection approximation typically fails for thick specimens due to multiple scatterings throughout the object. To the best of our knowledge, a 3D reconstruction approach that is capable of both properly modeling multiple scattering and providing isotropic voxel sizes in such scenarios is yet to be proposed. We report here a novel method to address this issue. Our method works by optimizing a 3D object function in such a way that the transmission signals produced by the object have a good match with the actual measurements. Using the multislice method [1], diffraction through the object can be appropriately accounted in the forward model. The optimization algorithm is implemented using automatic differentiation (AD), which saves the labor needed for manually deriving the derivative of the loss function with regards to the object function, and can flexibly meet any changes made to the model. Numerical studies have proven that our algorithm produces much better results than conventional tomography reconstruction methods in the beyond-DOF scenario. In addition, our algorithm is compatible with full-field imaging techniques such as point-projection x-ray microscopy (PPXM), which endows it with great potential to be used for high-throughput 3D imaging of samples beyond the DOF.

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### Confocal X-ray Fluorescence Microscopy at the Advanced Photon Source Sector 20

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X-ray fluorescence (XRF) is a powerful technique for elemental analysis in part owing to its minimal sample preparation requirements and sub-ppm-sensitivity. However, conventional XRF imaging generally requires thin samples, which is not always desirable or possible (e.g., for brittle samples or when non-destructive analysis is required). Non-destructive 3-D confocal XRF microscopy allows spatial discrimination of XRF photons in all three dimensions and enables high resolution x-ray spectroscopy, such as XANES, to be performed directly on a small region of interest within large samples. Polycapillaries are the most common collection optics used for a confocal XRF microscopy, but limit the technique to depth resolution of upwards of 10  $\mu\text{m}$  at 10 keV. The new confocal XRF microscopy capability at sector 20-ID, enabled by CHESS micro-channel arrays (CCA), [1] are capable of achieving depth resolution of 2–5  $\mu\text{m}$ . CCAs provide both an improvement in resolution and, in addition, invariant spatial resolution with the x-ray fluorescence energy. This capability has applications in environmental science, biology, and anthropology. Recent experiments include studies on mineral inclusions, human teeth, fish embryos, plants, and cultural artifacts. The sector 20-ID microscopy station is a KB mirror based microprobe providing a focus in the range 2–5 microns, and we can match the beam sizes to the CCAs spatial resolutions. We will present detailed current capabilities of the confocal technique at sector 20-ID.

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**A65****High Photon Flux XUV Source Driven by High Repetition Rate >100 kHz Fiber Laser**

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The recent development of high repetition rate lasers based on ytterbium-doped fiber amplifiers (YDFA), has paved the way to increase the repetition rate (>100 kHz) of coherent extreme ultra violet (XUV) sources generated by high harmonic generation (HHG). Increasing the repetition rate of HHG drivers comes with several advantages, such as increased photon flux [1,2], reduction of the acquisition time in coincidence experiments to study molecular dynamics such as COLTRIMS, and the possibility to study the electronic structure of matter via photoemission spectroscopy and microscopy, where low doses are needed to avoid space-charge effects [3].

Up to now, the majority of HHG studies and applications has been restricted to the low repetition rates of Ti:sapphire lasers. Commonly, Ti:sapphire lasers delivers 20 fs pulses at a central wavelength  $\lambda = 800$  nm, with pulse energies up to hundreds of mJ. However, the average power of these laser systems cannot easily be scaled beyond 10 W, restricting HHG at low repetition rates (up to 10 kHz).

YDFA can generate kW average powers [4] with pulse energies of hundreds of  $\mu\text{J}$  at a central wavelength  $\lambda = 1030$  nm. However, gain narrowing limits the pulse duration of high energy fiber CPA to above 250 fs and accessing the few-cycle regime requires two stages of nonlinear compression [5]. Long pulse durations limit the maximum intensity at the interaction zone (laser – noble gas), and therefore it limits the maximum photon energy generated by the HHG process.

Recently, an efficient few-cycle laser source based on a high-energy YDFA has been successfully developed [6]. The use of a broadband seeder, together with spectral shaping allows for the generation of high temporal quality 130 fs (40% shorter than previous state of the art), 250  $\mu\text{J}$  pulses at 200 kHz, corresponding to 1.5 GW of peak power and 50 W of average power. The unprecedented short pulse duration at this energy level allows compression down to the few-cycle regime using a single nonlinear compression stage. Spectral broadening in a Xenon-filled

capillary results in the generation of 14 fs and 120  $\mu\text{J}$  pulses at 200 kHz, corresponding to 24 W of average power [6].

We investigate the evolution of different XUV parameters, spectral width of harmonics, the cutoff energy, the photon flux and the efficiency of the XUV process, as a function of the pulse duration of the YDFA driving laser. We used a recently developed compact XUV source in a single pass HHG set-up with tight focusing configuration on a Neon gas jet and driven by an industrial YDFA that can be operated up to several MHz to generate HHG in three modalities: (1) directly with the output of laser model Tangerine (350 fs), (2) with a nonlinear compression down to 30 fs and (3) with few cycle pulses (14 fs) obtained after post-compression of Tangerine SP (Short Pulse).

We report a decrease of the spectral harmonics width  $\Delta E$ , down to 250 meV, by using directly the output of the Tangerine (350 fs). In contrast, the shortest driving pulse duration (14 fs) allowed us to reach photon energies up to 140 eV in Neon. These photon energies are suitable for several applications, for example time-resolved atomic inner shell spectroscopy [7]. The high repetition rate of the driving laser allows reaching a photon flux of up to  $2 \times 10^{12}$  Photons / s / eV. We will more generally discuss the dependence of XUV characteristics such as spectrum shape, spatio-spectral structures, and harmonic spectral width on the driving laser and XUV generation setup parameters.

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**A66****Multi-scale Imaging in Metal Additive Manufacturing**

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Powder bed additive manufacturing (AM) processes selectively melt or bind particles in successive thin layers of powder materials to build three-dimensional parts. They offer various advantages over conventional manufacturing methods, which include manufacturing complex parts directly from the design without the

requirement of tooling and on-demand manufacturing. This reduces the inventory of spares and decreases the lead time [1]. As a result of these advantages, AM of metallic materials is growing rapidly in fields of medical, aerospace, automobile, and defense industries [2,3]. Various physical processes affect the quality of parts manufactured using additive manufacturing processes, including melting and vaporization of material due to interaction with the laser, melt-pool and vapor depression zone dynamics, and powder behavior. The complex interaction between these processes leads to formation of defects in parts, which causes variability in mechanical properties [4]. In this study, various x-ray imaging techniques are used to study the powder feedstock and laser melting processes to understand the relationships between powder properties, process parameters, and built parts. Synchrotron x-ray tomography (beam line 2-BM) and transmission x-ray microscopy (beam line 32-ID-C) techniques were used to study the powder and built parts at various spatial resolutions in 3D. High-speed x-ray imaging and diffraction techniques were used to record the additive manufacturing processes and evolution of microstructure respectively. Different spatial and temporal resolutions provide valuable insights into formation of defects and microstructure in parts built using AM processes.

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## A67

### 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>.

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**A68****areaDetector: What's New?****M.L. Rivers**

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Recent enhancements to the EPICS areaDetector module will be presented.

- Support for 10 GBit Ethernet cameras from Point Grey/FLIR in new ADSpinnaker detector repository. These are next-generation cameras that are 6–8 times faster than 1 Gbit Ethernet cameras in wide use at the APS.
- Support for new Bruker Photon II detector.
- Support for BLOSC compression in HDF5 files.
- Support for automatic conversion of medm adl files to edm edl, caQtDM ui, and CSS-BOY opi files.
- Added GraphicsMagick to ADSupport so it can now be built on Linux and Windows.
- New features in ADLightField: StepAndGlue support, Entrance Port selection.
- Added ADEiger support for the Dectris Eiger detector to the areaDetector project.