

Monday Morning, November 10, 2014

Actinides and Rare Earths Focus Topic

Room: 301 - Session AC+AS+MI+SA+SS-MoM

Spectroscopy, Microscopy and Dichroism of Actinides and Rare Earths

Moderator: David Shuh, Lawrence Berkeley National Laboratory

8:20am AC+AS+MI+SA+SS-MoM1 **Novel Synthetic and Spectroscopic Techniques in Actinide Materials Chemistry, Stefan Minasian**, Lawrence Berkeley National Laboratory, *E. Batista*, Los Alamos National Laboratory, *C.H. Booth*, Lawrence Berkeley National Laboratory, *D. Clark*, Los Alamos National Laboratory, *J. Keith*, Colgate University, *W. Lukens*, Lawrence Berkeley National Laboratory, *S. Kozimor*, *R.L. Martin*, Los Alamos National Laboratory, *D. Nordlund*, SLAC National Accelerator Laboratory, *D. Shuh*, *T. Tyliczszak*, Lawrence Berkeley National Laboratory, *D. Sokaras*, SLAC National Accelerator Laboratory, *X.-D. Weng*, Los Alamos National Laboratory, *T.-C. Weng*, SLAC National Accelerator Laboratory **INVITED**

The development of a detailed, quantitative understanding of electronic structure and bonding for a broad range actinide materials remains a significant scientific challenge. Recent advances have shown that the 1s to np transition intensities measured by Cl and S K-edge X-ray absorption spectroscopy (XAS) directly relate to coefficients of covalent orbital mixing in M-Cl and M-S bonds. The scientific progress associated with these Cl and S XAS studies suggests that using synchrotron-generated radiation to quantify covalency for ligands beyond Cl and S would have a wide impact. The nature of chemical bonds between actinides and light atoms such as oxygen, nitrogen, and carbon is of particular interest because these interactions control the physics and chemistry of many technologically important processes in nuclear science. However, obtaining accurate light atom K-edge XAS spectra on non-conducting compounds is notoriously difficult, because the measurement is highly sensitive to surface contamination, self-absorption, and saturation effects. Fortunately, recent upgrades at synchrotron facilities, advancements in beamline instrumentation, and sample preparation methods suggest that these insights are now within reach. Specifically, comparing XAS spectra measured in transmission with a scanning transmission X-ray microscope (STXM) with those from non-resonant inelastic X-ray scattering (NIXS) and time-dependent density functional theory provides a sound basis for validation of bulk-like excitation spectra.

Herein, a new effort is discussed that employs these techniques to understand bonding interactions in two well defined series of f-element materials. The actinide sandwich complexes, "actinocenes," $(C_8H_8)_2An$ ($An = Th, Pa, U, Np, Pu$) have played a central role in the development of organoactinide chemistry. Results showed two contrasting trends in actinide-carbon orbital mixing, and evidence that covalency does not increase uniformly as the actinide series is traversed. Additionally, the C K-edge XAS spectrum of thorocene represents the first experimental evidence of a ϕ -type orbital interaction. Oxygen K-edge XAS measurements and DFT studies began the lanthanide dioxides LnO_2 ($Ln = Ce, Pr, Tb$), because their electronic structures are well-established from hard X-ray spectroscopies. Preliminary efforts to use lanthanide oxides and lanthanide organometallics as experimental benchmarks for quantitative determinations of covalency in d-block and f-block materials will also be discussed.

9:00am AC+AS+MI+SA+SS-MoM3 **X-ray Magnetic Circular Dichroism of Actinides, Andrei Rogalev, F. Wilhelm**, European Synchrotron Radiation Facility (ESRF), France **INVITED**

Actinides compounds, which are straddling the magnetic properties of rare-earths and transition metals, have been the subject of increasing interest due to their very different properties, such as Pauli paramagnets, localized and itinerant ferromagnets, and heavy fermion superconductors. The key parameter responsible for the large variety of magnetic properties is obviously degree of localization of the 5f states which are indeed involved in both the chemical bonding and the magnetism. To unravel the details of the electronic structure and magnetic properties of these 5f states, polarization dependent X-ray spectroscopy at the $M_{4,5}$ edges appears as the most suitable experimental tools. At the third generation synchrotron radiation facilities, small x-ray beam with flexible polarization sized down to few microns can be routinely achieved. This technique is thus perfectly suited for studying minute samples (a few micrograms) of transuranium materials. This talk reviews recent advances in use of polarized x-rays to

study local magnetic properties and electronic structure of actinides compounds.

The magnetic properties are mostly studied with X-ray Magnetic Circular Dichroism (XMCD). The great advantage of this technique is its capability to probe the orbital and spin magnetization of 5f states separately. XMCD experiments have been reported for a great number of uranium compounds and have permitted to understand, at least qualitatively, which is the ground state despite the difficulty over assigning a valency. It has also revealed differences between localized and itinerant systems that are not yet fully understood. To our knowledge there are very few reports on XMCD measurements on other trans-uranium materials. This is unfortunate, as the questions of localization of 5f states become more interesting as the 5f count increases. In order to improve our understanding of the magnetism of actinides, which is based up to now solely on uranium compounds, and thus better to describe the differences between localized and itinerant 5f systems, we report a thorough XMCD study of a series of ferromagnetic $AnFe_2$ Laves-phase compounds. Moreover, we show that additional information regarding exchange interaction between neighboring actinides atoms can be extracted from the XMCD measurements performed at absorption edges of other "nonmagnetic" atoms in the compounds.

Finally, we demonstrate that the study of the branching ratio in $M_{4,5}$ absorption spectra can bring valuable information regarding the coupling scheme, within which to discuss the electronic and magnetic properties of actinides atoms.

9:40am AC+AS+MI+SA+SS-MoM5 **Magnetic Circular Dichroism Measured with Transmission Electron Microscope, Jan Ruzs**, Uppsala University, Sweden **INVITED**

X-ray magnetic circular dichroism (XMCD; [1]) is an established experimental probe of atom-specific magnetic properties of lanthanides and actinides. In XMCD, a photon of well-defined energy and polarization is absorbed by an atom in the sample with a probability that is proportional to the number available unoccupied states with an energy that allows fulfilling the energy conservation and selection rules. An essential element of XMCD are so called sum rules [2,3], which relate the XMCD spectra to the spin and orbital angular momenta, respectively.

Recently, a new experimental method has been developed that is closely related to XMCD. It was named electron magnetic circular (or chiral) dichroism (EMCD) and it is measured with a transmission electron microscope (TEM) instead of a synchrotron beam-line. We will review the short history of this method starting from its proposal in 2003 [4], first experimental proof-of-the-concept in 2006 [5], formulation of the theory [6] and sum rules [7,8] in 2007 to the present state-of-the-art and early applications, for example [9-12]. Yet, despite intense efforts, EMCD is still in its development phase, particularly from the point of view of quantitative studies. On the other hand, qualitative EMCD experiments have reached resolutions below 2nm [13].

The primary advantages of the EMCD, when compared to XMCD, are costs, availability and lateral resolution. Even a state-of-the-art TEM is a device considerably cheaper than a synchrotron beam-line and as such it can be available locally to a research group. TEM is also a very versatile instrument that combines diffraction experiments, elemental analysis, local electronic structure studies via electron energy loss spectroscopy [14] and now also magnetism via EMCD.

- [1] J. L. Erskine, E. A. Stern, Phys. Rev. B **12**, 5016 (1975).
- [2] B. T. Thole et al., Phys. Rev. Lett. **68**, 1943 (1992).
- [3] P. Carra et al., Phys. Rev. Lett. **70**, 694 (1993).
- [4] C. Hebert, P. Schattschneider, Ultramicroscopy **96**, 463 (2003).
- [5] P. Schattschneider et al., Nature **441**, 486 (2006).
- [6] J. Ruzs, S. Rubino, and P. Schattschneider, Phys. Rev. B **75**, 214425 (2007).
- [7] J. Ruzs et al., Phys. Rev. B **76**, 060408(R) (2007).
- [8] L. Calmels et al., Phys. Rev. B **76**, 060409(R) (2007).
- [9] S. Muto et al., Nature Comm. **5**, 3138 (2013).
- [10] Z. H. Zhang et al., Nature Nanotech. **4**, 523 (2009).
- [11] Z.Q. Wang et al., Nature Comm. **4**, 1395 (2013).
- [12] J. Verbeeck et al., Nature **467**, 301 (2010).
- [13] P. Schattschneider et al., Phys. Rev. B **78**, 104413 (2008).
- [14] K. T. Moore and G. v.d. Laan, Rev. Mod. Phys. **81**, 235 (2009).

10:40am **AC+AS+MI+SA+SS-MoM8 The Microstructure of Plutonium Hydride Growth Sites**, *Martin Brierley, J.P. Knowles*, AWE, UK, *M. Preuss, A.H. Sherry*, University of Manchester, UK

Under certain conditions plutonium is able to form plutonium hydride during long term storage [1]. Plutonium is radioactive, decaying via release of an alpha particle. Alpha particles are particularly damaging within the body and every attempt should be made to limit the distribution of loose material. Plutonium hydrides have been shown to be pyrophoric when exposed to oxygen; a reaction that could potentially liberate loose particulate outside of suitable containment.

Previous work into the hydriding rate of plutonium has investigated the reaction rate of various hydrides on the surface of these materials; specifically the nucleation rate, the lateral growth rate and the specific hydriding rate [2, 3]. Plutonium is a reactive metal and quickly forms a semi-protective oxide layer in air. Upon exposure of an oxide-covered sample to hydrogen, hydride is formed at discrete sites on the surface, which then grow radially across the surface [1]. Recent work has suggested a grain boundary enhanced growth rate [4].

In the present study, the microstructure associated with selected plutonium hydride growth sites was studied to provide information regarding the nucleation and growth mechanisms that govern the formation of plutonium-hydride. The samples were ground to 600 grit and evacuated before being exposed to ultra-pure hydrogen at pressures between 10 mbar and 1000 mbar for sufficient time to have nucleated a number of hydride sites.

Post-test analysis was performed using Scanning Electron Microscopy (SEM) and Optical Microscopy (OM) to determine the microstructure of the hydride growth sites. The morphology of individual hydride growth sites indicates that the hydride-metal interface has a highly discontinuous boundary, resulting from enhanced grain boundary diffusion and spears of transformed material; the microstructure within the plutonium hydride growth sites indicates that a preferred growth habit was adopted by the hydride product.

References

- [1] J.M. Haschke and J.C. Martz, Los Alamos Science, 26 (2000) 266-267
- [2] G. W. McGillivray, J. P. Knowles, I. M. Findlay, M. J. Dawes, J. Nucl. Mater. 385 (2009) 212-215.
- [3] C. Kenney, R. Harker "Specific Hydriding Rates of δ -Plutonium", Presentation at Pu Futures, Keystone Colorado (2010)
- [4] C.K. Saw, J.M. Haschke, P.G. Allen, W. Mclean II, L.N. Dinh, J. Nucl. Mater. 429 (2012) 128-135

11:00am **AC+AS+MI+SA+SS-MoM9 Hydrides of U-Mo and U-Zr Alloys: Structure and Electronic Properties**, *Ladislav Havela, M. Paukov, I. Tkach, D. Drozdenko, M. Cieslar, Z. Matej*, Charles University, Czech Republic

When U metal (α -U) is exposed to H gas, it forms a stable hydride β -UH₃. The lattice expansion stabilizes the ferromagnetic order with the Curie temperature around 170 K. The metastable form, α -UH₃, could not be synthesized as a pure phase, and the admixture of β -UH₃ did not allow to determine reliably its intrinsic magnetic properties. We have been testing the reaction to H exposure of γ -U (bcc), which was synthesized as a single phase by combination of Mo or Zr doping into U and ultrafast cooling. We found that such alloys need high H₂ pressure and long exposure to absorb hydrogen. The products can be characterized by the formula UH₃Mo(Zr)_x. The hydrides with Mo have a structure corresponding to β -UH₃ with grain size around 1 nm, i.e. almost amorphous. Its ordering temperatures increase to 200 K for UH₃Mo_{0.18} and then decrease for higher Mo concentrations. The hydrides UH₃Zr_x exhibit the UH₃ structure (bcc U lattice filled with H atoms). Their Curie temperature weakly decreases with increasing Zr concentration and the extrapolation to Zr-free state indicates $T_C = 170$ K, i.e. identical to β -UH₃. The results can be compared with numerous hydrides obtained by hydrogenation of U₆X compounds (X = Mn, Fe, Co, Ni), all probably having similar magnetic properties. We present a detailed study of magnetic properties, electrical resistivity and specific heat. The structure characterization of initial alloys and the hydrides has been done by means of XRD, SEM with EBSD and TEM. The hydrides represent and new class of U materials, which exhibit, irrespective of details of composition or crystal structure, strong ferromagnetism with relatively very high ordering temperatures, quite surprising at materials at which the inter-U spacing does not exceed appreciably the Hill limit 340-360 pm. At last, the variations using double doping (both Mo and Zr) will be presented.

11:20am **AC+AS+MI+SA+SS-MoM10 Unraveling the Mystery of Reactively-Sputtered UO(4+x)**, *David Allred, R.S. Turlay, B.S. McKeon, A. Diwan, E.A. Scott, R.R. Vanfleet*, Brigham Young University
We recently found EDX and XPS evidence in reactive sputtered uranium oxide thin films of higher oxygen-to-uranium ratios than the 3-to-1 allowed

by stoichiometry. We used reactive, DC-magnetron sputtering in 100% oxygen to prepare uranium-oxide thin films on silicon wafer with the highest possible oxygen content to investigate this. Both EDX & XPS showed that the ratio of oxygen-to-uranium in freshly samples was at least 4-to-1, with compositions approached 5 to 1. The potential explanations are uranates or peroxides. Detecting hydrogen- and an element difficult to detect in thin films-is crucial in understanding what is happening chemically. Uranates require cations. The only one possible in our films would be hydrogen. Similarly, bulk uranium peroxides without water/hydrogen peroxide of hydration are not known. (We have found evidence of uranium trioxide being weekly hygroscopic and stored samples in a dry environment, nonetheless these samples show high oxygen contents as prepared.) We report our chemistry and structural (TEM and XRD) attempts to solve this mystery. We also report are measurement of extreme ultraviolet reflectance of this material. (ALS-beamline 6.3.2)

11:40am **AC+AS+MI+SA+SS-MoM11 Cathodoluminescence and Band Gap Studies of Single Crystal U_xTh_{1-x}O₂ (x = 0.00, 0.01, 0.22)**, *David Turner*, Oak Ridge Institute for Science and Education, *J. Reding, R. Hengehold, T. Kelly*, Air Force Institute of Technology, *J.M. Mann*, Air Force Research Laboratory, *J. Kolis*, Clemson University, *J. Petrosky*, Air Force Institute of Technology

Analyses of depth- and temperature-resolved cathodoluminescence experimental techniques have identified many previously unobserved spectral characteristics in U_xTh_{1-x}O₂ compounds grown using a slow growth hydrothermal method. Three U_xTh_{1-x}O₂ (x = 0.00, 0.01, 0.22) hydrothermally grown, single crystals were examined using cathodoluminescence. Unique luminescence features were identified as a function of uranium concentration. In the undoped and x = 0.01 U_xTh_{1-x}O₂, an electronic phase transition is observed as a 20 nm (0.21 eV) red-shift in the wavelength of maximum emission. This red-shift appears when the crystals are heated during both 5 and 10 keV electron beam irradiation. Conversely, a similar phase transition is not observed in the U_xTh_{1-x}O₂ alloy (x = 0.22). Instead, the wavelength of maximum emission remains constant at 305 nm (4.07 eV). Ultimately, the addition of uranium to the ThO₂ lattice increases the band gap of the material which is identified as a 10 nm (0.13 eV) blue shift if the luminescence. Finally, a quadrupole transition is observed in the uranium-containing crystals (O 2p to U 5f) at approximately 600 nm (2.07 eV).

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room: 312 - Session SA-MoM

Synchrotron Studies of Processes in Energy Conversion, Electronic Devices and Other Materials I

Moderator: Franz Himpsel, University of Wisconsin-Madison

8:20am **SA-MoM1 Looking Into Buried Interfaces with Soft/hard X-Ray Photoemission and Standing-Wave Excitation**, *Charles Fadley*, University of California, Davis

INVITED

I will present some new directions in synchrotron radiation soft x-ray photoemission (XPS, SXPS) and hard x-ray photoemission (HXPS, HAXPES, HIKE) [1-6], with illustrative examples of applications to a range of sample types. These involve combined SXPS and HXPS studies of buried layers and interfaces in magnetic and transition-metal oxide multilayers [1,2], as well as in semiconductor junctions [3]; solid-gas or solid-liquid interfaces with high ambient pressures [5]; band-offset measurements in multilayer structures [6]; and the use of standing waves from multilayer mirrors to enhance depth contrast in spectroscopy [1-5].

References

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, the Army Research Office, under MURI Grant W911-NF-09-1-0398, the Forschungszentrum Julich, Peter Grunberg Institute, and the APTCOM project of Le Triangle de Physique, Paris.

1 "Determination of layer-resolved magnetic and electronic structure of Fe/MgO by standing-wave core- and valence- photoemission", See-Hun Yang, Benjamin Balke, Christian Papp, Sven Döring, Ulf Berges, L. Plucinski, Carsten Westphal, Claus Schneider, Stuart S. P. Parkin, and Charles S. Fadley, Phys. Rev. B 84, 184410 (2011).

2 "Interface properties of magnetic tunnel junction La_{0.7}Sr_{0.3}MnO₃/SrTiO₃ superlattices studied by standing-wave excited photoemission spectroscopy", A. X. Gray et al., Phys. Rev. B 82, 205116 (2010); and A.X. Gray et al., Europhysics Letters 104, 17004 (2013).

3 “Nondestructive characterization of a TiN metal gate: chemical and structural properties by means of standing-wave hard x-ray photoemission spectroscopy”, C. Papp, G. Conti, et al. *J. Appl. Phys.* 112, 114501 (2012).

4 “Hard X-ray Photoemission with Angular Resolution and Standing-Wave Excitation”, C. S. Fadley, invited review, *J. Electron Spectrosc.* 190, 165-179 (2013)

5 “Chemical-state resolved concentration profiles with sub-nm accuracy at solid/gas and solid/liquid interfaces using standing-wave ambient-pressure photoemission (SWAPPS)”, S. Nemsak et al., in preparation

6 “Band Offsets in Complex-Oxide Thin Films and Heterostructures of SrTiO₃/LaNiO₃ and SrTiO₃/GdTiO₃ by Soft and Hard X-ray Photoelectron Spectroscopy”, G. Conti, A. M. Kaiser, A. X. Gray, S. Nemšák, G. K. Pálsson, J. Son, P. Moetakef, A. Janotti, L. Bjaalie, C.S. Conlon D. Eiteneer, A.A. Greer, A. Keqi, A. Rattanachata, A.Y. Saw, A. Bostwick, W.C. Stolte, A. Gloskovskii, W. Drube, S. Ueda, M. Kobata, K. Kobayashi, C. G. Van de Walle, S. Stemmer, C. M. Schneider and C. S. Fadley, *J. Appl. Phys.* 113 143704 (2013).

9:00am **SA-MoM3 Hard X-ray Photoelectron Spectra (HXPES) of Bulk Non-Conducting Silicate Glasses**, *Yongfeng Hu, Q.F. Xiao, X.Y. Cui, D. Wang*, Canadian Light Source, Canada, *G.M. Bancroft, H.W. Nesbitt, M. Biesinger*, University of Western Ontario, Canada

Bulk studies of non-conducting oxides and silicates, such as silicate glasses containing cations such as Na, K, Mg and Ca are important to obtain quantitative bulk information of bridging oxygen (Si-O-Si, so-called BO), non-bridging oxygen (Si-O-M, so-called NBO), and free oxygen (M-O-M). These studies have been so far limited to the XPS studies using spectrometers equipped with modern charge compensation systems, such as Kratos or ESCALAB 250Xi.^{1,2} Such measurements are very important for determining the chemical and physical properties of a wide variety of silicate minerals and glasses². Synchrotron-based hard X-ray photoelectron spectroscopy (HXPES) has recently been applied to the characterization of surfaces and interfaces of advanced materials. In this work, we will demonstrate that the HXPES, without any charge compensation system, can avoid the large differential charging problems usually seen with bulk non-conductors using conventional XPS instruments. These problems are overcome by depositing a thin metal coating on the glass surface and by taking advantage of the large and variable probing depth offered by HXPES. We show that the optimal O 1s linewidth, matching to that of the Krotos' results, can be obtained for the non-conducting silicate glasses using HXPES. Together with the high resolution Si 1s results, these HXPES data are critical for accurate analysis of the BO, NBO and free oxide content of these silicate glasses.

[1] H. W. Nesbitt, G.M. Bancroft, G.S. Henderson, R.Ho, K.N. Dalby, Y. Huang, Z. Yan, *J. Non-Cryst. Solids* 357 (2011) 170.

[2] H.W.Nesbitt, G.M. Bancroft, *Rev. Min. Geochem.* 78 (2014) 271.

9:20am **SA-MoM4 In Situ Study of Plasma Assisted Atomic Layer Epitaxy of III-N Semiconductors Using Synchrotron X-ray Methods**, *N. Nepal*, Naval Research Laboratory, *M.G. Erdem*, Boston University, *S.D. Johnson, V.R. Anderson*, Naval Research Laboratory, *A. DeMasi, K.F. Ludwig*, Boston University, *Charles Eddy, Jr.*, Naval Research Laboratory
Atomic layer epitaxy (ALE) is a relatively new method to grow crystalline materials in a layer-by-layer fashion by separating the growth reaction into two surface-mediated, self-limiting half reactions at relatively low temperatures. Recently, plasma assisted ALE (PA-ALE) has been used to grow epitaxial III-nitride films at temperatures from 180-500°C [1-2]. At these growth temperatures, the ad-atom mobility is low and the growth process is highly dependent on the quality of the growth surface. Thus, understanding the mechanism of nucleation and growth kinetics is very important to improving material quality. A promising method for *in situ* monitoring involves the use of high intensity coherent x-rays, such as from a synchrotron light source, and includes small angle reflectance/scattering, diffraction, and fluorescence.

We present initial *in situ* studies of the PA-ALE process using synchrotron x-ray radiation, and grazing incidence small angle x-ray scattering (GISAXS), x-ray reflectivity (XRR), and in-plane x-ray diffraction (XRD) measurements. Investigations focus on the *in situ* surface preparation process and initial stages of epitaxial growth of AlN and InN on GaN template layers. Experiments were conducted in a custom PA-ALE growth facility installed at beamline X21 of the National Synchrotron Light Source. Surface evolution during the *in situ* surface preparation process was monitored by GISAXS and the nucleation and growth processes for AlN and InN were monitored using GISAXS, XRR, and in-plane XRD. Atomic force microscopy (AFM), x-ray photoelectron spectroscopy and out-of-plane XRD were employed as post growth characterizations.

In situ XRR measurements of an optimized growth process for AlN on a 450°C substrate revealed a 0.08 nm/cycle growth rate and clearly shows

each half-cycle of the AlN growth process. *Ex situ* AFM measurements confirm that the surface roughness after growth was similar (RMS roughness = 0.74 nm) to that of the GaN substrate. We compare the *in situ* in-plane synchrotron XRD study with previous reports[2] of AlN/GaN grown in a Cambridge Nanotech Fiji reactor to assess the material quality grown in the *in situ* chamber. The in-plane XRD measurement on pre-grown ALE AlN confirms the epitaxial nature and wurtzite structure with 60 degree symmetry in Φ -scan. These early results demonstrate that *in situ* synchrotron x-ray characterization methods are a powerful tool for exploring the epitaxial nucleation and growth mechanisms of III-nitride layers by PA-ALE.

1. N. Nepal, et al., *J. Cryst. Growth and Des.* **13**, 1485 (2013).

2. N. Nepal, et al., *Appl. Phys. Lett.* **103**, 082110 (2013).

9:40am **SA-MoM5 Application of Synchrotron Radiation Based Hard X-ray Photoelectron Spectroscopy (HAXPES) to Characterise Semiconductor Device Structures**, *Greg Hughes, L. Walsh*, Dublin City University, Ireland, *J.C. Woicik*, National Institute of Standards and Technology (NIST), *P.K. Hurley*, Tyndall National Institute, Ireland
INVITED

Hard x-ray photoelectron spectroscopy (HAXPES) is emerging as a technique which has the capability to provide chemical and electronic information on much larger depth scales than conventional XPS. This has potential applications in the study of oxide/semiconductor and metal/semiconductor buried interfaces found in device structures, particularly after annealing cycles. In this presentation results of combined hard x-ray photoelectron spectroscopy (HAXPES) and electrical characterisation measurements on identical Si and III-V based metal-oxide-semiconductor (MOS) structures will be presented. The experimental findings obtained indicate that surface potential changes at the semiconductor/dielectric interface due to the presence of a thin metal gate layer can be detected with HAXPES. Changes in the semiconductor band bending at zero gate voltage and the flat band voltage for the case of metal gate layers derived from the semiconductor core level shifts observed in the HAXPES spectra are in agreement with values derived from C-V measurements.

The III-V material InGaAs, shows promise as the channel material in high speed n-MOSFETs however, the issue of low resistance source/drain (S/D) contacts to InGaAs remains. A possible solution is to find a self-aligned silicide like material (salicide) to act as the S/D contacts. The search for this material has recently focussed on Ni-InGaAs, due to its promisingly low R_s and its apparent abrupt interface with InGaAs. Results of a HAXPES study of the Ni-InGaAs alloy system has been undertaken in order to determine the nature of the Ni-InGaAs interface and its evolution as a function of annealing temperature. The results show that Ni readily interacts with InGaAs upon deposition at room temperature resulting in significant inter-diffusion and the formation of NiIn, NiGa, and NiAs alloys. This information when combined with x-ray absorption spectroscopy (XAS) measurements can be used to develop a structural and chemical compositional model of the Ni-InGaAs system as it evolves over a thermal annealing range of 250-500 °C.

10:40am **SA-MoM8 Correlative Probing of the Surface Chemistry and Electron Transport of Nanodevices in Operando Mode using Scanning Photoelectron Emission Microscopy**, *Andrei Kolmakov*, National Institute of Standards and Technology (NIST)
INVITED

The surface as well as interfacial properties of nanoscopic devices are intimately linked to their electronic transport properties. In addition, they have a strong dependence on their dimensions, faceting and stoichiometry. As a result, the traditional measurements on the ensembles of nanostructures would suffer from significant averaging effects and need to be replaced with testing of individual well characterized nanostructure. In this report, we demonstrate few examples of correlative imaging, spectroscopy and transport measurements on individual working nanodevices using capabilities of modern synchrotron radiation based photoelectron microscopy. In particular, the surface analysis of the operating MEMS nanowire sensor model device being coupled with scanning x-ray beam induced current microscopy correlates real time changes in conductance of the nanowire with formation of the specific surface groups upon redox reaction. The effect of the electrodes and electroactive defects in the devices on their performance will be discussed. The perspectives of the *in operando* device characterization at real world pressures and temperatures will be outlined.

11:20am **SA-MoM10 A NEXAFS Spectromicroscope for Structural and Chemical Imaging Analysis**, *Conan Weiland*, Synchrotron Research, Inc., *Z. Fu*, *C. Jaye*, *D.A. Fischer*, National Institute of Standards and Technology, *K. Scammon*, University of Central Florida, *P.E. Sobol*, *E.L. Principe*, Synchrotron Research, Inc.

INVITED

We present the development of a Large Area Rapid Imaging Analytical Tool (LARIAT MKII) for near edge x-ray absorption fine structure (NEXAFS) surface chemical and structural analysis. This analyzer utilizes magnetostatic and grid-less electrostatic lenses to maintain the lateral distribution of electrons into a 16 mega channel detector, allowing for a 180° collection angle for high collection efficiency enabling rapid parallel imaging. The system is in development for installation at the NIST SST beamline at NSLS II. Initial images from LARIAT MKII, currently installed at NSLS, will also be presented. The images demonstrate the system's imaging capabilities, with resolution approaching 5 μm for C K-edge images.

Monday Afternoon, November 10, 2014

Actinides and Rare Earths Focus Topic

Room: 301 - Session AC+AS+MI+SA+SS-MoA

Theoretical Modeling of f Electron Systems

Moderator: Ladislav Havela, Charles University, Czech Republic

2:00pm AC+AS+MI+SA+SS-MoA1 **Nonmagnetic Ground State of PuO₂**, *Jindrich Kolorenc*, Academy of Sciences of the Czech Republic **INVITED**

The correlated band theory implemented as a combination of the local density approximation with the dynamical mean-field theory is applied to PuO₂. We obtain an insulating electronic structure consistent with the experimental photoemission spectra, and a nonmagnetic ground state that is characterized by a noninteger filling of the plutonium f shell ($n_f \approx 4.4$). Due to a sizable hybridization of the f shell with the p states of oxygen, the ground state is more complex than the four-electron Russell-Saunders ³L₄ manifold split by the crystal field. The dynamical mean-field theory, which in the present case can be schematically viewed as an extension of the crystal-field model with hybridization terms, improves the agreement between the theory and experiment for the magnetic susceptibility [1]. Encouraged by the good accuracy achieved for PuO₂, we apply the theory to several other tetravalent actinide oxides.

[1] A. B. Shick, J. Kolorenc, L. Havela, T. Gouder, and R. Caciuffo, Phys. Rev. B **89**, 041109 (2014).

2:40pm AC+AS+MI+SA+SS-MoA3 **DMFT Modeling of Electronic Spectral Properties in Pu-based Actinides**, *Jian-Xin Zhu*, Los Alamos National Laboratory **INVITED**

Plutonium-based materials have been studied for many years due to their importance in nuclear energy applications. Scientifically, these materials exhibit highly complex properties. Pu metal shows a significant volume expansion and anomalous magnetic properties; while Pu-115 (like PuCoGa₅) are found to be superconductors. These intriguing phenomena originate from the special location of Pu in the Periodic Table, which is at the boundary between the light actinides that have itinerant 5f electrons and the heavy actinides with localized 5f electrons. They call out the notion of strong correlation of 5f electrons. In this talk, I will present a study of the electronic structure of Pu metals and its 115 compounds in the framework of the combination of local density functional approximation and dynamical mean-field theory. In particular, the results on momentum-resolved spectral functions will be presented and be compared with those based on the LDA only. In addition, the effect of Pu 5f electron occupancy on the electronic structure of these systems will also be discussed. The test of these results by future angle-resolved photoemission spectroscopy measurements will give a stringent constraint on the theoretical approach.

3:40pm AC+AS+MI+SA+SS-MoA6 **The Evolution in Pu Nanocluster Electronic Structure: From Atomicity to Three-Dimensionality**, *James Tobin, S.W. Yu, B.W. Chung*, Lawrence Livermore National Laboratory, *M.V. Ryzhkov*, Russian Academy of Science-Urals, *A. Mirmelstein*, Russian Federation Nuclear Lab (VNIITF)

The development of electronic structure in solid systems as a function of size has long been a subject of great interest and extensive scientific investigation. Experimentally, the transition, from nanoscale or mesoscopic to bulk behavior in metal clusters, was reported in 1981 by Mason and co-workers. Similarly, the evolution from two-dimensional to three-dimensional band structure in metal overlayers and the manifestation of nanoscale effects in compound semiconductor have also been observed. In the area of actinide materials, the progress has been slowed by the limitations imposed by the highly radioactive, chemically toxic and pyrolytic nature of these materials. Havela and Gouder and colleagues performed investigations upon Plutonium (Pu) ultra-thin films, deposited in situ by means of a discharge-plasma, and Trelenberg and co-workers developed an approach using laser ablation of Uranium (U). Gas phase studies of actinides have also been pursued including atoms, molecules and reactions. Recent theoretical studies include UO₂ molecules, solid actinide oxides, and actinide carbide clusters. A new approach to cluster calculations has been taken in this study. Past cluster calculations were arranged in such a way that the central atom would exist in a bulk like environment. In calculations herein, it is expected that the central atom will be in the most bulk-like environment as well. However, just as in any finite size object, there will be variation of potential at the positions of symmetry non-equivalent atoms within the simulated cluster. Hence, averaging over all of the atoms in the cluster will give a measure of the effect of size. We will use this aspect of

cluster calculations to investigate size related effects. Here, we report the result of the calculation of the electronic structure of clusters of Pu and their comparison to bulk spectroscopic results. Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract No. DE-AC52-07NA27344. Work at the RAS and VNIITF was supported in part by Contract B590089 between LLNL and VNIITF. The Advanced Light Source (ALS) in Berkeley and the Stanford Synchrotron Radiation Laboratory are supported

by the DOE Office of Science, Office of Basic Energy Science. For more detail see: M.V. Ryzhkov, A. Mirmelstein, S.-W. Yu, B.W. Chung and J.G. Tobin, "Probing Actinide Electronic Structure through Pu Cluster Calculations," Intl. J. Quantum Chem. **113**, 1957 (2013); COVER ARTICLE.

4:00pm AC+AS+MI+SA+SS-MoA7 **First-Principles Density Functional Theory Simulation on Rare-Earth-Based Oxides as Fast Oxygen Ion Conductors**, *Mamoru Sakaue, M. Alaydrus, H. Kasai*, Osaka University, Japan, *T. Ishihara*, Kyushu University, Japan

Development of novel fast ion conductors is a crucial issue for realizing solid oxide fuel cells (SOFCs) which can operate in low temperatures. While yttria-stabilized zirconia (YSZ) had been well-studied both by experiments and theories, exploration of other types of materials retaining high ionic conductivities in lower temperatures is still desired. Experimental studies in the recent twenty years have found some rare-earth-based oxides having higher ionic conductivities to be promising for operation below 600°C, and first-principles simulation studies on the materials have begun.

We studied atomic and electronic properties on oxygen-ionic conduction of LaGaO₃-, La₂GeO₅-, Pr₂NiO₄- and CeO₂-based materials by first-principles calculations based on density functional theory (DFT). We analyzed stable structures, electronic densities of states, oxygen migration paths and activation energies in the paths of pure and doped materials in order to evaluate their capabilities in application to electrolytes or electrodes. The obtained results of the activation energies showed good agreements with experiments in several aspects. However, for Pr₂NiO₄- and CeO₂-based materials that contain lanthanoid elements, there remains an open question about theoretical treatment of 4f electron states. The strong localization was found to affect oxygen ion motions fundamentally as well as electronic/magnetic properties. Then the strong electron-electron correlation modifies simple trends in activation energies found for the lanthanoid series within an approximation in which the correlation effects were neglected [1].

While fundamental reproduction of the strong electron-electron correlation in localized states by DFT is extremely difficult, empirical corrections by Hubbard *U* terms enable a practical solution to this problem. Here, the *U* value can be determined only by comparison with experiments in most cases because the value is affected by environment of the lanthanoid atoms. However, a theoretical study based on an empirical model demonstrated that the environment effects on 4f orbitals can be small if its strong localization is maintained [2]. In the presentation, we confirm this rule based on the results by the DFT first-principles calculations with Hubbard *U* corrections and discuss possibilities of computational materials design of lanthanoid-doped ceria (Ce_{1-x}Ln_xO_{2-x/2}) as electrolyte materials.

[1] M. Alaydrus, M. Sakaue, S. M. Aspera, T. D. K. Wungu, T. P. T. Linh, H. Kasai, T. Ishihara and T. Mohri, J. Phys. Condens. Matter **25**, 225401 (2013).

[2] E. Rogers, P. Dorenbos and E. van der Kolk, New J. Phys. **13**, 093038 (2011).

4:20pm AC+AS+MI+SA+SS-MoA8 **Electronic Structure, Magnetic Properties, and Magneto-Structural Transformations of Rare Earth Magneto-Caloric Materials**, *Durga Paudyal*, Ames Laboratory, *V.K. Pecharsky, K.A. Gschneidner, Jr.*, Ames Laboratory and Iowa State University **INVITED**

We present first principles modeling of structural and magnetic properties of Gd₅Ge₄ based magneto-caloric materials. The total energy as a function of the shear displacement of slabs confirms stability of experimentally observed crystal and magnetic structures. Small substitutions of the Gd by Y and Lu lead to a catastrophic loss of ferromagnetism, but the substitutions by La have no effect on the magnetism. Furthermore, substitutions of the Ge by Si exert chemical pressure and transform the antiferromagnetic O(II) to the ferromagnetic O(I) ground state. In addition, we present a pathway for estimating the magnetic entropy change in the room temperature giant magnetocaloric compounds, i.e. Gd₅Si₂Ge₂, by coupling first principles outputs with the established magneto-thermodynamic models. The theoretical values of the magnetic entropy change compare well with experimental results.

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. The research was performed at the Ames Laboratory, which is operated for the U.S. DOE by Iowa State University under contract # DE-AC02-07CH11358.

Novel Trends in Synchrotron and FEL-Based Analysis

Focus Topic

Room: 312 - Session SA-MoA

Synchrotron Studies of Processes in Energy Conversion, Electronic Devices and Other Materials II

Moderator: Charles Fadley, University of California, Davis

2:00pm **SA-MoA1 Synchrotron-based *In Situ* Study of PEMFC, SOFC, Battery and Supercapacitor Components, Benedetto Bozzini, Universita' del Salento - Italy** **INVITED**

Fuel cells and supercapacitors are electrochemical devices providing efficient and pollution-free production and transformation of electricity. Notwithstanding their environmental appeal, a host of materials-science problems – chiefly related to the limited durability of crucial functional components – are hindering the widespread application of these otherwise promising devices. Nanotechnology is foreseen to play a key role in the elimination of such drawbacks. Some nanotechnology solutions have already led to sensitive improvements of properties, functionality and performance of some components. However, the present knowledge is mostly at the macroscopic and empirical trial-and-error level and the answers to many questions require much deeper scientific understanding of the origin of degradation processes. In this regard, the development and implementation of appropriate methods for in-situ characterization of cell components at the functionally relevant length scales is highly required. Soft X-ray spectroscopies, namely X-ray absorption spectroscopy, X-ray emission (fluorescence) spectroscopy, resonant inelastic X-ray spectroscopy and X-ray photoelectron spectroscopy have been extensively employed for ex-situ characterization of materials used in electrochemical systems. Furthermore, adding spatial resolution capabilities by implementing proper optical solutions has opened unique opportunities for monitoring material changes and mass transport events occurring at submicron length scales. The input from these methods is providing correlative information about the status of the electrode surface and of the electrode/electrolyte interface and also of the processes occurring under operation conditions at the three phase boundary, namely the electrode-electrolyte-reactant interface¹⁻⁴. REFERENCES [1] B. Bozzini, A. Gianoncelli, P. Bocchetta, S. Dal Zilio, G. Kourousias, *Anal. Chem.* **86**, 664 (2014)

[2] B. Bozzini, M. Amati, L. Gregoratti, M. Kiskinova, *Sci. Rep.* **3**, 2848 (2013)

[3] B. Bozzini, A. Gianoncelli, C. Mele, M. Kiskinova, *Electrochim. Acta* **114**, 889 (2013)

[4] B. Bozzini, M. Kazemian Abyaneh, M. Amati, A. Gianoncelli, L. Gregoratti, B. Kaulich, Maya Kiskinova, *Chemistry – A European Journal* **18**, 10196 (2012)

2:40pm **SA-MoA3 Structure/Selectivity Studies of Promoted Rh/TiO₂ Catalysts under CO Hydrogenation Reaction Conditions, Robert Palomino, J. Magee, P. Carrillo Sanchez, Stony Brook University, M. White, Brookhaven National Laboratory and SUNY Stony Brook**

Rh-based catalysts are sought after for the conversion of syn gas (CO +H₂) to higher oxygenates due to their C-C coupling capabilities, but are highly selective to hydrocarbons. Through the addition of promoters (Fe, Mn, Mo), the selectivity can be altered to oxygenates by varying mechanisms.[1] Fe and Mo in particular have been known to enhance ethanol and other C₂₊-oxygenates through the suppression of methane. Unfortunately, little is known of the structure of these promoted catalysts under reaction conditions. This work focuses on the atomic structure determination of Fe- and Mo-promoted Rh/TiO₂ catalysts with varying promoter concentration. The atomic structure was monitored as a function of promoter concentration under reduced and CO hydrogenation conditions with synchrotron radiation at beamline X7B of the NSLS. X-ray diffraction (XRD) was utilized to elucidate the phase components in the catalysts, while Pair Distribution Function (PDF) analysis was used to determine the local atomic structure of the active components contained in the catalyst. By monitoring the evolution of phase and local atomic structure, we correlate the structure-selectivity relationship by direct comparison with selectivity measurements performed on the same catalysts.

1. Spivey, J.J. and A. Egbebi, *Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas*. Chemical Society Reviews, 2007. **36**(9): p. 1514-1528.

3:00pm **SA-MoA4 Synchrotron Infrared Nano-spectroscopy, Hans Bechtel, Lawrence Berkeley National Laboratory, E.A. Muller, R.L. Olmon, University of Colorado at Boulder, M.C. Martin, Lawrence Berkeley National Laboratory, M.B. Raschke, University of Colorado at Boulder**

By combining scattering-scanning near-field optical microscopy (s-SNOM) with mid-infrared synchrotron radiation, synchrotron infrared nano-spectroscopy (SINS) enables molecular and phonon vibrational spectroscopic imaging, with rapid spectral acquisition, spanning the full mid-infrared (500-5000 cm⁻¹) region with nanoscale spatial resolution. This highly powerful combination provides access to a qualitatively new form of nano-chemometric analysis with the investigation of nanoscale, mesoscale, and surface phenomena that were previously impossible to study with IR techniques. We have installed a SINS end-station at Beamline 5.4 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, making the s-SNOM technique widely available to non-experts, such that it can be broadly applied to biological, surface chemistry, materials, or environmental science problems. We demonstrate the performance of synchrotron infrared nano-spectroscopy (SINS) on semiconductor, biomineral and protein nanostructures, providing vibrational chemical imaging with sub-zeptomole sensitivity.

3:40pm **SA-MoA6 Synchrotron-Based Spectroscopy Shedding Light on Solar Cells, Franz Himpsel, University of Wisconsin-Madison** **INVITED**

After briefly discussing the role of photovoltaics in the current energy picture, this talk illustrates how spectroscopy with soft X-rays can assist the development of new types of solar cells with improved price/performance ratio. The starting point is the most general layout of a solar cell, which involves of a light absorber sandwiched between an electron donor and an electron acceptor. In contrast to the widely-used silicon solar cells, one can choose three different materials to optimize the four energy levels that are crucial for the performance of a solar cell. These are measured by a combination of X-ray absorption spectroscopy and photoelectron spectroscopy. Close coupling with first principles calculations makes it possible to discover and exploit systematic trends. Examples will be given, such as the combination of all three components in one molecule (donor- π -acceptor complexes [1],[2]). In addition to the energy levels one has to consider the lifetime of the photo-generated carriers. A future dream experiment will be discussed where the carriers are followed in real time on their way from the absorber to the contact electrodes, using pump-probe techniques at the latest generation of soft X-ray light sources. Such experiments have been performed in the UV/visible [3], but they would greatly benefit from the element- and bond-specific capabilities of X-ray absorption spectroscopy.

[1] A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, Md. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science* **334**, 629 (2011).

[2] I. Zegkinoglou, M.-E. Ragoussi, C. D. Pemmaraju, P. S. Johnson, D. F. Pickup, J. E. Ortega, D. Prendergast, G. de la Torre, and F. J. Himpsel, *J. Phys. Chem. C* **117**, 13357 (2013).

[3] G. Duvanel, J. Grilj, and E. Vauthey, *J. Phys. Chem. A* **117**, 918 (2013).

4:20pm **SA-MoA8 *In Situ* Soft X-Ray Absorption Spectroscopy for Investigation of Charge Storage and Actuation in Nanostructured Carbon Aerogels, J.R.I. Lee, M. Bagge-Hansen, B. Wood, T. Ogitsu, A. Wittstock, M. Worsley, Trevor Willey, M. Merrill, Lawrence Livermore National Laboratory, D. Prendergast, Lawrence Berkeley National Laboratory, I.C. Tran, M. Biener, T. Baumann, J. Biener, Lawrence Livermore National Laboratory, J.-H. Guo, Lawrence Berkeley National Laboratory, T.W. van Buuren, Lawrence Livermore National Laboratory**

Carbon aerogels (CAs) are a class of nanostructured, porous materials that have demonstrated applications in electrical energy storage (EES) due to their very high surface area, chemical and electrochemical stability, and relatively low cost. Tailoring these materials towards improved ESS performance can be significantly enhanced by a better understanding of nanostructured materials in aqueous environments under various potential gradients; therefore, we have pursued advanced in situ characterization techniques capable of probing the electronic structure and bonding of these electrode materials during charge-discharge cycling. We report the successful development of a cell for in situ soft x-ray absorption spectroscopy (XAS) studies of EES materials and the application of this cell to the investigation of CA supercapacitors. Our XAS measurements, combined with complementary ab initio modeling, reveal profound changes in the structure and bonding of the CAs in operando, which will be discussed in terms of their macroscopic physical properties. This work

performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

4:40pm **SA-MoA9 First-Principles Modeling of Near-Edge X-ray Spectroscopy for Lithium Compounds**, *John Vinson*, National Institute of Standards and Technology (NIST)

X-ray spectroscopy is a widely-used tool for probing local structural and chemical properties of materials. For devices such as batteries *operando* measurements are vital for understanding the structural changes that take place during the device's lifecycle. Computational modeling can assist experimental investigation by providing complementary data: pointing from proposed structure to observed spectra. The OCEAN spectroscopy package is capable of calculating K- and L-edge spectra of periodic or semi-disordered extended systems using a Bethe-Salpeter equation formalism. Here we present the OCEAN package and near-edge x-ray absorption calculations of lithium compounds. We showcase the effects of accounting for vibrational disorder as well as how a computational approach can be used to decouple the structural and charge-transfer effects on the x-ray spectra observed during (de)lithiation.

5:00pm **SA-MoA10 Soft X-ray Spectroscopy for Fundamental Understanding and Practical Optimization of Battery Materials**, *Wanli Yang*, Lawrence Berkeley National Laboratory **INVITED**

Improving the energy-density and safety of batteries remains a formidable and critical challenge for sustainable energy applications, especially for electric vehicles. The pressing demand calls for novel approaches based on modern material synthesis and advanced characterization tools. Synchrotron based soft x-ray spectroscopy is one of such incisive tools that probe the electronic states in the vicinity of the Fermi Level, which are directly related to battery operations.

This presentation will focus on the concepts of how the electronic structure revealed by soft x-ray spectroscopy could help the battery material research. The link between fundamental electron states and battery performance will first be explained in general^[1]. Several recent spectroscopic results will be discussed from both chemical and physical point of view: The chemical information delivered by soft x-ray indicates the complicated formation process of solid-electrolyte-interphases^[2]. The evolution of the transition-metal 3d states provides in-depth information of the phase transformation in positive electrodes^[3]. Key electronic states that could be directly detected by soft x-ray experiments provide clear guidelines for optimizing battery binder materials in negative electrodes^[4]. Additionally, *in-situ/operando* soft x-ray experiments reveal distinct charge dynamics in operating battery electrodes^[5]. Perspectives will be provided at the end on how to advance the battery material studies through novel instrumentation and methodology.

[1] Yang et al., JESRP 190, 64 (2013); [2] Qiao et al., Adv. Mater. Interf. 10.1002/admi.201300115 (2014); [3] Liu et al., JACS 134, 13708 (2012); [4] Liu et al., Adv. Mater. 23, 4679 (2011); [5] Liu et al., Nat. Commun. 4, 2568 (2013)

Tuesday Morning, November 11, 2014

Actinides and Rare Earths Focus Topic

Room: 301 - Session AC+AS+MI+SA+SS-TuM

Synchrotron Radiation and Laboratory Based Investigations of Actinides and Rare Earths

Moderator: David Geeson, AWE

8:00am **AC+AS+MI+SA+SS-TuM1 The Role of the 5f Band and Partial Occupancy in Actinide L3-edge XANES and RXES Measurements**, *Corwin Booth, S.A. Medling, Y. Jiang*, Lawrence Berkeley National Laboratory, *J.G. Tobin*, Lawrence Livermore National Laboratory, *P.H. Tobash, J.N. Mitchell, D.K. Veirs*, Los Alamos National Laboratory, *M.A. Wall, P.G. Allen*, Lawrence Livermore National Laboratory, *J.J. Kas*, University of Washington, *D. Sokaras, D. Nordlund, T.-C. Weng*, SLAC National Accelerator Laboratory, *E.D. Bauer*, Los Alamos National Laboratory

INVITED

Although actinide (An) L3-edge x-ray absorption near-edge structure (XANES) spectroscopy has been very effective in determining An oxidation states in insulating, ionically-bonded materials, such as in certain coordination compounds and mineral systems, the technique fails in systems featuring more delocalized 5f orbitals, especially in metals. Recently, actinide L3-edge resonant x-ray emission spectroscopy (RXES) has been shown to be an effective alternative. This technique is further demonstrated here using a parametrized partial unoccupied density of states method to quantify both occupancy and delocalization of the 5f orbital in alpha-Pu, delta-Pu, PuCoGa5, PuCoIn5, and PuSb2. These new results, supported by FEFF calculations, highlight the effects of strong correlations on RXES spectra and the technique's ability to differentiate between f-orbital occupation and delocalization. Potential temperature-dependent spectral changes in the hidden order compound URu2Si2 and the superconductor PuCoGa5 will be discussed.

8:40am **AC+AS+MI+SA+SS-TuM3 Actinide Research with Hard Synchrotron Radiation**, *Roberto Caciuffo*, European Commission, JRC-ITU, Germany

INVITED

Advanced x-ray synchrotron radiation techniques, addressing spatial and temporal fluctuations of structural and electronic degrees of freedom, hold outstanding scientific promises for the future of actinide research [1]. Indeed, by probing hidden order parameters and elementary electronic excitations with high sensitivity and resolution, element- and edge-specific (resonant and non-resonant) x-ray scattering experiments provide the bricks for building the novel conceptual frameworks necessary to unravel the complexity of actinides. Here, I will present selected results from these experiments and discuss what they tell us.

Whereas resonant x-ray diffraction (RXD) with photon energies tuned to the $M_{4,5}$ absorption edges of actinide ions are used to study the order of electric quadrupole moments in oxides and intermetallics [2-4], resonant x-ray emission spectroscopy (RXES) and non-resonant inelastic X-ray scattering (NIXS) are applied to study the bulk electronic configuration in solids, liquids and gases [5,6]. In particular, the high penetration depth of hard X-rays employed in NIXS enables flexible containment concepts, facilitating investigations of radioactive materials in the liquid phase or under extreme conditions. Finally, inelastic x-ray scattering (IXS) can be used to map phonon dispersion branches with an energy resolution comparable to the one afforded by inelastic neutron scattering, but using crystal samples with sizes orders of magnitude smaller than those required by neutrons.

In the first example, I will show how a combination of diffraction, RXES, and absorption near-edge spectroscopy experiments at high-pressure can be used to study the correlation between polymorphism, mixing of different electronic configurations, and hybridization effects in elemental americium [7]. The potential of RXD in elucidating the nature of "hidden order" will be illustrated by the examples of the low-temperature phases in NpO_2 [8] and URu_2Si_2 [9]. Then, I will present NIXS results interrogating the $O_{4,5}$ absorption edges of uranium and plutonium materials, and results of IXS studies of the vibrational dynamics in $PuCoGa_5$ and NpO_2 .

[1] R. Caciuffo, E. C. Buck, D. L. Clark, G. van der Laan, *MRS Bulletin* **35**, 889 (2010)

[2] P. Santini et al., *Rev. Mod. Phys.* **81**, 807 (2009)

[3] H. C. Walker et al., *Phys. Rev. Lett.* **97**, 137203 (2011)

[4] Z. Bao et al., *Phys. Rev. B* **88**, 134426 (2013)

[5] T. Vitova et al., *Phys. Rev. B* **82**, 235118 (2010)

[6] R. Caciuffo et al., *Phys. Rev. B* **81**, 195104 (2010)

[7] S. Heathman et al., *Phys. Rev. B* **82**, 201103(R) (2010)

[8] N. Magnani et al., *Phys. Rev. B* **78**, 104425 (2008)

[9] H. C. Walker et al., *Phys. Rev. B* **83**, 193102 (2011)

9:20am **AC+AS+MI+SA+SS-TuM5 Lumps, Bumps and Pyrophoric Powders - Nuclear Waste Viewed in a New Light**, *Tom Scott*, University of Bristol, UK, *C.A. Stitt, M. Hart*, Diamond Light Source Ltd., UK, *J. MacFarlane, A. Banos, H. Paraskevoulakos, K. Hallam*, University of Bristol, UK

INVITED

How do you look inside a nuclear waste package without breaking it open? This question is important when the contained corrosion products are potentially flammable and radioactive. Synchrotron x-rays have been used to perform micro-scale in situ observation and characterisation of uranium entrapped in grout; a simulation for some intermediate level waste. Using specially designed analysis cells X-ray tomography and x-ray diffraction have been used to generate both qualitative and quantitative data from a grout encapsulated uranium sample before, and after, deliberately constrained H_2 corrosion. Tomographic reconstructions determined the extent, rates and mechanisms of the oxidation reaction by assessing the relative densities between the materials and the volume of corrosion products. The oxidation of uranium in grout was shown to follow the anoxic $U + H_2O$ oxidation regime, and the pore network within the grout was observed to influence the induction period for the initiation of uranium hydride formation across the surface of the metal. Powder diffraction analysis identified the corrosion products UO_2 and UH_3 , and permitted measurement of corrosion induced stress. Together, x-ray tomography and diffraction provide a means of accurately determining the types and degree of uranium corrosion occurring, thereby offering a future means for studying the reactions occurring in real full-scale waste package systems.

11:00am **AC+AS+MI+SA+SS-TuM10 Isotopic Measurements of Uranium in Particles by SIMS**, *David Simons*, National Institute of Standards and Technology (NIST)

INVITED

Secondary ion mass spectrometry (SIMS) has become a primary tool for the International Atomic Energy Agency (IAEA) and its Network of Analytical Laboratories (NWAL) to monitor activities at uranium enrichment sites. IAEA inspectors collect samples by wiping surfaces within facilities with cloth wipes that are later distributed to the NWAL for analysis. At the laboratories particles are extracted from the wipes and searched by various means to find those that contain uranium. The uranium-bearing particles are analyzed by mass spectrometry for their isotopic composition that is the key signature to be compared with the declared use of the facility. Large-geometry (LG) SIMS instruments based on magnetic sector mass spectrometers with multicollector array detectors are used by five members of the NWAL to both search for the uranium particles and analyze those that are found. We have characterized the performance of this type of instrument and found that it can be set up with a mass resolving power that excludes nearly all mass spectral interferences from uranium isotopes while maintaining high instrument transmission and high abundance sensitivity. The total efficiency for uranium detection has been measured with monodisperse microspheres and found to exceed 1 %. Detection of $U236$ presents a special case because of interference from the $U235$ hydride ion that is removed by peak-stripping. The effect of the hydride on the uncertainty in the $U236$ abundance determination has been modeled for different uranium enrichments and hydride-to-parent ratios, and the effect of the particle substrate on hydride production has been investigated. The performance of LG-SIMS instruments for isotopic measurements of uranium in particles was recently demonstrated in the NUSIMEP-7 study organized by the Institute of Reference Materials and Measurements in which these instruments were able to detect and measure all uranium isotopes in particles smaller than 400 nm, including $U236$ at an isotopic abundance of 8×10^{-6} .

11:40am **AC+AS+MI+SA+SS-TuM12 X-ray Excited Auger Transitions of Pu Compounds**, *Art Nelson, W.K. Grant, J.A. Stanford, W.J. Siekhaus, W. McLean*, Lawrence Livermore National Laboratory

X-ray excited Pu NOO Auger line-shapes were used to characterize differences in the oxidation state of Pu compounds. The Auger line-shapes were combined with the associated chemical shift of the Pu $4f_{7/2}$ photoelectron line, which defines the Auger parameter and results in a reliable method for definitively determining oxidation states independent of binding energy calibration. Results show that PuO_2 , Pu_2O_3 , $PuH_{2.7}$ and Pu have definitive Auger line-shapes. These data were used to produce a chemical state (Wagner) plot for select plutonium oxides. This Wagner plot allowed us to distinguish between the trivalent hydride and the trivalent oxide, which cannot be differentiated by the Pu $4f_{7/2}$ binding energy alone.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room: 312 - Session SA-TuM

Characterization of Nanostructured and LD Materials Using Synchrotron-Based Methods

Moderator: Maya Kiskinova, Elettra-Sincrotrone Trieste,
Italy

8:00am **SA-TuM1 Analysis and Speciation of Nanoscaled Materials by Means of Grazing-Incidence and High-Resolution X-ray Spectrometry.** *Burkhard Beckhoff, M. Gerlach, I. Holfelder, P. Hönicke, J. Lubeck, M. Mueller, A. Nutsch, B. Pollakowski, C. Streeck, R. Unterumsberger, J. Weser,* Physikalisch-Technische Bundesanstalt (PTB), Germany **INVITED**

The development of efficient nanoscaled materials requires the correlation of the materials' functionality with their chemical and physical properties. To probe these properties, analytical methods that are both sensitive and selective at the nanoscale are required. The reliability of most analytical methods relies on the availability of reference materials or calibration samples, the spatial elemental composition of which is as similar as possible to the matrix of the specimens of interest. However, there is a drastic lack of reference materials at the nanoscale. We address this challenge by means of a bottom-up X-ray analytical method where all instrumental and experimental parameters are determined with a known contribution to the uncertainty of the analytical results. This approach does not require any reference materials but a complete characterization of the analytical instruments' characteristics. X-ray spectrometric methods allow for the variation of the analytical sensitivity, selectivity, and information depth needed to effectively reveal the spatial, elemental, and chemical specimen parameters of interest. Examples of interfacial speciation, elemental depth profiling as well as layer composition and thickness characterizations in various nanoscaled materials will be given.

References

- [1] R. Unterumsberger, B. Pollakowski, M. Müller, and B. Beckhoff, *Anal. Chem.* 83 (2011) 8623
- [2] R. Unterumsberger, M. Müller, B. Beckhoff, P. Hönicke, B. Pollakowski, S. Bjeoumikhova, *Spectrochim. Acta B* 78 (2012) 37
- [3] F. Reinhardt, J. Osán, S. Török, A.E. Pap, M. Kolbe and B. Beckhoff, *J. Anal. At. Spectrom.* 27 (2012) 248
- [4] A. Delabie, S. Sioncke, J. Rip, S. van Elshocht, G. Pourtois, M. Müller, B. Beckhoff, K. Pierloot, *J. Vac. Sci. Technol.* A30 (2012), 01A127
- [5] B. Pollakowski, P. Hoffmann, M. Kosinova, O. Baake, V. Trunova, R. Unterumsberger, W. Ensinger, and B. Beckhoff, *Anal. Chem.* 85 (2013) 193
- [6] C. Becker, M. Pagels, C. Zachaus, B. Pollakowski, B. Beckhoff, B. Kanngießer, and B. Rech, *J. Appl. Phys.* 113 (2013) 044519
- [7] C. Streeck, S. Brunken, M. Gerlach, C. Herzog, P. Hönicke, C.A. Kaufmann, J. Lubeck, B. Pollakowski, R. Unterumsberger, A. Weber, B. Beckhoff, B. Kanngießer, H.-W. Schock and R. Mainz, *Appl. Phys. Lett.* 103 (2013) 113904
- [8] J. Lubeck, B. Beckhoff, R. Fliegau, I. Holfelder, M. Müller, B. Pollakowski, F. Reinhardt and J. Weser, *Rev. Sci. Instrum.* 84 (2013) 045106
- [9] I. Holfelder, B. Beckhoff, R. Fliegau, P. Hönicke, A. Nutsch, P. Petrik, G. Roeder and J. Weser, *J. Anal. At. Spectrom.* 28 (2013) 549

8:40am **SA-TuM3 X-Ray Photoemission Spectromicroscopy: Recent Achievements and Future Applications.** *Claus Schneider,* Forschungszentrum Juelich GmbH, Germany **INVITED**

Complex material systems play a pivotal role in many areas of modern technology, such as information storage and processing or energy conversion and storage. In particular, modern information technology exploits the full potential of very different material systems for the meticulous control of alternative state variables. These state variables are used to represent the individual information bits and may be electron charges in semiconductor nanoelectronics, electron spins in the case of spintronics, or local redox configurations in resistive switching elements. Due to this broad range, the materials encompass intermetallic compounds, oxides or chalcogenides, elementary and compound semiconductors or even molecular components. In addition, the functional elements, for example, individual memory cells or transistor structures often involve nanometer dimensions and operate on nanosecond timescales or even below. This

imposes considerable challenges on the characterization of electronic, chemical and magnetic states in the steady state or during operation.

Immersion lens microscopy with synchrotron radiation has matured into a versatile and powerful tool to investigate a broad range of issues in condensed matter physics and materials science. In its energy-filtered version photoemission microscopy combines high-resolution imaging with spectroscopic capabilities in a unique fashion, enabling access to valence and core electronic states. The excitation with photons ranging from the soft to the hard x-ray regime ensures element selectivity and variable information depth. Choosing the polarization state of the synchrotron radiation enables one to distinguish different states of magnetic order, such as ferro- and antiferromagnets. The intrinsic time structure of the synchrotron radiation permits the study of processes with picosecond time-resolution via pump-probe approaches.

This contribution will review the present status of x-ray photoemission spectromicroscopy with emphasis on applications in information technology. In particular, we will cover model systems in spintronics and in resistive switching [1,2]. The results address both static properties and dynamic processes. We will also discuss new developments, such as photoemission microscopy with hard x-rays and the implementation of imaging spin polarimetry.

Y. Aoki, et al., *Nat. Commun.* (2014) 3473.

C. Lenser et al., *Adv. Funct. Mater.* (2014) online publ.

9:20am **SA-TuM5 Growth and Characterization of Low Dimensional Materials for Applications in Energy and Sensor Devices.** *Andrea Goldoni,* Elettra-Sincrotrone Trieste, Italy **INVITED**

Nanostructured low dimensional systems, in particular carbon nanotubes and oxide nanopillars, have a number of aspects that make them suitable for applications in the fields of environmental gas sensors and energy devices. Here we present the growth and characterization of some nanostructures of interest [1-3] made by well-ordered tin oxide nanopillars on ITO and hybrid/functionalized carbon nanostructures, suitable both as electrodes for solar and electrochemical cells, as well as for extremely fast (and sensitive) gas sensors [4-6].

[1] S. Hofmann et al., "In-situ observations of catalyst dynamics during surface-bound carbon nanotube nucleation", *Nano Letters* 7, 602 (2007); C. Mattevi et al., "In-situ XPS study of catalyst-support interactions and growth of carbon nanotube forests", *J. Phys. Chem. C* 112, 12207 (2008).

[2] L. D'Arsiè et al., "Tubular Sn-Filled Carbon Nanostructures on Indium Tin Oxide: Nanocomposite material for multiple applications", *Carbon* 65, 13 (2013).

[3] P. Mbuyisa et al., "Controlled Synthesis of Carbon-Based Nanostructures Using Aligned ZnO Nanorods as Templates", *Carbon* 50, 5472 (2012).

[4] F.M. Toma et al., "Efficient Water Oxidation at Carbon Nanotube/Polyoxometalate Electrocatalytic Interfaces", *Nature Chemistry* 2, 826 (2010); S. Piccinin, et al., "Unifying Concepts in Water Oxidation Catalysis: Thermodynamic and kinetic pathways powered by a molecular, tetraaruthenium-oxo complex as the blue-print of metal-oxide surfaces", *PNAS* 110, 4917 - 4922 (2013).

[5] F. Rigoni et al., "Enhancing the sensitivity of pristine carbon nanotubes to detect low-ppb ammonia concentrations in the environment", *Analyst* 138, 7392 (2013); F. Rigoni et al., "Water selective, high sensitivity gas sensors based on single-wall carbon nanotubes functionalized with indium tin oxide nanoparticles: towards low ppb detection of ammonia concentrations in the environment", submitted (2014).

[6] V. Aljani et al., "Extremely Sensitive and Fast Sensors Made of Vertical Nanostructures of SnOx on Indium Tin Oxide", submitted (2014).

11:00am **SA-TuM10 Novel 2D Electron Gases at the Surface of Transition-Metal Oxides: Role of Topology and Spin-Orbit Coupling.** *Andrés F. Santander-Syro,* Université Paris-Sud, France **INVITED**
Novel 2D electron gases at the surface of transition-metal oxides:

role of topology and spin-orbit coupling

Andrés F. Santander-Syro

CSNSM – Université Paris-Sud (France)

Transition-metal oxides (TMOs) are correlated-electron systems with remarkable properties, such as high-temperature superconductivity or large magnetoresistance. The realization of two-dimensional electron gases (2DEGs) at surfaces or interfaces of TMOs, a field of current active research, is crucial for harnessing the functionalities of these materials for future applications. Additionally, these 2DEGs offer the possibility to explore new physics emerging from the combined effects of electron correlations and low-dimensional confinement.

Recently, we discovered that a 2DEG is simply realized at the vacuum-cleaved surface of SrTiO₃, a transparent, insulating TMO with a gap of 3.5 eV. We directly imaged its multiple heavy and light subbands using angle-resolved photoemission spectroscopy [1]. In this talk, I will show that one can also create and tailor 2DEGs in other TMO surfaces, opening vast possibilities for the study of correlations in low dimensions in materials showing diverse functionalities. I will first discuss the specific case of KTaO₃, a wide-gap insulator with a spin-orbit coupling 30 times larger than in SrTiO₃. I will show that quasi-2D confinement in this system results in comparable scales for the Fermi energy, the subband splitting, and the spin-orbit coupling, leading to a complete reconstruction of the orbital symmetries and band masses [2]. Then, I will show that by choosing various surface terminations of different symmetries one can modify the electronic structure of the 2DEGs at the surface of TMOs [3]. Additionally, I will discuss the experimentally observed effects of spin-orbit coupling in the 2DEG at the surface of SrTiO₃. All these results demonstrate that, in TMOs, the strong correlations, together with the electron confinement and the surface-lattice symmetry, can lead to novel states at the surface that are not simple extensions of the bulk bands.

[1] A. F. Santander-Syro *et al.*, Nature **469**, 189 (2011).

[2] A. F. Santander-Syro *et al.*, Phys. Rev. B **86**, 121107(R) (2012).

[3] C. Bareille *et al.*, Sci. Rep. **4**, 3586 (2014).

11:40am **SA-TuM12 Effects of Interfacial Interaction: Electronic Structure of Graphene on Metallic and Insulating Surfaces**, *Petra Rudolf*, University of Groningen, The Netherlands **INVITED**

The interaction of graphene with substrates and its influence on the electronic properties is of paramount importance for designing novel electronic and optoelectronic devices. However, the capability of disentangling the surface contribution of the support from those of the graphene single layer is a challenging and unresolved problem. In this contribution I shall present results concerning the electronic states of a typical metallic interface, namely graphene/Cu, where the coupling is weak. These results will be compared to the electronic states of suspended graphene and graphene on an insulating substrate.

When the properties of the occupied electronic band structure were investigated by angle-resolved photoelectron spectromicroscopy, we demonstrated that a suspended CVD grown graphene membrane locally shows electronic properties comparable with those of samples prepared by micromechanical cleaving of graphite. CVD grown graphene on the Cu(111) surface was instead found to be slightly doped, while on an insulator surface it was demonstrated to fully preserve the intrinsic properties, implying that the graphene monolayer is totally decoupled as if it were freestanding and not doped.

The unoccupied surface states at the weakly coupled graphene/Cu interface were studied by non-linear angle resolved photoemission spectroscopy. In particular, by comparing the band dispersion of the unoccupied image potential states and the occupied surface states of the interfaces graphene/Cu(111) and graphene/ polycrystalline copper foil, we were able to identify and characterise the Shockley surface state and the n=1 image state of the Cu(111) surface and the symmetric n=1 image state of the single layer of graphene.

Tuesday Afternoon, November 11, 2014

Novel Trends in Synchrotron and FEL-Based Analysis

Focus Topic

Room: 312 - Session SA-TuA

Free Electron Laser and Synchrotron Studies at the Molecule-Surface Interfaces

Moderator: Zahid Hussain, ALS-LBNL

2:20pm SA-TuA1 FEL-Based Techniques to Explore Photochemistry and Transient States of Molecules on Surfaces, Wilfried Wurth, Universität Hamburg, Germany **INVITED**

New light sources based on linear accelerators such as the free-electron laser FLASH at DESY in Hamburg in the extreme ultraviolet, the Linac Coherent Light Source LCLS in Stanford as the world's first x-ray laser or FERMI at Elettra in Trieste as the first fully externally seeded free-electron laser provide ultrashort, extremely powerful short wavelength pulses with unprecedented coherence properties.

With these new sources it is possible to extend the well-established x-ray spectroscopic techniques for the investigation of the static electronic structure of matter like e.g. photoelectron and x-ray emission spectroscopy to probing the evolution of the electronic structure after controlled excitation in the time domain. The talk will review recent time-resolved x-ray spectroscopy experiments illustrating the opportunities for the study of ultrafast dynamics at surfaces. I will mainly discuss results which have been obtained in the framework of a large international Surface Science Collaboration at LCLS including groups from the US (SLAC in Stanford), from Sweden (University Stockholm), from Denmark (Danish Technical University), and from Germany (Fritz-Haber Institute and Helmholtz Center Berlin, and the Center for Free-Electron Laser Science (CFEL) at the University of Hamburg). These results show that with the new sources it is possible to characterize transient intermediates in surface reactions. Furthermore first steps towards monitoring surface reactions in real-time will be illustrated.

This work has been supported by German Ministry for Education and Science through the priority program FSP-301: "FLASH: Matter in the Light of Ultrashort, Extremely Intense X-ray Pulses"

References:

M. Dell'Angela et al., *Real-Time Observation of Surface Bond Breaking with an X-ray Laser*, *Science* 339, 1302 (2013)

M. Beye et al., *Selective Ultrafast Probing of Transient Hot Chemisorbed and Precursor States of CO on Ru(0001)*, *Phys. Rev. Lett.* 110, 186101 (2013)

T. Katayama et al., *Ultrafast soft X-ray emission spectroscopy of surface adsorbates using an X-ray free electron laser*, *Journal of Electron Spectroscopy and Related Phenomena* 187, 9 (2013)

3:00pm SA-TuA3 Real-time X-ray Photoelectron Spectroscopy Studies of Electronic Dynamics at Molecule-Semiconductor Interfaces, Oliver Gessner, Lawrence Berkeley National Laboratory **INVITED**

Interfacial charge transfer processes in molecular and nanoscale systems play an increasingly important role in emerging concepts for renewable energy technologies. Rational design decisions, however, rely on our capability to monitor the pathways of charge carriers on an atomic scale and with a temporal resolution that is commensurate with the timescales of interfacial electron motion. We introduce a new approach to characterize the location of a migrating electron at a molecule-semiconductor interface with sub-nanometer spatial sensitivity and sub-picosecond temporal resolution. Employing the unique capabilities of the Linac Coherent Light Source (LCLS) X-ray Free Electron Laser we use femtosecond time-resolved X-ray photoelectron spectroscopy (tr-XPS) to monitor the nature of an intermediate state that precedes free charge carrier generation in dye-sensitized ZnO nanocrystals after photoexcitation with visible light. Using the element specificity of inner-shell photoemission lines and, in particular, their sensitivity to transient local valence electronic structures, tr-XPS employs the Ru center of the dye molecule as a local reporter atom to provide a unique perspective on ultrafast interfacial charge flow. The underlying physics are explored in a concerted effort with constrained density functional theory (CDFT) calculations of the interfacial electronic structure. The results are discussed with respect to a significantly reduced rate of free charge carrier generation in N3/ZnO systems compared to other material combinations such as N3/TiO₂.

Femtosecond time-resolved experiments at the LCLS are complemented by a new picosecond time-resolved XPS effort at the Advanced Light Source

(ALS). Using a novel time-stamping technique in combination with a high-power picosecond laser system, tr-XPS experiments on dye-sensitized semiconductor substrates can be performed with up to MHz repetition rates in all operating modes of the ALS (multi-bunch and two-bunch). The measurements simultaneously monitor chemical shifts of particular photolines and transient surface photovoltages of the semiconductor substrate. Results will be discussed with respect to a possible correlation between intramolecular electron dynamics and transient interfacial charge carrier concentrations in the semiconductor. Routes and first steps toward the implementation of *in operando* X-ray studies of interfacial photoelectrochemical processes will be outlined.

4:20pm SA-TuA7 Unraveling Topological Properties of Spintronic Materials Using Coherent X-rays, Sujoy Roy, Lawrence Berkeley National Laboratory **INVITED**

Understanding new topological states in condensed matter systems is a current research topic of tremendous interest due to both the unique physics and their potential in device applications. The topological magnetic phases have exotic spin texture, and in some cases can be moved coherently over macroscopic distances with very low currents. Recently discovered skyrmions is an example of such a topological phase that manifest in magnetic systems as a hexagonal lattice of spin vortices. In this talk we will discuss our observation of the skyrmions using resonant soft x-ray scattering in Cu₂SeO₃ and demonstrate the unexpected existence of two distinct skyrmion sub-lattices that arise from inequivalent Cu sites with chemically identical coordination numbers and valency. The skyrmion sublattices are rotated with respect to each other implying a long wavelength modulation of the lattice. The coupled response of these sublattices to external magnetic field suggests a secondary interaction term that has not been predicted. We will also describe an artificial spin ice system whose origin lies in geometrical frustration that comes from the topology of a well-ordered structure rather than from disorder. We observed that under certain applied magnetic field the spin ice exhibits a magnetic structure that can impart orbital angular momentum into the photon beam thereby creating a vortex beam. Further, the vortex beam can be manipulated by an applied magnetic field. Creating an x-ray vortex beams may enable new x-ray based techniques such as coherent control of excitations in quantum material, trapping and rotation of quasiparticles or biomolecules with free electron laser x-ray sources.

Work is funded by U.S. DOE.

5:00pm SA-TuA9 Where are the Electrons? Charge Transfer and Dissociation from a Femtosecond Electronic-Structure Perspective, Philippe Wernet, Helmholtz-Zentrum Berlin (HZB), Germany **INVITED**

Molecular structure and chemical bonding determine the dynamic pathways of molecules in their multidimensional landscapes and hence define the outcome of chemical reactions. Characterizing chemical bonding in short-lived reaction intermediates and transient states of molecules is hence the key to understanding chemical selectivity.

Spectroscopy with femtosecond light pulses with energies ranging from the ultraviolet to the x-ray regime enables a unique approach to the atomic-scale chemical dynamics as it allow for a complete mapping of the electronic structure of atoms and molecules during chemical reactions [1]. Time-resolved femtosecond x-ray spectroscopy in particular reveals chemical bonding both in real time of the reaction and from the atom's perspective in an element-selective way [2].

Here we present our view on charge-transfer and dissociation reactions both in the gas phase and in solution from a femtosecond electronic-structure perspective. We apply femtosecond laser pulses from laboratory laser sources and from large scale x-ray free-electron lasers to map the electronic structure evolution in prototypical systems. Our results reveal how the transient electronic structure and the nuclear dynamics are coupled and they elucidate the role of the solvent from a chemical-bonding perspective.

Detailed insight into the various cases is discussed and an outlook for the investigation of chemical reaction dynamics with x-ray laser spectroscopy is given.

References

[1] Ph. Wernet, M. Odellius, K. Godehusen, J. Gaudin, O. Schwarzkopf, W. Eberhardt, "Real-time evolution of the valence electronic structure in a dissociating molecule", *Phys. Rev. Lett.* 103, 013001 (2009).

[2] Ph. Wernet, "Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions", *Phys. Chem. Chem. Phys.* 13, 16941 (2011).

5:40pm **SA-TuA11 Layer Speciation and Electronic Structure Investigation of Hexagonal Boron Nitride Thin Film by Scanning Transmission X-ray Microscopy.** *Jian Wang*, Canadian Light Source Inc., Canada, *Z. Wang*, University of Western Ontario, Canada, *H. Cho, M.J. Kim*, Korea Institute of Science and Technology, Republic of Korea, *T.-K. Sham*, University of Western Ontario, Canada, *X. Sun*, Soochow University, China

Thin films of hexagonal boron nitride (hBN) exhibit a honey cone structure similar to that of graphene, with sp^2 hybridized boron and nitrogen atoms alternately bonded in the basal plane. This unique structure leads to some excellent properties such as high chemical and thermal stabilities, enhanced thermal and electrical conductivity in the basal plane, and versatile doping capabilities. Thus hBN thin films have attracted increasing attentions in many fields. However, unlike graphene, the partly ionic B-N bond in hBN reduces electron-delocalization and creates a large band gap (5.2 eV) in the ultraviolet (UV), making hBN a wide band gap semiconductor and a promising deep UV light emitter. Therefore, an in depth understanding of the morphology and the electronic structure of individual hBN thin films will be of great importance in the development of sophisticated technologies. Synchrotron based scanning transmission X-ray microscopy (STXM) using a nanoscaled focused soft X-ray beam (~ 30 nm) provides an excellent combination of microscopic examination and chemical/electronic structure speciation via XANES spectroscopy for individual nanomaterials. In this work, chemical imaging, thickness mapping and layer speciation have been performed on a multilayered CVD hBN film with thickness from single layer up to 9 layers by STXM. Spatially-resolved XANES directly from discrete layers have been extracted and compared. Notably a double feature σ^* exciton state and a stable high energy σ^* state were observed at the boron site, and the boron projected σ^* DOS, especially the first σ^* exciton, is sensitive to surface modification, particularly in the single layer regions which show detectable contaminants and defects. Nitrogen site has shown no exciton character. The distinct exciton effect on boron and nitrogen was interpreted to the partly ionic state of hBN. Bulk XANES spectroscopy of hBN thin films was also measured to confirm the spectro-microscopic STXM result. Finally, we compare the XANES (i.e. unoccupied electronic structure) of hBN with that of graphene to elucidate the similarities and origins of the corresponding spectroscopic features.

6:00pm **SA-TuA12 Reference-free, In-depth Characterization of Nanoscaled Materials by Combined X-ray Reflectivity and Grazing incidence X-ray Fluorescence Analysis.** *Philipp Hönicke, M. Müller*, Physikalisch-Technische Bundesanstalt, Germany, *B. Detlefs*, CEA-LETI, France, *C. Fleischmann*, IMEC, Belgium, *B. Beckhoff*, Physikalisch-Technische Bundesanstalt, Germany

The accurate in-depth characterization of nanoscaled layer systems is an essential topic for today's developments in many fields of materials research. Thin high- κ layers [1], gate stacks and ultra-shallow dopant profiles are technologically relevant for current and future electronic devices. Nanolaminate composites, consisting of alternating layers of different materials with a nanometer scale thickness, are being developed for energy storage and memory applications [2]. However, the metrological challenges to sufficiently characterize such complex systems require a further development of the current analytical techniques.

Synchrotron-based Grazing Incidence X-ray Fluorescence (GIXRF) analysis has already been shown to be capable of contributing to the in-depth analysis of nanoscaled materials [3,4]. Essential for the quality of the results obtained with GIXRF is the calculation of the underlying X-ray standing wave field. This requires accurate knowledge of the optical properties of the system under investigation. Usually, this cannot be obtained from tabulated data due to the complexity of the sample in terms of layer thicknesses and material combinations and because of the fundamentally different material properties at the nanoscale.

The combination of GIXRF with X-Ray Reflectometry (XRR), provides access to the optical properties of the sample and has been shown to improve the characterization reliability of GIXRF [3]. Employing the novel in-house built instrumentation [5] and radiometrically calibrated detectors at the laboratory of the Physikalisch-Technische Bundesanstalt at the BESSY II synchrotron radiation facility, this combined method allows for reference-free quantitative in-depth analysis [3,4,6]. The capabilities of the combined XRR-GIXRF method are demonstrated by means of several nanoscaled layer systems as well as ultra-shallow dopant profiles.

[1] R.D. Clark, *Materials* 7(4), (2014), 2913.

[2] J. Azadmanjiri et al., *J. Mater. Chem. A* 2, (2014), 3695.

[3] P. Hönicke et al., *J. Anal. At. Spectrom.* 27, (2012), 1432.

[4] M. Müller et al., *Materials* 7(4), (2014), 3147.

[5] J. Lubeck et al., *Rev. Sci. Instrum.* 84, (2013), 045106.

[6] P. Hönicke, M. Müller, B. Beckhoff, *Solid State Phenomena* 195, (2013), 274.

Tuesday Evening Poster Sessions

Novel Trends in Synchrotron and FEL-Based Analysis

Focus Topic

Room: Hall D - Session SA-TuP

Synchrotron Analysis Poster Session

SA-TuP1 Soft X-ray Spectroscopy Reveals Chemical Information beneath the Surface of Organic Photovoltaic Devices, *Claudia Fleischmann*, IMEC, Belgium, *P. Hönicke, M. Müller, B. Beckhoff*, Physikalisch-Technische Bundesanstalt (PTB), Germany, *E. Voroshazi, J. Tait, T. Conard*, IMEC, Belgium, *W. Vandervorst*, IMEC, KU Leuven Belgium

While inorganic photovoltaic devices (PV) remain the main choice for large-scale energy production, *organic photovoltaic devices* (OPV) show great potential for future, environmentally friendly energy sources. Their semi-transparency, light-weight and unique opto-electrical properties combined with the possibility to shape OPV devices at will enable new applications where PV has never been used before. Similar to their inorganic counterparts, the underlying physical mechanisms and hence the performance and efficiency of organic devices is directly linked to their physicochemical properties. Revealing these properties is often very challenging due to the limited sensitivity and specificity of standard analytical techniques used for inorganic semiconductor characterization. In addition, it is highly desirable to probe the device structure as close as possible to a real one, which typically comprises organic-inorganic interfaces, intermixed phases being based on the same constituent atoms, or multilayer structures of a few tens to hundreds of nanometer thickness.

In this contribution we will examine the capabilities of *Near-Edge X-ray Absorption Fine Structure Spectroscopy* (NEXAFS) for the chemical characterization of (complete) bulk-heterojunction OPV device structures based on conjugated polymers and fullerene derivatives including P3HT, PCDTBT, DPP and PCBM. We will show that the high chemical sensitivity of the carbon K-edge (~290eV) NEXAFS permits to distinguish between the common organic semiconductors in these devices, providing a tool for compositional analysis and miscibility studies. By using fluorescence yield detection the information depth is extended far beyond the surface, in contrast to electron yield detection, allowing to probe non-destructively the bulk properties of (buried) layers in the OPV structure. In this context, we will also illustrate the remaining metrology challenges and investigate the sensitivity of the sulfur and nitrogen K-edge NEXAFS to be used for degradation studies. Finally, we will discuss the stability of these organic materials under x-ray irradiation, which is particularly critical for synchrotron radiation-based methods.

SA-TuP2 Exact, Efficient Calculation of Synchrotron Radiation--Proximity and Angle Effects, *Eric Shirley*, NIST

We evaluate synchrotron radiation for a circular orbit using Graf's addition theorem for Bessel functions. Using Debye's and Olver's asymptotic expansions, the exact radiation fields can be calculated without recourse to assuming large distance from the tangent point and without using truncations as in Schwinger's work. Thus, the present results should be both numerically robust and efficient, requiring no numerical integration. The results are applied to assessing the accuracy of the Schwinger formula for radiometric applications. The formulas are particularly well suited for long wavelengths and for measurements at end stations close to the storage ring. Application areas are typically UV and x-ray instrument calibration for such purposes as found on environmental satellites. By carrying out this work, we can gain a quantitative sense on the accuracy of various approximations that can be made, and hence their consequential suitability.

Authors Index

Bold page numbers indicate the presenter

— A —

Alaydrus, M.: AC+AS+MI+SA+SS-MoA7, 5
Allen, P.G.: AC+AS+MI+SA+SS-TuM1, 8
Allred, D.D.: AC+AS+MI+SA+SS-MoM10, 2
Anderson, V.R.: SA-MoM4, 3

— B —

Bagge-Hansen, M.: SA-MoA8, 6
Bancroft, G.M.: SA-MoM3, 3
Banos, A.: AC+AS+MI+SA+SS-TuM5, 8
Batista, E.: AC+AS+MI+SA+SS-MoM1, 1
Bauer, E.D.: AC+AS+MI+SA+SS-TuM1, 8
Baumann, T.: SA-MoA8, 6
Bechtel, A.: SA-MoA4, 6
Beckhoff, B.: SA-TuA12, 12; SA-TuM1, 9; SA-TuP1, 13
Biener, J.: SA-MoA8, 6
Biener, M.: SA-MoA8, 6
Biesinger, M.: SA-MoM3, 3
Booth, C.H.: AC+AS+MI+SA+SS-MoM1, 1;
AC+AS+MI+SA+SS-TuM1, 8
Bozzini, B.: SA-MoA1, 6
Brierley, M.: AC+AS+MI+SA+SS-MoM8, 2

— C —

Caciuffo, R.: AC+AS+MI+SA+SS-TuM3, 8
Carrillo Sanchez, P.: SA-MoA3, 6
Cho, H.: SA-TuA11, 12
Chung, B.W.: AC+AS+MI+SA+SS-MoA6, 5
Cieslar, M.: AC+AS+MI+SA+SS-MoM9, 2
Clark, D.: AC+AS+MI+SA+SS-MoM1, 1
Conard, T.: SA-TuP1, 13
Cui, X.Y.: SA-MoM3, 3

— D —

DeMasi, A.: SA-MoM4, 3
Detlefs, B.: SA-TuA12, 12
Diwan, A.: AC+AS+MI+SA+SS-MoM10, 2
Drozdhenko, D.: AC+AS+MI+SA+SS-MoM9, 2

— E —

Eddy, Jr., C.R.: SA-MoM4, 3
Erdem, M.G.: SA-MoM4, 3

— F —

Fadley, C.S.: SA-MoM1, 2
Fischer, D.A.: SA-MoM10, 4
Fleischmann, C.: SA-TuA12, 12; SA-TuP1, 13
Fu, Z.: SA-MoM10, 4

— G —

Gerlach, M.: SA-TuM1, 9
Gessner, O.: SA-TuA3, 11
Goldoni, A.: SA-TuM5, 9
Grant, W.K.: AC+AS+MI+SA+SS-TuM12, 8
Gschneidner, Jr., K.A.: AC+AS+MI+SA+SS-MoA8, 5
Guo, J.-H.: SA-MoA8, 6

— H —

Hallam, K.: AC+AS+MI+SA+SS-TuM5, 8
Hart, M.: AC+AS+MI+SA+SS-TuM5, 8
Havela, L.: AC+AS+MI+SA+SS-MoM9, 2
Hengehold, R.: AC+AS+MI+SA+SS-MoM11, 2
Himpfel, F.J.: SA-MoA6, 6
Hoenicke, P.: SA-TuM1, 9
Holfelder, I.: SA-TuM1, 9
Hönicke, P.: SA-TuA12, 12; SA-TuP1, 13
Hu, Y.F.: SA-MoM3, 3
Hughes, G.: SA-MoM5, 3
Hurley, P.K.: SA-MoM5, 3

— I —

Ishihara, T.: AC+AS+MI+SA+SS-MoA7, 5

— J —

Jaye, C.: SA-MoM10, 4
Jiang, Y.: AC+AS+MI+SA+SS-TuM1, 8
Johnson, S.D.: SA-MoM4, 3

— K —

Kas, J.J.: AC+AS+MI+SA+SS-TuM1, 8
Kasai, H.: AC+AS+MI+SA+SS-MoA7, 5
Keith, J.: AC+AS+MI+SA+SS-MoM1, 1
Kelly, T.: AC+AS+MI+SA+SS-MoM11, 2
Kim, M.J.: SA-TuA11, 12
Knowles, J.P.: AC+AS+MI+SA+SS-MoM8, 2
Kolis, J.: AC+AS+MI+SA+SS-MoM11, 2
Kolmakov, A.: SA-MoM8, 3
Kolorenc, J.: AC+AS+MI+SA+SS-MoA1, 5
Kozimor, S.: AC+AS+MI+SA+SS-MoM1, 1

— L —

Lee, J.R.I.: SA-MoA8, 6
Lubeck, J.: SA-TuM1, 9
Ludwig, K.F.: SA-MoM4, 3
Lukens, W.: AC+AS+MI+SA+SS-MoM1, 1

— M —

MacFarlane, J.: AC+AS+MI+SA+SS-TuM5, 8
Magee, J.: SA-MoA3, 6
Mann, J.M.: AC+AS+MI+SA+SS-MoM11, 2
Martin, M.C.: SA-MoA4, 6
Martin, R.L.: AC+AS+MI+SA+SS-MoM1, 1
Matej, Z.: AC+AS+MI+SA+SS-MoM9, 2
McKeon, B.S.: AC+AS+MI+SA+SS-MoM10, 2
McLean, W.: AC+AS+MI+SA+SS-TuM12, 8
Medling, S.A.: AC+AS+MI+SA+SS-TuM1, 8
Merrill, M.: SA-MoA8, 6
Minasian, S.: AC+AS+MI+SA+SS-MoM1, 1
Mirmelstein, A.: AC+AS+MI+SA+SS-MoA6, 5
Mitchell, J.N.: AC+AS+MI+SA+SS-TuM1, 8
Mueller, M.: SA-TuM1, 9
Muller, E.A.: SA-MoA4, 6
Müller, M.: SA-TuA12, 12; SA-TuP1, 13

— N —

Nelson, A.J.: AC+AS+MI+SA+SS-TuM12, 8
Nepal, N.: SA-MoM4, 3
Nesbitt, H.W.: SA-MoM3, 3
Nordlund, D.: AC+AS+MI+SA+SS-MoM1, 1;
AC+AS+MI+SA+SS-TuM1, 8
Nutsch, A.: SA-TuM1, 9

— O —

Ogitsu, T.: SA-MoA8, 6
Olmon, R.L.: SA-MoA4, 6

— P —

Palomino, R.: SA-MoA3, 6
Paraskevoulakos, H.: AC+AS+MI+SA+SS-TuM5, 8
Paudyal, D.: AC+AS+MI+SA+SS-MoA8, 5
Paukov, M.: AC+AS+MI+SA+SS-MoM9, 2
Pecharsky, V.K.: AC+AS+MI+SA+SS-MoA8, 5
Petrosky, J.: AC+AS+MI+SA+SS-MoM11, 2
Pollakowski, B.: SA-TuM1, 9
Prendergast, D.: SA-MoA8, 6
Preuss, M.: AC+AS+MI+SA+SS-MoM8, 2
Principe, E.L.: SA-MoM10, 4

— R —

Raschke, M.B.: SA-MoA4, 6
Reding, J.: AC+AS+MI+SA+SS-MoM11, 2
Rogalev, A.: AC+AS+MI+SA+SS-MoM3, 1
Roy, R.: SA-TuA7, 11
Rudolf, P.: SA-TuM12, 10
Rusz, J.: AC+AS+MI+SA+SS-MoM5, 1
Ryzhkov, M.V.: AC+AS+MI+SA+SS-MoA6, 5

— S —

Sakaue, M.: AC+AS+MI+SA+SS-MoA7, 5
Santander-Syro, A.F.: SA-TuM10, 9
Scammon, K.: SA-MoM10, 4
Schneider, C.M.: SA-TuM3, 9
Scott, E.A.: AC+AS+MI+SA+SS-MoM10, 2
Scott, T.: AC+AS+MI+SA+SS-TuM5, 8
Sham, T.-K.: SA-TuA11, 12
Sherry, A.H.: AC+AS+MI+SA+SS-MoM8, 2
Shirley, E.L.: SA-TuP2, 13
Shuh, D.: AC+AS+MI+SA+SS-MoM1, 1
Siekhaus, W.J.: AC+AS+MI+SA+SS-TuM12, 8
Simons, D.: AC+AS+MI+SA+SS-TuM10, 8
Sobol, P.E.: SA-MoM10, 4
Sokaras, D.: AC+AS+MI+SA+SS-MoM1, 1;
AC+AS+MI+SA+SS-TuM1, 8
Stanford, J.A.: AC+AS+MI+SA+SS-TuM12, 8
Stitt, C.A.: AC+AS+MI+SA+SS-TuM5, 8
Streeck, C.: SA-TuM1, 9
Sun, X.: SA-TuA11, 12

— T —

Tait, J.: SA-TuP1, 13
Tkach, I.: AC+AS+MI+SA+SS-MoM9, 2
Tobash, P.H.: AC+AS+MI+SA+SS-TuM1, 8
Tobin, J.G.: AC+AS+MI+SA+SS-MoA6, 5;
AC+AS+MI+SA+SS-TuM1, 8
Tran, I.C.: SA-MoA8, 6
Turley, R.S.: AC+AS+MI+SA+SS-MoM10, 2
Turner, D.: AC+AS+MI+SA+SS-MoM11, 2
Tyliszczak, T.: AC+AS+MI+SA+SS-MoM1, 1

— U —

Unterumsberger, R.: SA-TuM1, 9

— V —

van Buuren, T.W.: SA-MoA8, 6
Vandervorst, W.: SA-TuP1, 13
Vanfleet, R.R.: AC+AS+MI+SA+SS-MoM10, 2
Veirs, D.K.: AC+AS+MI+SA+SS-TuM1, 8
Vinson, J.: SA-MoA9, 7
Voroshazi, E.: SA-TuP1, 13

— W —

Wall, M.A.: AC+AS+MI+SA+SS-TuM1, 8
Walsh, L.: SA-MoM5, 3
Wang, D.: SA-MoM3, 3
Wang, J.: SA-TuA11, 12
Wang, Z.: SA-TuA11, 12
Weiland, C.: SA-MoM10, 4
Weng, T.-C.: AC+AS+MI+SA+SS-MoM1, 1;
AC+AS+MI+SA+SS-TuM1, 8
Weng, X.-D.: AC+AS+MI+SA+SS-MoM1, 1
Wernet, Ph.: SA-TuA9, 11
Weser, J.: SA-TuM1, 9
White, M.: SA-MoA3, 6
Wilhelm, F.: AC+AS+MI+SA+SS-MoM3, 1
Willey, T.M.: SA-MoA8, 6
Wittstock, A.: SA-MoA8, 6
Woicik, J.C.: SA-MoM5, 3
Wood, B.: SA-MoA8, 6
Worsley, M.: SA-MoA8, 6
Wurth, W.: SA-TuA1, 11

— X —

Xiao, Q.F.: SA-MoM3, 3

— Y —

Yang, W.L.: SA-MoA10, 7
Yu, S.W.: AC+AS+MI+SA+SS-MoA6, 5

— Z —

Zhu, J.-X.: AC+AS+MI+SA+SS-MoA3, 5