Actinides and Rare Earths Focus Topic
Room 202C - Session AC+MI+SA-WeM

Magnetism, Complexity, and Superconductivity in the Actinides and Rare Earths

Moderators: Melissa Denecke, University of Manchester, UK, David Geeson, AWE, James Tobin, UW Oshkosh

8:00am **AC+MI+SA-WeM-1 Strong electron-electron Interactions in the Actinides: Using Organometallics to Probe Delocalization Effects**, *Corwin Booth*, Lawrence Berkeley National Laboratory **INVITED**

Systems exhibiting strong electron-electron interactions remain at the forefront of inquiry into complex properties of condensed matter systems due to their exciting properties (eg. superconductivity) and their resistance to being understood on a fundamental level. A bottleneck toward a better understanding has been the difficulty of the required many-body calculations for extended solids. Alternatively, calculations on small molecules require fewer and better approximations, potentially offering a better description. Although strong electron-electron interactions are well established in extended solids, recent work on lanthanide organometallic coordination compounds has demonstrated the importance of such interactions, fueled by the propensity for certain 4f orbitals to be partially delocalized. Meanwhile, recent work on the actinides challenges the canonical view that the 5f electrons can bond in the light actinides but are essentially localized in the heavier actinides. A major stumbling block for such work is the paucity of known structures for elements beyond Am in the periodic table.

For the discussion presented here, work on Ce and Yb organometallics will provide context in terms of f-occupancy and in bonding characteristics and the effect on magnetism. The role of strongly electron interactions will be described in terms of configuration interaction (CI) and related calculations. Occupancy is measured using Ln L_{III}-edge x-ray absorption near-edge structure (XANES) techniques, and local structure (EXAFS) measurements demonstrate the final effect on the bonding at the metal center. Of particular interest is what happens in formally Ce(IV) systems that exhibit strong interactions.

XANES measurements of actinides are more difficult to interpret and will be discussed. The focus will be, however, on EXAFS measurements across the An series in the presence of strongly oxidizing ligands. Chosen ligands include hydroxypyridonone (HOPO), with less oxidizing ligands, such as diethylenetriaminepentaacetic acid (DTPA) used for comparison. Cations include Th, U, Pu, Am, Cm, Bk, and Cf. Discussions will center on nearest-neighbor bond lengths, using DFT calculations as a guide. The surprising role of covalency in the late actinides will be considered, both in terms of the EXAFS results and in terms of the edge shifts.

This work was supported by the U.S. Department of Energy (DOE), Office of Science (OS), Office of Basic Energy Sciences (OBES), under Contract No. DE-AC02-05CH1123.

8:40am **AC+MI+SA-WeM-3 Structure and Magnetism of U-based Thin Films and Heterostructures**, *Evgeniya Tereshina-Chitrova*, Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic; *L Havela,* Charles University, Prague, Czech Republic; *T Gouder, Z Bao,* Institute for Transuranium Elements, Germany; *M Dopita,* Charles University, Prague, Czech Republic; *R Caciuffo,* Institute for Transuranium Elements, Germany **INVITED**

Uranium is the basic component of most nuclear fuels. The production of uranium-based films has advantage over bulk materials studies as it allows performing advanced physics and chemistry experiments on small amounts of radioactive material and on its clean and smooth surfaces. Other interesting field is uranium magnetism. Although uranium itself is non-magnetic, uranium compounds display a rich variety of magnetic phenomena intimately related to the variable character of the 5f electron states [1]. Additional degrees of freedom can be used in thin films, in which the reduced dimensionality and structure modifications far exceed the limits imposed by thermodynamics, obeyed in bulk systems. We review the achievements in the field of sputter-deposited films, in which variations of deposition conditions can dramatically suppress crystallinity of the deposited material. The 5f itinerant magnetic systems (as US or UN [2]) react to the low substrate temperatures and high deposition rates by decreasing ordering temperatures and eventually by the loss of U magnetic moments. The strong ferromagnetism of uranium hydride is, on the other hand, almost insensitive, which underlines its local-moment character.

The possibility to combine films of various materials on the nanostructure scale can also give rise to new functionalities. For example, the exchange bias (EB) effect [3], arising as a result of combination of a ferromagnet biased by exchange interaction at the interface to an antiferromagnet, is particularly interesting if uranium magnetics are involved. The new ingredient, strong spin-orbit interaction, can lead to very strong magnetic anisotropy, which represents an essential parameter. We have been systematically studying films of Fe_3O_4 (ferromagnet) grown using different substrates on the top UO_2, playing the role of biasing antiferromagnet [4]. The resulting high bias field (> 0.2 T) and a proximity effect, in which the high Curie temperature of Fe_3O_4 provides the EB functionality even at temperatures exceeding ordering of UO_2, demonstrate the promising aspects of using actinides in this non-traditional way.

[1] V. Sechovsky, L. Havela, in: Magnetic Materials, K.H.J. Buschow (Ed.), Elsevier, Amsterdam, 1998, Vol. 11, p. 1.

[2] L. Havela et al., JALCOM 408-412, p. 1320 (2006).

[3] W. H. Meiklejohn and C. P. Bean, Phys. Rev. B 102, 1413 (1956).

[4] E.A. Tereshina et al., Appl. Phys. Lett. 105(12),122405 (2014).

9:20am **AC+MI+SA-WeM-5 Field Induced Lifshitz Transitions in URu2Si2**, *E Calegari,* Univ Federale Santa Maria, Brazil*; S Magalhaes,* Universidade Federale Rio Grande do Sul, Brazil*; Peter Riseborough,* Temple University **INVITED**

We report calculations on an unusual phase of the Under-screened Anderson Lattice (UAL) model, the so called spin-dependent inter-orbital density wave that has been proposed as describing the ``Hidden Order" (HO) phase of URu2Si2.

We determine the effects of an applied magnetic field. Since the order parameter describes an ordering in the x-y plane, the electronic properties of the system are anisotropic below the critical temperature THO. We show that the magnetic susceptibility becomes anisotropic below THO. Furthermore, for fields applied along a spontaneously chosen hard axis, THO decreases towards zero and that the HO transition changes from second order to first order at a large value of the magnetic field. Also, we find that the system undergoes a cascade of field-induced Lifshitz transitions and also show how these properties originate from the dependence of the quasi-particle bands on the orientation of the applied field. The good qualitative agreement with experimental findings provides strong support for the proposed description of the HO phase as a spin-dependent inter-orbital density wave phase.

11:00am **AC+MI+SA-WeM-10 New Form of Uranium Hydride - UH2**, *Ladislav Havela*, M Paukov, M Dopita, L Horak, P Minarik, M Divis, I Turek, Charles University, Prague, Czech Republic*; D Legut,* VSB-Technical University of Ostrava, Czech Republic*; T Gouder, A Seibert, F Huber,* European Commission - Joint Research Centre*; E Tereshina-Chitrova,* Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic

Most of *f*-elements form with hydrogen both di- and trihydrides. Actinide and rare-earth dihydrides occur, as a rule, in the CaF_2 structure type. Uranium represents an exception, only UH_3 is present in the binary phase diagram. It exists in two different structure types. The metastable form α-UH_3 forms in the Cr_3Si structure type, which is in fact *bcc* U lattice filled with hydrogen. The stable form β-UH_3 has a larger cubic cell with two different U sites. Both forms are ferromagnets with the total U moment of ≈ 1 μ_B/U and the Curie temperature T_C ≈ 165 K. We have recently synthesized UH_3 thin films using a reactive sputter deposition. XRD analysis indicated the β-UH_3 structure, modified by a pronounced (00l) texture and compressive residual strains imposed by the deposition dynamics. Magnetization measurements proved T_C = 165 K.

The sputter deposition on a cooled substrate (*T* = 170 K) using Si wafer the crystal structure turned different. The deposited material is undoubtedly cubic, of the *fcc* type, and the lattice parameter a = 5.3598 ± 0.0014 Å is very close to that of PuH_2 (a = 5.359 Å) and NpH_{2+x} (a = 5.343-5.355 Å). Hence we can assume that UH_2 in the fluorite structure has been formed. The key role in stabilization plays likely the effect of substrate (Si has a = 5.431 Å) in combination with low temperature deposition. The UH_2 film was subsequently subjected to magnetization measurements, which indicated a ferromagnetic ground state with T_C ≈ 125 K. This is lower than in the UH_3 phases, although the U-U spacing in UH_2 should be higher, 3.78

Å, than in both UH_3 phases (3.31 and 3.60 Å for β- and α-UH_3, respectively). This fact points to the U-U interaction being more important than the U-U spacing. The ferromagnetic state is also the ground state obtained from ab-initio calculations. Scalar relativistic calculations (LDA) for experimental lattice parameter yield the spin moment $μ_S$ = 2.0 $μ_B$/U. LDA+U (U = 2.25 eV) gives the equilibrium lattice parameter a = 539.9 Å, i.e. 0.7% larger than the experimental one, the ferromagnetic ground state with (111) easy-magnetization direction and the magnetic anisotropy energy E_a = 9 meV. The total moment 0.45 $μ_B$/U consists of 2.59 $μ_S$ and -3.04 $μ_L$.

11:20am AC+MI+SA-WeM-11 Tuning of Electronic Properties of U- and RE-Metallic Systems by H Absorption, *Silvie Maskova,* Charles University, Prague, Czech Republic*; K Miliyanchuk,* Ivan Franko National University of Lviv, Lviv, Ukraine*; A Kolomiets,* Lviv Polytechnic National University, Lviv, Ukraine*; L Havela,* Charles University, Prague, Czech Republic

The sensitivity of the interactions in the intermetallic systems to modification of the crystal structure makes the experimental techniques involving alteration of the atomic arrangement especially important. Various studies under compression are well-known examples of such methods. From this point of view hydrogenation can be treated as a complementary technique that provides „negative" pressure. Hydrides can be defined as compounds for which the hydrogen absorption leads to the modifications of the crystal structure, such as pure lattice expansion or the formation of a new structure. As a result, the new compounds (hydrides) exhibit qualitatively new physical properties and such modifications provide us with additional information on the peculiarities of interatomic interactions in the initial compounds.

As an example, we will compare the impact of H absorption on U- and RE-compounds using A_2T_2X (A = Rare-Earth (RE) or actinide, T = transition metal, X = p-metal) compounds crystallizing in the tetragonal Mo_2FeB_2 structure type (space group $P4/mbm$). U_2T_2X interact with H_2 only at high pressure (≈ 100 bar) reaching 2 H/f.u. The H absorption produces a lattice expansion (lower than 10 %), while the tetragonal structure is preserved. Higher H concentrations, which can be achieved in some RE_2T_2X compounds (up to 8 H atoms/f.u), lead to amorphization or structure symmetry changes (with volume expansion exceeding 20 %), imposed by a minimum H-H distance requirement.

Magnetic properties of U-compounds strongly depend on the U-U distances. Hydrogen intrusion modifies the lattice by expanding it without changing the crystal-structure type leading to a 5f band narrowing. As a consequence, doping of U intermetallics by interstitial hydrogen leads to stronger magnetic properties. On the other hand, the hydrogen absorption has opposite effect on magnetic properties of RE_2T_2X compounds. For RE compounds, hydrogenation affects mainly the inter-site exchange interaction, which is weakened presumably by reducing the concentration of conduction electrons, responsible for the RKKY interaction.

11:40am AC+MI+SA-WeM-12 Magnetic Structures of U_nRhIn_{3n+2} Materials, *Attila Bartha, M Klicpera,* Charles University, Prague, Czech Republic*; P Cermak,* Forschungszentrum Juelich GmbH, Germany*; B Ouladdiaf,* Institute Laue-Langevin, France*; J Custers,* Charles University, Prague, Czech Republic

In the past decade, U-compounds crystallizing in the $HoCoGa_5$-type structure (P4/mmm), frequently referred to as 115, have been in the focus of attention in experimental and theoretical research. Vigorous activities have been motivated by the high superconducting transition temperature of T_c = 8.7K in $PuRhGa_5$ [1] and T_c = 18.5K in $PuCoGa_5$ [2]. No further superconductivity has been reported in neither U-115 nor in the closely related U_2TGa_8 compounds (T = transition metal). However, interesting magnetic properties have been observed: neutron scattering experiments revealed that $UNiGa_5$ exhibits the G-type antiferromagnetic (AFM) phase, while $UPdGa_5$ and $UPtGa_5$ exhibit the A-type AFM state. Note that G-type indicates a 3D Néel state, while A-type refers to a layered AF structure where spins align FM in the ab plane and AFM along the c axis [3]. The difference in the two magnetic structures is significant since it implies a sign change of the nearest-neighbor (NN) interaction.

Here we report on the magnetic structures of $URhIn_5$ and U_2RhIn_8, two new members of the $U_nT_mX_{3n+2m}$ (X=In,Ga) family of compounds [4]. $URhIn_5$ displays AFM order below T_N = 98K. The observed increase of the resistivity for current parallel [100], [110] and [001] are reminiscent to a spin-density

wave (SDW) type of transition with the gap opening first along the [001] direction [5]. U_2RhIn_8 enters the AFM state at T_N = 117K. No increase in resistivity in the vicinity of T_N is found which would hint to a SDW gap opening. Neutron diffraction experiments on $URhIn_5$ were performed at the Heinz Maier-Leibnitz Zentrum (MLZ) in Garching using the triple axis spectrometer PANDA. Single crystals with accumulated mass of 10mg where glued on an Al-plate. Our results confirmed the magnetic propagation vector ***k***=(1/2,1/2,1/2) predicted by NMR experiments [6] and a magnetic moment of 1.65 $μ_B$/U^{3+}. The neutron study on U_2RhIn_8 has been conducted at ILL, Grenoble using D10 on only one single crystal with m ≈ 1mg. Analysis revealed a propagation vector ***k***=(1/2,1/2,0) and an ordered moment of 1.7 $μ_B$/U^{3+}. UIn_3, $URhIn_5$ and U_2RhIn_8 all show G-type AFM phase. While the c-axis parameter differs significantly the a lattice parameter equals 4.601Å, 4.621Å and 4.6056Å respectively, being a change of less than 1% pointing to the fact that the NN coupling is important for the type of magnetic structure.

[1] F. Wastin *et al.*, J.Phys.Condens.Matter **15,** S2279 (2003)

[2] J.L. Sarrao *et al.,* Nature (London) **420,** 297 (2002)

[3] T. Hotta, Phys.Rev. B **70,** 054405 (2004)

[4] A. Bartha *et al.*, J.Magn.Magn.Mater. **381,** 310 (2015)

[5] A. Bartha *et al.*, Acta Phys.Pol. A **127,** 339 (2015)

[6] H. Sakai *et al.* Phys.Rev. B **88,** 045123 (2013)

12:00pm AC+MI+SA-WeM-13 Insights into the Magnetic Dead Layer in $La_{0.7}Sr_{0.3}MnO_3$ Thin Films from Temperature, Magnetic Field and Thickness Dependence of their Magnetization, *Navid Mottaghi,* M Seehra, R Trappen, S Kumari, C Huang, S Yousefi, G Cabrera, A Romero, M Holcomb, West Virginia University

Detailed dc magnetization (M) measurements of a 7.6 nm $La_{0.7}Sr_{0.3}MnO_3$ thin film samples is investigated. The sample was fabricated by pulsed laser deposition. Zero-field-cooled (ZFC) M vs. applied field (H) cooled down to T = 5 K reveal the presence of negative remanent magnetization (NRM) as well as in ZFC M vs. temperature (T) measurements in H = 50 Oe and 100 Oe. ZFC and FC (field-cooled) protocols are used to determine the blocking temperature T_B in different H. Isothermal hysteresis loops at different T are used to determine the temperature dependence of saturation magnetization (M_S), remanence (M_R) and coercivity H_C. The M_S vs. T data are fit to the Bloch law, M_S (T) = M_0 (1 − B$T^{3/2}$), showing a good fit for T < 100 K and yielding the nearest-neighbor exchange constant $J/k_B ≅ 18$ K. The variations of T_B vs. H and H_C vs. T are well described by the model often used for randomly oriented magnetic nanoparticles with magnetic domain diameter ≈ 9 nm present in the dead-layer of thickness d =1.4 nm. Finally, the data available from literature on the thickness (D) variation of Curie temperature (T_C) and M_S of LSMO films grown under 200, 150, and 0.38 mTorr pressures of O_2 are analyzed in terms of the finite-size scaling, with M_S vs. D data fit to M_S (D) = M_S(b)(1-d/D) yielding the dead layer thickness d = 1.1 nm, 1.4nm and 2.4 nm respectively.

Applied Surface Science Division
Room 204 - Session AS+NS+SA-WeM

Beyond Traditional Surface Analysis

Moderators: Mark Engelhard, EMSL, Environmental Molecular Sciences Laboratory, Kathryn Lloyd, DuPont

8:00am AS+NS+SA-WeM-1 Solar Wind Interaction with Carbonate Deposits on Asteroid (1) Ceres' Surface: The Role of Surface Analysis in Laboratory Planetary Science, *Catherine Dukes,* G Rodriguez Lopez, C Bu, University of Virginia

Bright deposits of anhydrous carbonates across the dark background of dwarf-planet Ceres have been identified by Dawn's VIR spectrometer with a composition that varies from natrite with minor amounts of ammonium bicarbonate within the Cerealia and Vinalia Faculae to magnesite, calcite, and dolomite in other high-albedo regions [1]. These deposits are expected to derive from the aqueous alteration of volatile-containing silicates, forming a viscous brine below Ceres' solid crust. Hydrated salts from this reservoir are deposited on the planetary surface by extrusion through vents or co-ejected by jets of sub-surface water ice. Water loss in the material occurs with exposure to the low pressure environment on Ceres' surface as a function of exposure time, even at temperatures < 240 K [2].

Unprotected from the impacts of solar particles, cosmic rays, and meteorites, anhydrous salts undergo chemical and physical change (space weathering), which can be remotely identified by optical reflectance. The

effect of solar-wind ions on carbonates can be simulated in the laboratory, and the correlation between surface composition and morphology with optical change can be used to infer physical processes occurring on airless planetary bodies. We investigate the stability of carbonates and measure systematic darkening with 4 keV He-ion fluence, a potential geologic chronometer for Ceres' bright deposits.

Carbonate powders are pressed into pellets, then introduced into vacuum (10^{-9} Torr) and cooled to ~110/200 K.

An external-beam from an FT-IR is used to perform *in-vacuo* reflectance measurement. Spectra were acquired at varied fluence, equivalent to solar irradiation of ~300 - 30,000 years at 2.8 A.U. Changes in surface composition and molecular chemistry were investigated by *in-situ* X-ray photoelectron spectroscopy (XPS).

Blueish luminescence of sodium carbonates with He^+ is observed. Vis-NIR darkening (~80%) of natrite (Na_2CO_3)occurs after 10^{18} He cm^{-2}, with reddening of the visible spectral slope. Similar darkening is noted for 1.3 - 5 µm, along with attenuation of carbonate overtones. Concomitant XPS measurement shows a reduction of carbon and oxygen, with enhancement of sodium. Exposure of the darkened sample to 10,000 L H_2O-vapor results in brightening to > 80%.

Ion-induced darkening of Ceres' natrite deposits is expected to occur on a time-scale of 100 - 1000 years, and can be reversed by exposure to water vapor. For deposits of varied albedo, this suggests that the brightest areas are the most recent deposits or the most recently exposed to water.

[1] DeSantis et al. (2016) Nature 536, 54-57

[2] Bu et al. (2017) Icarus doi.org/10.1016/j.icarus.2017.12.036

8:20am **AS+NS+SA-WeM-2 Looking Deeper and Smaller: Enhancing XPS by Hard X-ray Probes and High-resolution Imaging**, *Olivier Renault,* CEA/LETI-University Grenoble Alpes, France*; C Zborowski,* University of Southern Denmark, Denmark*; J Rueff,* Synchrotron SOLEIL, L'orme des Merisiers, France*; Y Yamashita, S Ueda,* NIMS, Japan*; G Grenet,* Lyon Institute of Nanotechnology, France*; S Tougaard,* University of Southern Denmark, Denmark

X-ray photoelectron spectroscopy (XPS) has become a mature technique with a widespread use spanning from fundamental research to R&D labs. In parallel, the intrinsic complexity of materials and systems to be analyzed by XPS has increased. Some of the limitation of XPS are of concern if a non-destructive, non-invasive analytical protocol is the key issue. These are, especially, the poor lateral resolution and the poor bulk sensitivity, making impossible the analysis of microscopic features and buried interfaces in a reliable way.

In this contribution, we review the capabilities of current and novel techniques to get into: (i) high lateral resolution and quantitative micro-analysis using spectroscopic imaging implemented by X-ray PhotoElectron Emission Microscopy (XPEEM); (ii) high depth sensitivity offered by Hard X-ray Photoelectron Spectroscopy (HAXPES), coupled or not with inelastic background analysis to futher enhance information depth up to nearly 100 nm.

We will highlight the capabilities of each techniques by different practical examples in the field of 2D materials [1] and device technology [2, 3], emphasizing particularly the perspectives offered by novel laboratory hard X-ray sources [4].

[1] H. Kim, O. Renault et al., Physical Review B, 2016. 94(8): p. 081401.

[2] P. Risterucci, O. Renault et al., Applied Surface Science, 2017, 402: p. 78-85.

[3] C. Zborowski, et al., Applied Surface Science, 2018. 432(Part A): p. 60-70.

[4] O. Renault, E. Martinez, et al., Surf. Interface Anal. 2018 (in press).

8:40am **AS+NS+SA-WeM-3 Reenvisioning Amphiphilicity: Translating Cell Membrane Design Principles to Synthetic 2D Materials**, *Shelley Claridge,* Purdue University **INVITED**

2D materials such as graphene exhibit unique electronic and mechanical properties that promise substantial advantages in applications ranging from nanoelectronics to human health. Such interfaces are often functionalized noncovalently with lying-down phases of functional molecules to avoid disrupting electronic structure within the basal plane. Interfacial structures have commonly been characterized down to sub-nm scales using scanning probe techniques such as STM, either in vacuum, or at a solid-liquid interface with a nonpolar liquid (e.g. octadecene). However, molecules used in this approach are often structurally similar to amphiphiles such as fatty acids and phospholipids found in biological cell membranes, suggesting possible utility in *aqueous* environments. At the same time, the overall surface chemistry is strikingly different than that of the cell membrane -- in essence, the surface chemistry is that of a repeating cross-section of a lipid bilayer, with both hydrophilic and hydrophobic components exposed, forming a striped amphiphilic structure with sub-10-nm periodicity.

As 2D materials are integrated into hybrid materials and devices, this noncovalent amphiphilic interfacial structure raises two classes of significant questions requiring interfacial analysis: *(1) How do noncovalent lying-down ligand layers respond to solution or thermal processing?* What are the best ways to probe controlled *disordering* across scales from nm to mm at an interface with a polar liquid? If ligand dynamics vary with structure, to what extent can design principles from the cell membrane be invoked to control chemical functionality and reactions at the interface? *(2) Can noncovalently-adsorbed layers be patterned to template further interactions with the environment?* Lying-down phases of phospholipids and fatty acids present 1-nm-wide stripes of ordered chemical functional groups, suggesting the possibility of controlling processes such as crystallization, phase segregation, or analyte binding. We examine these questions, again developing approaches to characterize interface structure across the range of relevant length scales, and invoking structural design principles from the cell membrane.

9:20am **AS+NS+SA-WeM-5 Microstructural Effects on Surface Potential of Amorphous Solid Water**, *Caixia Bu, C Dukes,* University of Virginia

Amorphous solid water (ASW) formed by vapor deposition on substrates <~130 K is of interest for its abundance in Earth's upper atmosphere, icy planetary bodies, and throughout the interstellar medium, as well as its use as model material in many disciplines. Two crucial characteristics of ASW are a self-induced negative surface potential and formation of nanopores [1]. Here, we examine the role of microstructure, including nanopores, on the spontaneous surface potential of ASW, and describe the complementary experimental techniques used, which have application for other microporous solids.

ASW films were deposited by directed vapor beams onto a He-cooled quartz-crystal microbalance (QCM) under ultra-high vacuum. The integrated pore volume (porosity) was calculated by combining the areal mass measured via QCM and thickness measured by UV-visible interferometry. The integrated surface area was indicative by the abundance of incompletely coordinated surface water molecules (H_2O) on the pores, using the O-H dangling bonds (DBs) measured by FT-IR spectroscopy. An *in-situ* Kelvin probe measured film surface potential. A long-distance optical microscope monitored film morphology *in vacuo*. Annealing effects were investigated by heating the film at 1.8 K/min.

The magnitude of the negative surface potential ($|V_s|$) increased linearly with film thickness at rates ($|\Delta V_s/\Delta L|$) that decreased with increasing growth temperature (T_g = 10–110 K), keeping deposition angle at θ = 0° (angle between vapor beam and QCM normal); at T_g = 30 K, the $|\Delta V_s/\Delta L|$ decreased with increasing θ (= 10–75°). ASW porosity showed no dependence on T_g at θ = 0°, but increased significantly with increasing θ. The H_2O DBs decreased/increased with increasing T_g/θ, showing similar trends as the $|\Delta V_s/\Delta L|$. Upon heating, the most striking result was that the DB at ~3720 cm^{-1} (from two-coordinated H_2O) and the $|V_s|$ had similar temperature-dependent evolutions. By correlating all measurements, we propose that the observed intrinsic ASW surface potential results from aligned incompletely-coordinated H_2O on the pore surfaces [2].

The $|V_s|$ decreased abruptly when ASW thickness exceeded a critical value (L_c), and cracks appeared in the optical images of the films. The L_c, ~1–5 µm (T_g = 10–50 K; θ = 0–55°), increased with T_g and θ, suggesting dependences on the microporous structure. We explain such dependences of L_c in the context of Griffith theory and estimate the tensile strength of ASW to be ~25–40 MPa [3].

[1]Raut et al., *J. Chem. Phys.***127**, 204713 (2007); [2]Bu et al., *J. Chem. Phys.***143**, 074702 (2015); [3]Bu et al., *Appl. Phys. Lett.***109**, 201902 (2016).

9:40am **AS+NS+SA-WeM-6 Speciation and Reactivity of Organic Matter in Uranium Mine Wastes from Laguna- New Mexico: An Application of Surface Sciences in Environmental Systems.**, *Carmen A. Velasco, A Ali,* University of New Mexico*; C Osburn,* North Carolina State University*; K Artyushkova, J Cerrato,* University of New Mexico

The co-occurrence of organic matter and uranium in the Jackpile Morrison formation, New Mexico was investigated using spectroscopy, microscopy,

and water chemistry techniques to better understand the effects of organic matter on uranium (U) binding from abandoned U mine wastes. Samples were collected from the Jackpile Mine (JP)- New Mexico. The mean concentration of acid extractable content for mine waste from the JP was 2.61±0.09% U. Results from microprobe mapping suggest that U particles are surrounded by carbon (C) inclusions, while results from XRF analyses showed 2.78% (JP) carbon (C). Loss on ignition (LOI) analysis showed that 19.90±0.95% of organic carbon within the samples. Thermal gravimetric analysis (TGA) show the maximum weight loss between 105°C and 505°C, confirming that change on mass after the LOI is likely due to the loss of organic content of the samples. Analyses using XPS suggest that changes occur on the C binding and U oxidation state after modifying the pH in batch experiments. Emission Matrix (EMM) identified humic-acid and fulvic-acid like components present in the organic matter comprised in the mine waste, which is consistent with the organic functional groups detected by XPS. These findings suggest that uranium minerals are possibly complexed carboxylic functional groups from humic-and fulvic like substances. This study identified the relevance of considering the binding of U and C in mine wastes to better understand U mobilization in the environment.

*This work was awarded the best talk award at the 2018 NMAVS Symposium (Albuquerque-May2018)

11:00am AS+NS+SA-WeM-10 Optical Constants Measured for Iridium and Samarium by Reflection Electron Energy-loss Spectroscopy Spectra, *LiHao Yang, H Xu,* University of Science and Technology of China; *A Sulyok, M Menyhard,* Institute for Technical Physics and Materials Science Centre for Energy Research, Hungarian Academy of Sciences (MTA); *K Tokesi,* Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI), Hungary; *Z Ding,* University of Science and Technology of China, China

The optical properties, as one of the most important physical properties of materials, arouse a continuous interest of researchers. Accurate measurement of optical data by optical methods in a photon energy range up to 100 eV is still insufficient as special experimental conditions are required during the measurements in vacuum ultraviolet region (20-50 eV). In recent years a well-established technique based on the reflection electron energy loss spectroscopy (REELS) has been developed to obtain optical constants in a rather wide range of electron energy loss. The REELS method does not require a complicated process for preparation of samples and the incident electron energy is usually around a few keV. However, the REELS spectrum usually contains not only bulk excitation but also surface excitation. To remove the surface excitation effect from the REELS spectrum in data analysis, Da et al. [1] have developed a reverse Monte Carlo (RMC) method for the derivation of the energy loss function (ELF) which is directly related to optical constants of a solid.

In the present work, reflection electron energy loss spectra of Ir and Sm were measured at several primary energies ranging from 0.5 keV up to 2 keV and in a wide energy-loss range. Polycrystalline Ir and Sm samples were cleaned by Ar+ ion bombardment. To minimize the surface roughening and damage, glancing incidence angle of 80° with respect the surface normal and low projectile energy of 1 keV were applied with the rotated sample during the sputtering. Cleanliness of surface was checked by continuous detection of main Auger peaks of C and O. A reverse Monte Carlo simulation was performed to extract ELFs of these metals from experimental REELS spectra. All the ELFs have produced REELS spectra in a good agreement within the experimental uncertainty. The reliability of the obtained optical data has been confirmed by applying the Thomas-Ritchie-Kuhn (f-sum rule) and the perfect-screening sum rules (p-sum rule). The good agreement indicates that RMC treats accurately the surface excitation effect which is well removed from the final ELF. Comparisons of our data with other sources from experimental measurements are given.

The work was support by the National Natural Science Foundation of China (No. 11574289) and Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (2nd phase) under Grant No. U1501501.

Reference:

[1] B. Da, Y. Sun, S. F. Mao, Z. M. Zhang, H. Jin, H. Yoshikawa, S. Tanuma, and Z. J. Ding, J. Appl. Phys. 113, 214303 (2013).

11:20am AS+NS+SA-WeM-11 X-Ray Photoelectron Spectroscopy and Electrical Modeling of Electrowetting on Dielectric Devices, *Pinar Aydogan Gokturk,* Bikent University, Turkey; *B Ulgut, S Suzer,* Bilkent University, Turkey

Electrowetting on dielectrics (EWOD) is a process of changing the contact angle of a droplet sitting on the dielectric covered electrode by the application of external electric field. In majority of the electrowetting experiments reported in the literature, water or aqueous salt solutions are used and ambient medium is either the air, or another immiscible liquid like oil. In this study, for the first time two non-aqueous liquids; (i) polyethylene glycol with an average molecular weight of 600 Da, and (ii) DEME-TFSI ionic liquid, both with low vapor pressure and volatility, are used as droplets in the UHV chamber of an x-ray photoelectron spectrometer (XPS) with traditional electrowetting on dielectric device geometry. With the experimental determination on tracing the electrical potential developments on and around the droplet, using the shifts in the binding energy positions of peaks coming from the liquid and/or the substrate, under imposed AC and DC electrical fields, we are aiming to shed light on the numerous models employed for simulating the electrowetting phenomenon. Additionally, using XPS and incorporating real capacitors and resistors, we mimic and check on the commonly used models used for simulating the electrical behavior of the EWOD systems. Possible and accepted electrical circuit models are also used to simulate the XPS data.

11:40am AS+NS+SA-WeM-12 Near Ambient Pressure XPS Study of Oxygen Binding to the Surface of Transition Metal-nitrogen-carbon Electrocatalysts for Oxygen Reduction, *K Artyushkova, Yechuan Chen, P Atanassov,* University of New Mexico

The most promising class of platinum group metal-free materials for oxygen reduction reaction (ORR) is based on graphene-like carbon containing nitrogen and transition metal (MNC). It is well established that nitrogen coordination with metal in the carbon network of MNC materials is directly related to ORR activity; however, the exact nature of the active sites is still debated even after over 50 years of research.

The mechanism of oxygen reduction reaction in metal-nitrogen-carbon (MNC) catalysts has been studied by a combination of spectroscopic and theoretical structure-to-activity studies. Using inhibitors that have unique spectral signatures and have strong binding to the active sites allows elucidating the relationship between the chemistry of active sites and its activity.

We will report laboratory-based and near ambient pressure (NAP-XPS) analysis for series of electrocatalysts belonging to Fe-N-carbon families. X-ray photoelectron spectroscopic analysis of the interaction of complexing agents based on phosphonate and *in situ* monitoring of oxygen binding to metal-free active sites provides an important insight into the reaction mechanism. The effect the nitrogen chemistry and the type of iron on the oxygen binding was investigated by NAPXPS under an oxygen environment at operating temperature of the fuel cell. Preferential oxygen binding to different types of nitrogen and iron moieties in presence and absence of inhibitor was followed by spectroscopic changes in high-resolution nitrogen photopeak.

12:00pm AS+NS+SA-WeM-13 Surface Chemistry of Scandium, *Michael Brumbach, D Casalnuovo, E Barnat, C Winters, D Robinson Brown, C Snow, A Grillet,* Sandia National Laboratories

Manipulation of metal surface chemistry through vacuum gas dosing has been demonstrated for many years. Additionally, ex situ preparation methods, ion sputtering, and/or in vacuo thermal treatment are all known to change surface properties through oxidation, removal of oxide, change in microstructure, altering contaminants, or other mechanisms. While these studies have been performed for decades, there are few examples of these experiments for pure scandium films. Furthermore, few examples of dosing clean scandium surfaces under vacuum have been published. In this work, scandium films were treated with UV/ozone ex situ cleaning, ion sputtering, and thermal treatment under UHV. These surfaces were then exposed to different gases in the millitorr pressure range for extended periods of time. An optical emission spectrometer was used to monitor the composition of the dosing gas. Surfaces were analyzed before and after dosing. In concert with the gas analyses, the changes in surface chemistry of scandium could be correlated to the dosing species. This work discusses the X-ray photoelectron peak fitting of scandium and the changes in chemistry that can be observed through surface exposures.

Wednesday Morning, October 24, 2018

Department of Energy's National Nuclear Security Administration under
contract DE-NA0003525.

Actinides and Rare Earths Focus Topic
Room 202C - Session AC+AS+SA-WeA

Chemistry and Physics of the Actinides and Rare Earths

Moderators: Krzysztof Gofryk, Idaho National Laboratory, Ladislav Havela, Charles University, Czech Republic, David Shuh, Lawrence Berkeley National Laboratory

2:20pm AC+AS+SA-WeA-1 New Directions in f-Block Separations Chemistry based on Metal and Ligand Redox Activity, *Eric Schelter, A McSkimming,* University of Pennsylvania; *J Su,* Los Alamos National Laboratory,; *T Cheisson, H Fang,* University of Pennsylvania; *L Moreau,* Lawrence Berkeley National Laboratory, Berkeley; *B Cole, B Manor, M Gau, P Carroll,* University of Pennsylvania; *E Batista, P Yang,* Los Alamos National Laboratory; *C Booth,* Lawrence Berkeley National Laboratory; *Y Qiao, J Bogart,* University of Pennsylvania **INVITED**

Chemical separations of mixtures of cations in the context of nuclear waste processing for lanthanide/actinide mixtures and ore processing of rare earth elements remain some of the most challenging to achieve selectivity. We have been developing new or improved methods to address these challenges using redox chemistry. For example, by changing ligand characteristics it may be possible to attain unusual oxidation states, in the case of actinides, that would enable selective separations. This talk will include discussion of some of our efforts to manifest chemical distinctiveness in actinide redox chemistry and the associated electronic structures of such complexes. In a parallel effort, we have been developing separations chemistry for rare earth cations based on kinetic resolution. Kinetic resolution has only rarely been applied in metal separations chemistry and represents an interesting new direction. Using a redox active ligand, a predictive system for inter-rare earth partitioning and separations will be described.

3:00pm AC+AS+SA-WeA-3 Bond Distance Variations for Lanthanide and Actinide Compounds and its Implication, *Tsuyoshi Yaita,* Japan Atomic Energy Agency, Japan; *S Suzuki, T Kobayashi, H Shiwaku,* Materials Sciences Research Center, Japan Atomic Energy Agency, Japan **INVITED**

Lanthanide and actinide are f-electron filling series and the properties of the series on their chemical behavior are very similar if valence states are same, while an electronic configuration of the inner shell for each element is slightly different compared to the similarity in size, and the value of special elements such as Nd and Dy used as neodymium magnet is high in the use of high-tech products. Regarding actinides series, radiotoxic Am is paid for attention in the geological disposal of radioactive waste and the R&D for partitioning and transmutation technique is performed. Accordingly, intra-series separation for lanthanide and actinide with similarity in chemical behavior would be quite important for the recovery of noble metal used as high-tech parts and treatment of high-level waste prior to geological disposal, resulting that the development of useful separation system could improve economic efficiency and reduction of environmental load.

On these backgrounds, we focus on the intra-series separation for lanthanide and actinide, especially, the relationship between variation of separation efficiency in the series and systematics of structure and electronic structure, and then, we try to propose new separation concept. Especially, in this talk, we talk about the variation of hydration or complex bond distances for trivalent actinide and lanthanide series based on X-ray crystallography and EXAFS and the interpretation based on the SX-XAS/XES and theoretical calculation.

4:20pm AC+AS+SA-WeA-7 Spectroscopic Studies of Trivalent Actinide Coordination, *Benjamin Stein, M Kerlin, A Morgenstern, E Batista, S Bone, S Cary,* Los Alamos National Laboratory; *J Lezama Pacheco,* SLAC National Accelerator Laboratory; *S Kozimor, P Yang,* Los Alamos National Laboratory **INVITED**

Radioisotopes have a rich history in medicine, with their use dating back to the earliest studies of radioactivity. Only recently, however, have α-particle emitting radionuclides been considered for medical applications. Targeted alpha therapy utilizes the unique properties of α-emitting radionuclides to selectively kill cancer cells, with the short range of α-particles causing minimal collateral damage to nearby healthy cells. Actinium-225 (^{225}Ac) has been identified by the Department of Energy Isotope Program Long Range plan as an isotope of high national interest for targeted alpha therapy, due to its favorable half-life (10 days) and 4 α-emissions in the decay chain. However, if the ^{225}Ac is not securely bound to the targeting vector this effectiveness results in very high toxicity to off-target (i.e. healthy) cells. Due to the high radioactivity and limited supply of all actinium isotopes, very little fundamental chemistry is known about this elusive element. Utilizing the unique radiological facilities at Los Alamos, we have been able to use microscopic amounts (~30 micrograms) of the longer-lived isotope actinium-227 (half-life of 22 years) for chemical studies. Utilizing this isotope, we have developed handling and containment techniques to perform "classic" spectroscopic and chemical studies in support of developing actinium chelates to advance the use of ^{225}Ac in targeted alpha therapy. During these studies of actinium coordination chemistry we have also made comparisons with the more "traditional" trivalent actinides, in particular americium and curium. We will discuss our latest EXAFS, NMR, and computational results on these difficult to handle elements by presenting a comparison of acetate and phosphonate binding, and how this informs chelator development.

5:00pm AC+AS+SA-WeA-9 Speciation of Rare Earth Elements in Coal Harvesting Byproducts, *Xu Feng, M Council-Troche, J Morris, A Noble, R Yoon,* Virginia Polytechnic Institute and State University

Rare earth elements (REEs) are critical for the development of renewable energy resources, national security, and advanced manufacturing. With the recent closure of the rare earth mine in California, the U.S. relies entirely on foreign imports mainly from China, which poses serious economical and national security concerns. According to a study commissioned by the National Energy Technology Laboratory (NETL), the U.S. coal and coal byproducts contain ~11 million metric tons of recoverable REEs, only a small fraction of which could satisfy the domestic need [1].

Recent USGS studies showed that the REEs in U.S. coals are preferentially partitioned to clay minerals [1], suggesting that the clay byproducts may be a major source of the critical materials. Ion-adsorbed REEs in clay appear to exist as two distinct forms: (1) ionic species adsorbed by coulombic attraction which is thought to be the primary form in REE-adsorbed clay deposits in South China, and (2) colloidal REEs formed by hydrolysis, each requiring a unique extraction strategy. However, the conditions under which the ion-exchange clays were formed in the U.S. coals and accompanying mineral matter may be different from those for the South China ion-adsorption clays, and the specific speciation of REEs in U.S. coal materials is currently unknown. It is, therefore, critical to study the fundamental mechanisms by which REEs are adsorbed on clay minerals in aqueous media to develop effective targeted extraction strategies.

In this work, X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical state of representative light and heavy rare earth elements on artificial REE-adsorbed clay samples. Characteristic REE $3d_{5/2}$ features of the artificial clay sample, including the peak position of the two multiplet-split components, the magnitude of the multiplet splitting and the intensity ratio of each multiplet-split component, were compared to those of the high-purity REE standards such as $REE(OH)_3$, REE_2O_3 and $REECl_3$ to provide insight into the identification of REE speciation on the artificial sample. XPS results suggest that $REE(OH)_3$ is the primary REE species on the artificial REE-adsorbed clays. Furthermore, X-ray Adsorption Spectroscopy (XAS) was used to probe the speciation of representative light and heavy REEs in natural coal and coal byproduct samples by comparing the oxidation states and specific bonding environments to those of REE standard materials.

[1] Bryan, R. C., D. Richers, H.T. Andersen, and T. Gray, "Assessment of Rare Earth Elemental Contents in Select United States Coal Basins," Document No: 114-910178-100-REP-R001-00, January 2015.

5:20pm AC+AS+SA-WeA-10 Exotic Electronic Properties of Strongly Correlated Compounds $NpPd_3$ and $PuPd_3$, *Krzysztof Gofryk,* Idaho National Laboratory; *J Griveau, E Colineau,* Institute for Transuranium Elements; *K McEwen,* University College London; *W Nellis,* Harvard University; *J Smith,* Los Alamos National Laboratory

Actinides are characterized by the coexistence of localized and itinerant (delocalized) 5*f*-states near the Fermi energy. This dual nature of the 5*f*-electrons leads to many complex phenomena that are observed in these strongly correlated materials, spanning magnetic ordering, heavy-fermion ground state, unconventional superconductivity, and/or "non-Fermi liquid" state. The electronic properties of the strongly correlated electron systems are related to the formation, near the Fermi level, of a narrow band with large density of states and in spite of intensive theoretical and experimental efforts their nature is still not well understood. This behavior is well emphasized in AnPd$_3$ (An-U, Np, Pu) system. UPd$_3$ crystalizes in the hexagonal crystal structure and shows four phase transitions below 7.8 K, attributed to a succession of antiferroquadrupolar orderings of the

uranium ions localized on the quasi-cubic sites of the $d$hcp structure. Depending on a heat treatment, NpPd$_3$ crystalizes in hexagonal and cubic crystal structures. The hexagonal NpPd$_3$ (h-NpPd$_3$) exhibits two transitions at 30 and 10 K. It has been suggested that the low temperature transition might be due to ordinary antiferromagnetic ordering while the high temperature one might be caused by a quadrupolar order. The cubic NpPd$_3$ (c-NpPd$_3$) orders antiferromagnetically below 52 K and the magnetic and transport measurements suggests that the transition is first order. PuPd$_3$ crystalizes in the cubic structure and shows an antiferromagnetic order below 24 K. To explore the influence of electronic correlations on the physical properties in the AnPd$_3$ system, here we present our detailed magnetic, thermodynamic, and transport studies of NpPd$_3$ and PuPd$_3$.We show that all results obtained present characteristic behaviors of 4f- and 5f-electron strongly correlated materials. The magnitude and overall temperature dependence of the electrical resistivity, magnetostesitivity, Hall and Seebeck effect, and heat capacity of NpPd$_3$ and PuPd$_3$ are archetypal of materials with Kondo interactions. Our measurements also reveal an unusual magnetic ordering in c-NpPd$_3$. At T$_N$, the specific heat exhibits an extremely large peak [as large as 1000 J/(mol K)] and the magnetic susceptibility shows a clear jump. The transport properties of c-NpPd$_3$ indicate a dramatic reconstruction of the electronic structure at the Néel temperature, probably accompanied by a large change in the Fermi surface topology, which shows up as pronounced anomalies at this temperature in the electrical resistivity, the magnetoresistivity, and the Seebeck and the Hall coefficient. We will discuss implications of these results.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 202A - Session SA+AS+MI-WeA

Hard X-Ray Photoemission for Probing Buried Interfaces
Moderators: Zahid Hussain, ALS-LBNL, Olivier Renault, CEA-University Grenoble Alps, France

2:20pm **SA+AS+MI-WeA-1 Element-resolved Electronic Band Structure of Ga(Mn)As Measured by Standing-wave Hard X-ray Angle-resolved Photoemission**, **Slavomir Nemsak,** Advanced Light Source, Lawrence Berkeley National Laboratory; *M Gehlmann, C Kuo,* University of California, Davis; *T Lee,* Diamond Light Source Diamond House, Harwell Science and Innovation Campus; *L Plucinski,* Forschungszentrum Juelich GmbH, Germany; *J Minar,* University of West Bohemia; *C Schneider,* Forschungszentrum Juelich GmbH, Germany; *C Fadley,* University of California, Davis

Electronic band structure of the dilute magnetic semiconductor Ga$_{(1-x)}$Mn$_x$As was obtained using hard X-ray angle-resolved photoemission. The element- and site-sensitivity of the measurements was achieved by forming a strong X-ray standing-wave generated by Bragg reflection from the (111) atomic planes of both undoped GaAs and Mn-doped thin films. Due to the uneven occupancy of (111) planes by either Ga(Mn) or As atoms, the element-specific band structure can be obtained with a help of the SW modulation in core levels. Measured momentum- and element-resolved bulk electronic structure was compared to element-projected Bloch spectral functions with excellent agreement between experiment and theory. Apart from the site specific decomposition of the electronic structure, the SW measurements also confirmed a substitutional presence of Mn atoms at the Ga sites. This novel technique should be applicable to a broad range of complex materials.

2:40pm **SA+AS+MI-WeA-2 Probing Surface Band Bending of Polar GaN by Hard X-ray Photoemission Combined with X-ray Total Reflection**, **Shigenori Ueda,** NIMS, Japan

GaN is known as a polar semiconductor due to an alternative stacking of Ga and N layers along the c-axis. Ohsawa *et al*. [1] showed the difference in valence band spectral shapes of the bulk Ga- and N-polar GaN single crystals by using polarization dependent hard X-ray photoemission spectroscopy (HAXPES). In general, HAXPES is a bulk-sensitive probe [2], and take-off angle (TOA) dependent of photoelectron gives depth information [3]. However, the decrease of the photoemission intensity occurs in lower TOA, and the valence band spectra depend on TOA [3] due to the matrix element effect [4].

In this work, HAXPES combined with X-ray total reflection was used to obtain a depth-resolved electronic structure instead of TOA dependent measurements. The change of incidence angle within 1 degree around the critical angle of X-ray total reflection drastically changes the attenuation length of X-ray in solids.

We have measured the core-level and valence band HAXPES spectra of commercially available bulk single crystalline GaN for Ga and N polar faces in the case of inelastic mean free path of 2.17, 3.73, and 7.69 nm. Undoped n-type GaN crystal with fine polished surfaces was used. For the Ga-polar face, large band bending behavior was observed, while the band bending was small for the N-polar face. The Ga 3s and N 1s core-level spectra also showed the polarity dependent band bending behavior. We found that GaN near the surface is degraded in both the polar faces. This result suggests that high quality single crystalline GaN with fine surface treatment is required for detecting the intrinsic electronic structure of GaN. Finally we note that HAXPES combined with X-ray total reflection is useful method for depth-resolved electronic structure measurements, since the data acquisition time in this method is 10 or more faster than that in TOA dependent measurement, and the matrix element effect is almost negligible in this method.

References

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[3] M. Lozac'h *et al*., Sci. Technol. Adv. Mater. **14**(2013) 015007.

[4] S. M. Goldberg, C. S. Fadley, and S. Kono, J. Electron Spectrosc. Rel. Phenom. **21**(1981) 285.

3:00pm **SA+AS+MI-WeA-3 Interfaces in Cycled Battery Electrodes: Insights from HAXPES Studies**, **Julia Maibach,** Karlsruhe Institut of Technology (KIT), Germany **INVITED**

Rechargeable ion batteries such as lithium and sodium ion batteries generally consist of a negative electrode, a positive electrode and an ion conducting electrolyte. The contacts between the different materials are key to the electrochemical energy storage process and at the surfaces of the electrodes and at the interfaces to the electrolyte, reactions crucial to long-term, safe battery operation take place. Due to its surface and chemical sensitivity, photoelectron spectroscopy has therefore become a widely used tool to characterize and understand the processes and phenomena in these electrochemical energy storage systems.

Looking in more detail, a battery electrode itself is a complex system as it consists of many different components such as the active storage material, conductive additives as well as binders to keep the particles attached to a metal foil, which acts as a current collector. This complexity of mixed materials and morphologies further increases when the electrodes are cycled electrochemically due to the desired storage processes and due to reactions with the battery electrolyte leading to interface layer formation.

These highly complex systems of cycled battery electrodes bring new challenges when studied with photoelectron spectroscopy. In this presentation, observed peak shifts for cycled battery electrodes will be discussed in depth. Particular emphasis will be given to the buried interfaces. Here, hard x-ray photoelectron spectroscopy (HAXPES) is one of the few available techniques that can access the buried interface while maintaining the chemical information from the delicate battery interface layers. Based on HAXPES experiments, the role of the buried interfaces and their importance in both battery operation as well as in photoelectron spectroscopy characterization of cycled electrodes will be discussed.

Additionally, spectral changes due to electrode potentials as well as lithiation effects will be discussed. These strongly depend on the nature of the active material and therefore need to be considered carefully to achieve consistent data interpretation. Combining all presented effects, a strategy for photoelectron spectroscopy experiments on cycled battery electrodes will be proposed that takes buried interfaces into account.

4:20pm **SA+AS+MI-WeA-7 Development of Ambient Pressure HAXPES and other HAXPES Measurements at SPring-8 for Buried Interface**, **Yasumasa Takagi,** Japan Synchrotron Radiation Research Institute (JASRI), Japan **INVITED**

A near ambient pressure photoelectron spectroscopy measurement that use with hard X-rays (AP-HAXPES) were conducted at the BL36XU of SPring-8. The AP-HAXPES system with a commercial differential pumping-type spectrometer (R4000 HiPP-2, Scienta Omicron Inc.) was installed in the beamline. The excitation light of 7.94 keV focused to a beam size of 20 μm x 20 μm on the sample surface was used. The standard aperture size at the top of the front cone in the spectrometer is a diameter of 300 μm. In this report, we replaced the front cone with our home-made one with an

aperture diameter of 30 μm to increase the pressure limit in the AP-HAXPES measurement. Meanwhile, we have adapted the working distance of 60 μm in order not to perturb the gas environment at the sample surface.

We measured the XPS spectra of the Au(111) surface grown on a mica substrate under various gas pressures using the AP-HAXPES equipment. The intensity decay of the Au 4f spectra with an increasing gas pressure from 1 Pa to 100 kPa. Here we use "100 kPa" as the atmospheric pressure. The XPS measurement was not affected by the ambient gas at a pressure of 1 Pa. As the gas pressure increased, the signal intensity decreased because the photoelectrons were scattered by the ambient gas while passing through the sample to the detector. Although the signal intensity was very weak at the atmospheric pressure, the peaks of $4f_{5/2}$ and $4f_{7/2}$ can be detected. The signal-to-noise ratio can be improved by a prolonged acquisition time. The $4f_{7/2}$ and $4f_{5/2}$ peaks are clearly found in the spectrum at the atmospheric pressure in an acquisition time of 30 min. The Shirley background was subtracted from the spectrum, and the plots were fitted with a Voigt function. The curve fitting result shows that the energy difference between the $4f_{7/2}$ and $4f_{5/2}$ peaks is 3.7 eV and the intensity ratio $4f_{7/2}:4f_{5/2}$ is almost 4:3. These values are in good agreement with the standard value of the Au 4f peaks. Thus, a photoelectron spectroscopy under atmospheric pressure was successfully obtained using an aperture of 30 μm.

5:00pm **SA+AS+MI-WeA-9 Operando HAXPES Investigations of La Manganite-based Resistive Memories**, *Eugénie Martinez,* CEA/LETI-University Grenoble Alpes, France; *B Meunier,* Univ. Grenoble Alpes, CEA, LETI & LMGP, CNRS, France, France; *D Pla,* Univ. Grenoble Alpes, LMGP, CNRS, France; *R Rodriguez-Lamas,* Univ. Grenoble Alpes, LMGP, CNRS France, France; *M Burriel, C Jimenez,* Univ. Grenoble Alpes, LMGP, CNRS, France; *J Rueff,* Synchrotron SOLEIL, France; *Y Yamashita, S Ueda,* NIMS, Japan; *O Renault,* CEA/LETI-University Grenoble Alpes, France

The use of perovskite oxides in resistive random access memories (RRAMs) is considered for the next generation of non-volatile memories (NVMs) [1]. Indeed, their highly tunable ionic and electronic transport properties open new possibilities for multilevel storage capacity. In particular, manganese oxides, such as $LaMnO_{3+d}$ (LMO), are among the most promising candidates [2].The switching mechanism is related to oxygen transport, yielding to the creation and annihilation of oxygen vacancies through the functional layer. However, two main mechanisms based on filaments or 2D interfacial effects must be discriminated to better understand and control the devices properties.

We investigate here the key role of oxygen in the switching mechanism of LMO-based RRAMs using hard X-ray photoelectron spectroscopy (HAXPES). This technique allows learning about electrochemical reactions involved in the structure with sufficient depth sensitivity. Operando HAXPES was performed at Soleil and SPring-8 to investigate in-situ resistive switching. Measurements were done while biasing the memory with opposite polarities, to reach successively low and high resistance states. In particular, a chemical analysis of the interface between the active electrode and the LMO was done after *Set* and *Reset* operations.

Results show modifications of the oxygen core level spectra. The peak assigned to interfacial LMO shifts as a function of bias voltage, contrary to the bulk LMO component. These results highlight variations in charges concentration at the electrode/LMO interface, as a result of creation/annihilation of interfacial defects, such as oxygen vacancies. Complementary trends regarding La3*d* and Mn3*s*/2*p* spectra will be discussed in terms of oxidation and reduction phenomena, related to variations of the oxygen content at the electrode/LMO interface.

[1] Jin YL, Jin KJ, Ge C, Lu HB, Yang GZ, Resistive switching phenomena in complex oxide heterostructures, Modern Physics Letters B, 2013;27(29)1330021.

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5:20pm **SA+AS+MI-WeA-10 Combining Hard and Soft X-ray Angle-resolved Photoemission to Probe the Bulk Electronic Structure of Engineered Quantum Solids**, *Alexander Gray,* Temple University   **INVITED**
Angle-resolved photoelectron spectroscopy, or ARPES, is a powerful and well-established experimental technique for probing the momentum-resolved electronic structure of matter. In this talk, I will discuss several promising new directions in this field, which stem from experimental and theoretical studies wherein angle-resolved photoemission is carried out at

higher excitation energies, namely in the soft and hard x-ray regimes. I will focus specifically on the recent studies of novel engineered quantum materials and heterostructures, which aim at gaining a clear understanding of the depth-dependent nanoscale evolution of materials' electronic properties at the surface, in the bulk, and across the buried interfaces by using multiple modalities of hard and soft x-ray angle-resolved photoemission both separately and in tandem with each other.

6:00pm **SA+AS+MI-WeA-12 Surface/Interface Coupling in Buried Oxide Interfaces**, *Conan Weiland,* National Institute of Standards and Technology (NIST); *A Rumaiz,* Brookhaven National Laboratory; *G Sterbinsky,* Argonne National Laboratory; *J Woicik,* National Institute of Standards and Technology (NIST)
Oxide interfaces can host a variety of properties not found in the bulk materials. The interface between LaAlO3 (LAO) and SrTiO3 (STO) is a prototypical example; the interface of these two insulators can show conductivity, ferromagnetism, and even superconductivity. The source of these interface properties is still a matter of debate, with potential explanations including electronic reconstruction due to the polar discontinuity at the interface, chemical intermixing, and oxygen vacancies at either the interface or LAO surface. Hard x-ray photoelectron spectroscopy (HAXPES) is an excellent tool to probe these interfaces due to the enhanced and tunable probe depth afforded by a synchrotron source. We have used a combination of variable kinetic energy HAXPES and ambient pressure soft x-ray photoelectron spectroscopy (AP-XPS) to investigate the interplay between LAO film and surface structure and the LAO/STO interface. We find Al surface enrichment for most LAO films, while AP-XPS shows significant band shifts in the presence of water vapor. The role of these LAO surface features on the LAO/STO interface conductivity will be discussed.

Thursday Morning, October 25, 2018

Actinides and Rare Earths Focus Topic
Room 202C - Session AC+AS+SA-ThM

Nuclear Power, Forensics, and Other Applications
Moderator: Ladislav Havela, Charles University, Czech Republic

8:00am AC+AS+SA-ThM-1 Electron Microscopy in Nuclear Forensics, *Edgar Buck, D Reilly, J Schwantes, J Soltis, T Meadows, D Meier, J Corbey,* Pacific Northwest National Laboratory **INVITED**
Recent advances in electron microscopy both in terms of spatial resolution, sensitivity, and the ability to perform in-situ chemistry experiments, present enormous opportunities to the nuclear forensic field. Extraction of specific particles of interest with dual-beam SEM-FIB instruments can be readily applied plutonium-contaminated materials. Furthermore, other developments in microscopy have enabled in-situ monitoring of interfacial processes and 3D tomographic views of specimens and phases. Several new advances in technology have enabled great advances and potential for nuclear science including nuclear forensics. These include dual-beam ion-electron systems for precise sample isolation and preparation, the electromagnetic lens aberration-corrector, high-count capacity x-ray detector systems, faster digital cameras, high performance electron backscattered diffraction systems in combination with 3D visualization tools, application of cryoTEM methods to material science, as well as micro-fabricated in-situ cells that enable direct observation of chemical and electrochemical processes in the EM. The application of these technologies to nuclear forensics will be discussed.

8:40am AC+AS+SA-ThM-3 New Frontiers with Fission Track Analysis and TOF-SIMS Techniques, *Itzhak Halevy,* Nrcn Israel, Israel; *R Radus,* Ben Gurion University, Israel; *S Maskova,* Charles University, Prague, Czech Republic; *A Kogan, S Samuha, D Gridchin, E Grinberg, E Boblil, N Haikin,* IAEC-NRCN, Israel; *I Orion,* Ben-Gurion University -Negev, Israel; *A Weiss,* Faculty of Engineering, Bar-Ilan University, Israel **INVITED**
Illicit trafficking of radioactive materials is known to exist from the early days of radioactive era. The nuclear forensics deals with recognizing the materials and processes of the radioactive industry. The properties of the materials can give a hint about the source of material and its original use.

The most common radioactive material involved in illicit trafficking is uranium. Uranium is a common natural element which can be found everywhere. The cosmogenic uranium is well known and defined. The natural enrichment of uranium is varying within a small range around 0.72 % and is indicative to its source. The enrichment of the anthropogenic uranium can vary much depending on the purpose and use of the material. Different enrichments are known for individual nuclear power plants, research reactors and military uses.

Measuring the uranium properties can indicate its enrichment, presence of other elements or impurities and can help in finding its attribution, namely its origin.

To learn more about the history of found material accurate isotopic measurements are needed.

The ratio between ^{230}Th and ^{234}U can give a good estimation of how much time passed from the last chemical cleaning of the material. This technique is called radio-chronometry or age dating.

We developed new Lexan detectors with much better signal to noise ratio to improve sensitivity and reduce the false alarm.

New Automated software can recognize the fission track (FT) automatically and give the parameters of the track, like: roundness, intensity, number of tracks and color histogram. In that program we can add ROI (region of interest) or to cancel a false positive FT identification.

Analytical equipment like TOF-SIMS (Time Of Flight - Secondary Ion Mass Spectrometry) and ICP-MS (Inductively Coupled Plasma - Mass Spectrometer located at the Geophysical survey Israel - GSI) together with new FTA software give new frontiers to the nuclear forensic research .

A microscope equipped with TOF-SIMS gives the ability to measure quantitatively, the ratio between the different isotopes and molecules. Using the scanning electron microscope, we are able to choose the desired particle which can be then analyzed using the TOF-SIMS. TOF-SIMS is a technique capable to distinguish not only between elements but also different isotopes. Knowing the ratio between the isotopes is very important as it can help us to classify the material looking for its possible origin. Morphology and depth profile than give other insight to the

processes that the sample went through. Nano manipulators can extract the particle and transfer it to a different technique.

9:20am AC+AS+SA-ThM-5 Predictive Nuclear Forensics: Fundamental Frameworks to Fill Missing Pieces, *Jenifer Shafer, M Koehl, A Baldwin, D Wu,* Colorado School of Mines; *R Rundberg,* Los Alamos National Laboratory; *M Servis,* Washington State University; *T Kawano,* Los Alamos National Laboratory **INVITED**
Understanding the origin of nuclear forensic signatures provides the benefit of understanding how these signatures can be compromised and provides a framework to predict signatures that might arise under various conditions. The ability to predict signatures is particularly useful for the nuclear forensics community since only a limited number of samples exist. Frequently access to these samples can be further constrained due to classification boundaries. This talk provides two examples of how fundamental chemical and physical phenomena can be leveraged to understand signature origins, thus enabling a more robust nuclear forensics capability. The first study focuses on understanding how organic phase aggregation chemistry in the PUREX process can dictate trace metal, such as fission or corrosion product, partitioning patterns. By understanding how trace metals partition, information regarding the processing history, including the reprocessing site, could be ascertained. Trace metal partitioning patterns were studied by producing radiotracers in the USGS 1 MW TRIGA reactor. The influence of extractant aggregation on trace metal partitioning was then assessed using a combination of diffusion NMR spectroscopy and small angle neutron scattering. The second study focuses on understanding how cumulative fission product yields can describe the incident neutron energy. Fission yield curves of uranium-235 have a decrease in valley radionuclide production when the incident neutron energy is in the epithermal energy regime. This decrease in valley radionuclide production seems tied to the excitation of the uranium-236 to the 3- spin state. The octupole deformation of the 3- spin state enables more asymmetric fission than typically encountered with fast or thermal neutrons and thus suggests the structure of the excited uranium-236 compound nucleus could be, in part, responsible for cumulative fission product yields. These two studies highlight how fundmental science enables signature development.

11:00am AC+AS+SA-ThM-10 Soft X-ray Synchrotron Radiation Spectromicroscopy Studies of Radioactive Materials, *David Shuh,* Lawrence Berkeley National Laboratory; *A Altman,* Lawrence Berkeley National Laboratory and UC Berkeley; *D Kilcoyne, S Minasian, J Pacold, D Smiles, T Tyliszczak, D Vine,* Lawrence Berkeley National Laboratory; *L He, J Harp, M Meyer,* Idaho National Laboratory; *C Degueldre,* University of Lancaster, Switzerland
Soft X-ray synchrotron radiation methodologies are being developed and employed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory (LBNL) to elucidate the electronic structure of radioactive and actinide materials. Results from these investigations have begun to provide improved fundamental knowledge that can be used as a scientific basis for the enhanced design of actinide materials, complexes, ligands, and the overall understanding of actinide materials. The experimental developments at the ALS have centered on studies of radioactive materials with the soft X-ray scanning transmission X-ray microscope (STXM) at Beamline 11.0.2 for spatially-resolved near-edge X-ray absorption spectroscopy (XAS). The spectromicroscopy capabilities of the STXM provide the means to determine the speciation and composition in a range of actinide materials, particularly those of technological and environmental interest with spatial resolution that can reach to the true nanoscale. A particular emphasis has been on the use of light atom (B, C, N, O, F, Na, Mg, Al, Si) ligand K–edge XAS technique to determine the electronic structure characteristics in an array of unique and relevant materials. Furthermore, there are a host of additional electron energy level thresholds (such as the L–edges of the transition metals, the M–edges of the lanthanides, and others) that can be probed by near-edge XAS in the soft X-rays.

Recently, STXM spectromicroscopy studies have been extended to focused ion beam (FIB) prepared radioactive and irradiated material specimens in collaboration with Idaho National Laboratory. Future scientific developments and applications of soft X-ray spectromicroscopy investigations utilizing ptychography and in-operando methodologies will be discussed.

11:20am **AC+AS+SA-ThM-11 Comparison of the Oxidation Rates for Alpha Versus Delta Plutonium by X-ray Photoelectron Spectroscopy**, *Art Nelson, S Donald, D Roberts, W McLean,* Lawrence Livermore National Laboratory

X-ray photoemission spectroscopy (XPS) was used to characterize differences in the oxidation rates for polycrystalline α-Pu versus δ-Pu related to variations in grain size and surface electronic structure. The evolution of the Pu 4f core-level chemical shift as a function of oxygen exposure at ambient temperature was quantified in oxidation profiles. In addition, the X-ray excited Pu NOO Auger line-shapes were combined with the chemical shift of the Pu $4f_{7/2}$ photoelectron line that defines the Auger parameter and results in a reliable method for determining oxidation states independent of binding energy calibration. The oxidation profiles reveal that α-Pu oxidizes faster than δ-Pu, both resulting in the $PuO_2/Pu_2O_3/Pu$ oxide structure. This data was used to a produce chemical state (Wagner) plot for select plutonium oxides.

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

11:40am **AC+AS+SA-ThM-12 A Single-Stage AMS Detector for Secondary Ion Mass Spectrometry and its Applications to Nuclear Materials Analyses**, *David Willingham, E Groopman, K Grabowski,* U.S. Naval Research Laboratory; *L Sangely,* International Atomic Energy Agency; *A Meshik, O Pravdivtseva,* Washington University in St. Louis; *D Weisz, K Knight,* Lawrence Livermore National Laboratory

Secondary ion mass spectrometry (SIMS) has long been applied to the analysis of isotopic heterogeneities in nuclear materials. Few other methodologies can compete with the ability of SIMS to measure the isotopic composition of nuclear materials with high accuracy and precision with micrometer spatial resolution. Like many other mass spectrometry techniques, however, the presence of molecular isobaric interferences at any given mass-to-charge complicate interpretation of SIMS measurements. Uranium isotopes, for example, can be valuable and informative markers for the process of enriching uranium for nuclear fuel for the production of nuclear energy. In addition to the major uranium isotopes (^{238}U and ^{235}U), the minor isotope ^{236}U is of interest because it is an indication for the presence in the sample of uranium reprocessed from spent nuclear fuel. The resolving power needed to separate ^{236}U from the molecule $^{235}U^1H$, however, is greater than 38,000 - far beyond most the mass resolution of commercially available SIMS instruments. One solution to this problem is to use a Single-Stage Accelerator Mass Spectrometer (SSAMS) to accelerate secondary ions to a high enough energy (300keV) to enable molecular dissociation within a stripper gas while retaining good transmission, followed by SIMS-based detection. At the U.S. Naval Research Laboratory, we have developed the Naval Ultra-Trace Isotope Laboratory's Universal Spectrometer (NAUTILUS) to achieve this goal. Using the NAUTILUS, we accomplish molecule-free isotopic analysis of nuclear materials without sacrificing the benefits of SIMS. In this work, we demonstrate the broad applications of the NAUTILUS to areas of nuclear materials analyses including uranium bearing particle analysis for nuclear Safeguards, analysis of the Oklo natural nuclear reactor, and analysis of uranium doped silicate glasses as working reference analogs for nuclear fallout materials. The NAUTILUS represents a new era in SIMS analyses of complex materials with specific application to nuclear materials and general application to the SIMS community as a whole.

12:00pm **AC+AS+SA-ThM-13 Physicochemical Properties of Ag in Annealed ZrN/SiC/Ag Heterostructures Used to Simulate TRISO Nuclear Fuels**, *Jeff Terry, M Warren, R Seibert,* Illinois Institute of Technology

Silicon carbide (SiC) is used as a supportive and protective barrier in the cladding of tristructural-isotropic (TRISO) nuclear fuel particles. Previous studies both of surrogate surfaces and irradiated fuel have shown that the fission product silver (Ag) exhibits transport into and sometimes through the SiC barrier with temperatures above 500 °C. This silver release can cause safety concerns for maintenance workers due to plate-out on in-reactor components. Although an exact diffusion mechanism for Ag in SiC is unknown, a solution is needed to prevent this effect. The use of a ZrN protective coating may mitigate Ag transport and potential release. This study examines the transport of Ag in SiC through the use of surrogate multilayered thin-films. Thin films of subsequent layers of SiC, Ag, SiC, and ZrN deposited by pulsed-laser ablation deposition (PLD) under a range of annealing temperatures up to 1200 °C are studied. After heating, X-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM),

and energy-dispersive X-ray spectroscopy (EDS) was used to examine the surface of the ZrN. Initial results show that Ag does not readily diffuse through the ZrN layer like it does through SiC. The results and implications of this study will be discussed.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 202A - Session SA+MI-ThM

Ultra-fast Dynamics for Magnetic and Quantum Systems

Moderator: Claus Michael Schneider, Forschungszentrum Juelich GmbH, Germany

8:00am **SA+MI-ThM-1 New Opportunities at the APS: Using Intermediate Energy X-rays to Investigate Collective Behavior in Interacting Electron Systems**, *Jessica McChesney, F Rodolakis,* Argonne National Laboratory

In an effort to address one of the grand challenges for condensed matter physics in the 21st century, namely to gain an understanding of the physics of materials which exhibit collective electronic phenomena, the Advanced Photon Source has developed the intermediate-energy x-ray (IEX) beamline. Now fully operational, this beamline enables the investigation of collective behavior in interacting electron systems using two distinct but complementary techniques: angle-resolved photoemission spectroscopy and resonant soft x-ray scattering. In this talk, I will discuss some of the unique capabilities of the beamline and present several examples of collective behavior in interacting electron systems including electron-phonon coupling, spin and charge density waves and orbital ordering in high-temperature superconductors, transition metal oxides, topological insulators and heavy fermion materials.

8:20am **SA+MI-ThM-2 Observation of Surface Recombination in Ultra-fast Carrier Dynamics of $La_{0.7}Sr_{0.3}MnO_3$ Thin Films**, *Saeed Yousefi Sarraf, G Cabrera, R Trappen, N Mottaghi, S Kumari, C Huang, A Bristow, M Holcomb,* West Virginia University

Perovskite oxides (ABO_3) are a promising class of transition metal oxides that have attracted significant attention in material science due to diverse range of properties. Many studies on structural and magnetic properties have been done on perovskite oxides to base the multifunctional devices made by and proposed for these materials. Yet another very important property of perovskite oxides is that many of their band gaps are in the visible range. These gaps make these oxides a suitable choice for photovoltaic applications. However, despite the very critical role this property plays in light harvesting devices, there has been a limited understanding about the carrier dynamics of these materials, which inform us about the efficiencies of photovoltaic devices, especially in lower thicknesses. Since by decreasing the film thickness, the surface to bulk ratio increases and surface electrons dominate the bulk electrons, surface recombination might occur as an extra channel of energy relaxation, which decreases the device efficiency. Perovskite oxide $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films were fabricated with different thicknesses by pulsed laser deposition on (100) $SrTiO_3$ single crystal substrates. Our films' quality were checked by in situ RHEED patterns and oscillations, X-ray diffraction and reflectivity, magnetometry and atomic force microscopy. Ultra-fast carrier dynamics were studied by a degenerate reflectivity pump probe setup at 800nm for different film thicknesses and different pump powers. For films with a thickness above ~20nm three different recombination were observed, attributed to electron phonon relaxation, spin lattice phonon assists relaxation and thermal diffusion relaxation. However, for films thinner than ~20nm an extra relaxation mechanism was observed, which we attributed to surface recombination. This optics work was funded by the American Chemical Society (PRF #56642-ND10); sample growth and optimization were supported by NSF (DMR-1608656).

8:40am **SA+MI-ThM-3 Non-equilibrium Control of Charge & Spin Motion in Quantum Materials**, *Hermann Dürr,* Uppsala University, Sweden**INVITED**

A key driver of modern information technology is the quest for "smaller and faster" information processing and storage. The ultimate speed limit is the speed of light. Therefore, the idea to probe, change and control properties of materials with the help of light has long intrigued researchers in materials science. Of particular interest are magnetic materials which in nanostructured form are used for data storage, memory and processing. In this talk I will show several examples the unique potential of using

femtosecond soft x-ray pulses from x-ray free electron lasers such as the LCLS to probe in real time ultrafast spin dynamics in nanoscale systems and during all-optical magnetic switching. Understanding and ultimately engineering the evolving electron, spin and lattice motion on the time- and lengthscales associated with the relevant interactions promises new ways for storing and processing of information.

9:20am SA+MI-ThM-5 XUV-transient Grating: Probing Fundamental Excitations at the Nanoscale, *Laura Foglia, F Capotondi, R Mincigrucci, D Naumenko, E Pedersoli, A Simoncig, G Kurdi, M Manfredda, L Raimondi*, Elettra-Sincrotrone Trieste, Italy; *N Mahne*, IOM-CNR, Italy; *M Zangrando, C Masciovecchio, F Bencivenga*, Elettra-Sincrotrone Trieste, Italy **INVITED**
Nonlinear optical spectroscopies take advantage of multiple light-matter interactions via the Nth-order susceptibilities, to disentangle and selectively access the many interacting degrees of freedom that characterize complex systems. Indeed, the control on photon parameters (frequency, arrival time, polarization, etc.) for each field independently gives rise to a manifold of experimental techniques that allow to monitor, on ultrafast timescales, structural changes, spin and electron dynamics, collective phenomena as well as to selectively probe correlations among different excitations. Among the nonlinear processes, third order, or four-wave-mixing (FWM), interactions occur in all materials independently of their symmetry, and are thus the most widely used in applications. While nowadays these techniques are well established at optical wavelengths, their birth required the invention of the laser. Similarly, their extension to sub-optical wavelengths (XUV and X-ray), envisioned theoretically more than a decade ago, had to wait until the recent development of free electron lasers (FELs). XUV-FWM will allow exploiting core-hole resonances to address correlations among low-energy excitations and core states as well as monitoring charge and energy transfer processes. Additionally, it will extend the accessible wavevector range to the mesoscopic regime (0.1-1 nm^{-1}), which is fundamental to investigate, e.g., lattice dynamics in nanostructures and disordered systems as well as transport phenomena at the nanoscale.

Here I report on the demonstration of XUV four-wave-mixing response in a transient grating (TG) approach, exploiting the unique properties of the seeded FEL source FERMI and of two dedicated setups: TIMER and mini-TIMER. All-XUV TG data allowed us to determine the phonon and thermal dynamics of several semiconductors in an uncharted length-scale range, extending down to ≈20 nm. The results are compared with those of XUV pump/optical probe TG, evidencing different couplings to the electronic subsystem.

Additionally, I present the first evidence of FWM processes stimulated by FEL pulses at different wavelengths, obtained exploiting the multi-color capabilities of FERMI and will discuss the foreseen implementation of second order wave-mixing techniques for the chemical and interface specific probing of electronic processes.

11:00am SA+MI-ThM-10 Study of Photo-induced Dynamics in Quantum Materials using Femtosecond Time-resolved X-ray Scattering, *Wei-Sheng Lee*, SLAC National Accelerator Laboratory **INVITED**
It remains a great challenge to characterize and understand photo-induced dynamics in quantum materials when it is driven out-of-equilibrium by ultrafast photon pulses. Time-resolved x-ray scattering, enabled by x-ray free electron laser, can track the time-evolution of the magnetic, charge, and lattice degrees of freedom with femtosecond time resolution, providing new insights into the photo-induced dynamics. In this presentation, I will first highlight photo-induced dynamics of spin and charge orders in striped nickelate. The strong coupling between spin and charge orders still survives, despite that both orders have been strongly suppressed by photo-excitations [1,2]. In addition, by resonantly pumping a bond-stretching phonon using mid-IR pulses, we observed lattice-driven dynamics that is different from hot-electron-driven dynamics induced by optical pumping across the band gap [3]. Then, I will discuss phenomena associated with coherent lattice oscillations by highlighting the measurement of atomic displacement of a coherent A1g mode in an iron-based superconductor $BaFe_2As_2$, which can be correlated with accompanied electronic variations [4]. In particular, a quantitative "lock-in" comparison between electronic band structure obtained by time-resolved ARPES and the measured atomic displacements allows us to directly obtain orbital-specific electron-phonon coupling strength without any prior assumption of the electronic band structures [5]. Finally, I will showcase a proof-of-principle time-resolved RIXS experiment on CDW ordered $1T-TiSe_2$ as an outlook for the future time-resolved x-ray scattering experiment in the next generation x-ray free electron laser, such as the LCLS-II.

1. W. S. Lee et al.. Phase fluctuations and the absence of topological defects in photo-excited charge ordered nickelate. Nature Communications 3, 838 (2012).

2. Y. D. Chuang, W. S. Lee et al., Real-Time Manifestation of Strongly Coupled Spin and Charge Order Parameters in Stripe-Ordered La1.75Sr0.25NiO4 Nickelate Crystals Using Time-Resolved Resonant X-Ray Diffraction. Phys. Rev. Lett. 110, 127404 (2013).

3. W. S. Lee et al., Non-equilibrium Lattice-driven Dynamics of Stripes in Nickelates using Time-Resolved X-ray Scattering. Phys. Rev. B 95, 121105(R) (2017).

4. S. Gerber, et al., Direct characterization of photo-induced lattice dynamics in BaFe2As2. Nature Communication 6, 7377 (2015).

5. S. Gerber, S.-L. Yang et al., Femtosecond electron-phonon lock-in via photoemission and x-ray free-electron laser. Science 357, 71 (2017).

11:40am SA+MI-ThM-12 HAXPES Lab- A Home Lab System for HAXPES Measurements, *S Eriksson*, Scienta Omicron; *Anna Regoutz*, Imperial College London, UK
During the past decade, increased attention has been shown to hard X-rays in the photoelectron spectroscopy field. This is mainly due to the increased information depth enabled by the higher photon energies. Such bulk sensitive measurements could previously only be performed at dedicated synchrotron radiation facilities. The beam lines providing this type of radiation are heavily booked, so access to the experimental setups is thus limited. Higher excitation energies also enables bulk sensitive measurements of deep core levels not accessible with standard XPS.

Here we present a newproduct featuring a monochromized X-ray source giving out Ga Ka radiation at 9.25keV and a wide acceptance angle hemispherical electron analyzer, both combined on a simple to use vacuum system. The base system can easily be customized by adding separate modules such as a MBE- or preparation chamber or a glove box. With this system, a new set of possible experiments opens up in the home laboratory: investigations of buried interfaces, in operando devices, real world samples, etc.

The X-ray source consists of a MetalJet X-ray tube and the electrons which are accelerated into this jet generate an intense Ga Ka radiation. These X-rays are monochromized using a newly developed monochromator. The small spot size of 20 μm provided by the liquid jet source is maintained throughout the passing of the monochromator and only slightly broadened to about 50μm. In order to allow for easy adjustment of the X-ray focal point relative to the electron analyzer, the entire assembly of monochromator and source can be moved down to a precision of a few micrometers. The hemispherical electron analyzer is configured for high kinetic energies allowing for detection of the full energy range the source provides and a large acceptance angle of +/- 30 degrees. The overall system resolution is shown to be <0.5 eV.

We present data taken from polycrystalline gold and silicon wafers with a surface layer of silicon dioxide with a controlled thickness as well as transistor stacks and energy related materials.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 202A - Session SA+AS+HC+SS-ThA

IoT Session: Multi-modal Characterization of Energy Materials & Device Processing

Moderators: Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy, Slavomir Nemsak, Advanced Light Source, Lawrence Berkeley National Laboratory

2:20pm **SA+AS+HC+SS-ThA-1 Revealing Structure-Function Correlations in Fuel-Cells and Batteries.**, *Klaus Attenkofer, E Stavitski, M Liu, D Lu, M Topsakal, D Stacchiola, M Hybertsen,* Brookhaven National Laboratory **INVITED**

To reveal the structure and even more important, the structure-function correlation of materials are essential prerequisites to the optimization and rational design of materials in energy storage and conversion applications. The complex processes resulting in the function typically involve not only the initial chemical reaction but a wide range of reorganizations, phase transitions, and transport phenomena which finally determine the efficiency of the material and its reliability in applications. The characterization challenge of visualizing changes on multiple length scales of ordered and disordered materials is one aspect of the characterization problem; to correlate the identified changes with the function of the material and distinguish the essential changes from other non-correlated alternation is the second equally important task.

In the talk we will show on various examples from the field of fuel cells and batteries, how high throughput hard X-ray spectroscopy can be combined with data analytics and theory to reveal the atomic structure of the ordered and disordered materials. In a next step a true imaging tool like transmission electron microscopy is used to verify this structure. The high throughput aspect of this approach provides not only a new opportunity to use database approaches to guarantee an unbiased method for the structure identification and optimization with a "field of view" in the nanometer range but also provides a new strategy to use data analytics, especially data mining approaches, to establish the structure-function correlation. The combination of ex-situ and operando experiments provides a statistical relevant data quantity and a diversity of the data necessary to this approach and is minimizing at the same time challenges caused by sample damage.

3:00pm **SA+AS+HC+SS-ThA-3 Soft X-ray Spectroscopy for High Pressure Liquid**, *Ruimin Qiao, J Guo, W Chao,* Lawrence Berkeley National Laboratory **INVITED**

Soft X-ray spectroscopy (~50-1500eV), including both X-ray absorption and emission, is a powerful tool to study the electronic structure of various energy materials. Its energy range covers the K-edge of low-Z elements (e.g. C, N, O and F) and the L-edge of transition metal. Important information such as chemical valence, charge transfer and different ligand field could be directly extracted from the spectra. However, its application has been largely limited in materials that could be placed in vacuum (such as solid, below-ambient-pressure gas and liquid) because of the short penetration depth of soft x-ray. In this presentation, I will talk about the recent development of soft x-ray spectroscopy for high pressure liquid(up to 400 bars) at Advanced Light Source in Lawrence Berkeley National Lab.

4:00pm **SA+AS+HC+SS-ThA-6 Surface Action Spectroscopy Using FHI FEL Infrared Radiation**, *Zongfang Wu, H Kuhlenbeck, W Schöllkopf, H Freund,* Fritz-Haber Institute of the Max Planck Society, Germany

In model catalysis and general surface science studies, the vibrational characterization of a surface is usually performed with HREELS (high-resolution electron energy loss spectroscopy) or IRAS (infrared reflection absorption spectroscopy). Both methods have disadvantages: HREELS suffers from its low resolution and (in the case of ionic samples) the presence of intense multiple phonon losses, while IRAS requires normalization of the spectrum with the spectrum of a reference sample, which leads to a contamination of the spectrum with features of the reference sample. Action spectroscopy with rare-gas messenger atoms [A. Fielicke et al., Phys. Rev. Lett. 93, 023401 (2004)] is an established method for vibrational spectroscopy of gas-phase clusters that avoids these disadvantages. Rare-gas atoms attached to gas-phase clusters may desorb when the incident infrared (IR) radiation is in resonance with a cluster vibration. The fragmentation rate, as monitored with a mass spectrometer, represents a vibrational spectrum, which can be used to draw conclusions

regarding the cluster structure. Clusters, in this case deposited on a surface, are also highly relevant in model catalysis since they greatly influence catalytic reaction paths of supported catalysts. Both cluster shape and size matter. With this topic in mind a new apparatus for the application of IR FEL radiation to action spectroscopy of solid surfaces was set up at the Fritz Haber Institute (FHI), the $V_2O_3(0001)/Au(111)$ (~10 nm thick) and a $TiO_2(110)$ single crystal surface were studied as first test systems. The machine is connected to the FHI FEL, which is able to provide intense and widely tunable (3 – 60 μm) IR radiation. For $V_2O_3(0001)/Au(111)$ the well-characterized vanadyl surface vibration and other surface vibrations could be detected, while bulk states turned out to be invisible to the method. Presumably, anharmonic vibrational coupling between the primary excited vibration and the rare-gas vs. surface vibration leads to desorption. This explains the surface sensitivity of the method as well as its insensitivity to bulk vibrations. In the case of the $TiO_2(110)$ single crystal also rare-gas desorption resulting from an IR induced increase of the crystal temperature could be observed. This led to a better understanding of polaritons in rutile.

4:20pm **SA+AS+HC+SS-ThA-7 Spectroscopic Insight into Resistive Switching Processes in Oxides**, *C Baeumer, C Schmitz,* Forschungszentrum Juelich GmbH, Germany*; A Kindsmüller,* RWTH Aachen University, Germany*; N Raab, V Feyer, D Mueller, J Hackl, S Nemsak,* Forschungszentrum Juelich GmbH, Germany*; O Mentes, A Locatelli,* Elettra-Sincrotrone Trieste, Italy*; R Waser, R Dittmann,* **Claus Michael Schneider**, Forschungszentrum Juelich GmbH, Germany

Nonvolatile memories play an increasing role in modern nanoelectronics. Among the various storage concepts, resistive switching promises a high scalability. In oxides, the physical mechanism behind resistive switching involves electrically controlled local redox processes, which result in the formation and migration of oxygen vacancies. We studied these redox processes and their influence on the resistive switching in the model systems $SrTiO_3$(STO) and $ZrO_2$with a full suite of synchrotron-radiation based spectroscopy techniques. The resistive switching in STO proceeds via the growth of nanoscale conductive filaments, which poses considerable challenges to the spectroscopic characterization. Employing nanospectroscopy in an *operando* configuration we could unanimously relate the conductivity changes between the ON (low resistance) and OFF states (high resistance) to the redox-induced changes of the valencies and the formation of oxygen vacancies [1,2]. The retention time of the ON state in STO is determined by a reoxidation of the previously oxygen-deficient region and can be controlled by inserting an oxygen diffusion barrier. With respect to the reproducibility of the switching process, we find that the individual switching event is governed by a competition within a network of subfilaments, which has been created in the initial forming step. Upon resistive switching, one of these subfilaments becomes the current-carrying filament. However, during repeated switching the different subfilaments may become active, resulting in a cycle-to-cycle variation of the location and shape of the current-carrying filament, which determines the low-resistance state [3].

[1] C. Baeumer, C. Schmitz, A. Marchewka, D. N. Mueller, R. Valenta, J. Hackl, N. Raab, S. P. Rogers, M. I. Khan, S. Nemsak, M. Shim, S. Menzel, C. M. Schneider, R. Waser and R. Dittmann, Nat Commun **7** (2016) 12398.

[2] A. Kindsmüller, C. Schmitz, C. Wiemann, K. Skaja, D. J. Wouters, R. Waser, C. M. Schneider and R. Dittmann, APL Materials **6** (2018) 046106.

[3] C. Baeumer, R. Valenta, C. Schmitz, A. Locatelli, T. O. Mentes, S. P. Rogers, A. Sala, N. Raab, S. Nemsak, M. Shim, C. M. Schneider, S. Menzel, R. Waser and R. Dittmann, ACS Nano **11** (2017) 692.

4:40pm **SA+AS+HC+SS-ThA-8 Visualizing Electronic Structures of Topological Quantum Materials by Synchrotron Based Photoemission Spectroscopy**, *Yulin Chen,* Oxford University, UK **INVITED**

The electronic structure of matter is critical information that determine its electric, magnetic and optical properties. The precise understanding of such information will not only help understand the rich properties and physical phenomena of quantum materials, but also guide the design of their potential applications.

Angle-resolved photoemission spectroscopy (ARPES) is an effective method in determining the electronic structures of materials: with its energy and momentum resolution, ARPES can directly map out dispersions of electronic bands in the reciprocal space with critical parameters (such as the energy gap and width of bands, carrier type, density and the Fermi-velocity, etc.).

In this talk, I will first give a brief introduction to this powerful experimental technique, its basic principle and the rich information it can yield by using synchrotron radiation light source, then focus on its recent application to topological quantum materials (including some of our works on topological insulators, Dirac and Weyl semimetals [1]). Finally, I will review the recent development in ARPES and give a perspective on its future directions and applications.

[1] Science, 325, 178 (2009), Science, 329, 659 (2010), Nature Nanotechnology, 6, 705 (2011), Nature Chemistry, 4, 281 (2012), Nature Physics, 9, 704 (2013), Science, 343, 864 (2014), Nature Materials, 13, 677 (2014), Nature Physics, 11, 728 (2015), Nature Materials, 15, 27(2016), Nature Communications 7, 12924 (2016), Nature Communications, 8, 13973 (2017).

5:20pm **SA+AS+HC+SS-ThA-10 Electronic Structure of FeO, γ-Fe$_2$O$_3$ and Fe$_3$O$_4$ Epitaxial Films using High-energy Spectroscopies**, *German Rafael Castro,* Spanich CRG BM25-SpLine Beamline at the ESRF,, France*; J Rubio Zuazo,* Spanish CRG BM25-SpLine at the ESRF, France*; A Chainani,* Condensed Matter Physics Group, NSRRC, Taiwan, Republic of China*; M Taguchi,* RIKEN SPring-8 centre, Japan*; D Malterre,* Institut Jean Lamour, Universite de Lorraine, France*; A Serrano Rubio,* Spanich CRG BM25-SpLine Beamline at the ESRF, France

Today, one of the materials science goals is the production of novel materials with specific and controlled properties. Material composites, which combine different materials, with specific and defined properties, mostly of multilayer thin films, are a promising way to create products with specific properties, and, in general different of those of the constituents. The chemical, mechanical, electric and magnetic properties of such materials are often intimately related to their structure, composition profile and morphology. Thus, it is crucial to yield with an experimental set-up capable to investigate different aspects related with the electronic and geometric structure under identical experimental conditions, and, in particular, to differentiate between surface and bulk properties. There are few techniques able to provide an accurate insight of what is happening at these interfaces, which in general are buried by several tens of nanometres inside the material. The Spline beamline Branch B at the ESRF, the European Synchrotron, offers unique capabilities in this respect.

In this contribution we will present the study of the electronic structure of well-characterized epitaxial films of FeO (wustite), γ-Fe$_2$O$_3$ (maghemite) and Fe$_3$O$_4$ (magnetite) using Hard X-ray Photoelectron Spectroscopy (HAXPES), X-ray Absorption Near Edge spectroscopy (XANES) and electron energy loss spectroscopy (EELS). We carry out HAXPES with incident photon energies of 12 and 15 keV in order to probe the bulk-sensitive Fe 1s and Fe 2p core level spectra. Fe K-edge XANES is used to characterize and confirm the Fe valence states of FeO, γ-Fe$_2$O$_3$ and Fe$_3$O$_4$ films. EELS is used to identify the bulk plasmon loss features. A comparison of the HAXPES results with model calculations for an MO6 cluster provides us with microscopic electronic structure parameters such as the on-site Coulomb energy U_{dd}, the charge-transfer energy Δ, and the metal-ligand hybridization strength V. The results also provide estimates for the ground state and final state contributions in terms of the d^n, $d^{n+1}L1$ and $d^{n+2}L2$ configurations. Both FeO and γ-Fe2O3 can be described as charge-transfer insulators in the Zaanen-Sawatzky-Allen picture with $U_{dd} > \Delta$, consistent with earlier works. However, the MO6 cluster calculations do not reproduce an extra satellite observed in Fe 1s spectra of γ-Fe$_2$O$_3$ and Fe$_3$O$_4$. Based on simplified calculations using an M2O7 cluster with renormalized parameters, it is suggested that non-local screening plays an important role in explaining the two satellites observed in the Fe 1s core level HAXPES spectra of γ-Fe$_2$O$_3$ and Fe$_3$O$_4$.

5:40pm **SA+AS+HC+SS-ThA-11 Single-Bunch Imaging of Detonation Fronts Using Scattered Synchrotron Radiation**, *M Nielsen, J Hammons, M Bagge-Hansen, L Lauderbach, R Hodgin, K Champley, W Shaw,* Lawrence Livermore National Laboratory*; N Sinclair,* Washington State University*; Trevor Willey,* Lawrence Livermore National Laboratory

Radiographic imaging using a series of single pulses from synchrotron storage rings or x-ray free-electron lasers gives new insight into dynamic phenomena. One limitation of these sources is that the native and natural beam size at most end-station hutches is, at best, of mm-scale dimensions. Here, we describe a method for collecting full-field, radiographic images of cm-scale phenomena using focused pink-beam and scattering the x-rays, effectively creating point-source images. Although currently photon starved and highly dependent on parameters chosen (such as source-to-object and source-to-detector distances, scattering material, etc.) we are continuously improving the technique. At the Dynamic Compression Sector at the Advanced Photon Source, we use this capability to image detonation phenomena, particularly direct imaging of detonator performance, imaging initiation and run-up to detonation, imaging differences in ideal vs. non-ideal explosives, and have a goal to determining density during detonation at 10's of microns in resolution. In this presentation, we summarize our progress developing and using this technique in creating movies of dynamic phenomena as fast as 153.4 ns between frames, and as a method for imaging samples prior to, for example, collecting dynamic small-angle x-ray scattering or diffraction to observe nanodiamond growth kinetics and composition evolution during detonation.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room Hall B - Session SA-ThP

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic Poster Session

SA-ThP-1 Relative Sensitivity Factors in Hard X-ray Photoelectron Spectroscopy up to 10 keV for Quantitative Analysis, *Satoshi Yasuno*, Japan Synchrotron Radiation Research Institute, Japan*; N Ikeno,* Aichi Synchrotron Radiation Center, Japan*; H Oji,* Nagoya University Synchrotron Radiation Research Center, Japan

Hard X-ray photoelectron spectroscopy (HAXPES) has been attracting considerable attention since it can probe the chemical and electronic states of the bulk and buried interface lying at depths of several tens of nm due to its large probing depth.[1] In the last decade, HAXPES have been applied to various research fields, such as electronic devices, organic materials, and rechargeable batteries. However, the quantitative analysis of the HAXPES measurement related to the relative sensitivity factors(RSFs), standard materials and theoretical calculations in hard X-ray region, have not previously been reported in detail. Therefore, in this study, we investigated the procedures of quantitative analysis for HAXPES and development of the RSFs data base in the hard X-ray region. Here, we focused the database of the RSFs of compounds provided by Wagner.[2] According to Wagner's RSFs principle, the absolute value of the sensitivity factor will vary with the matrix because of the variability of the mean free path λ, by contrast the relative sensitivity factor will hardly vary because the ratio λ_1/λ_2 for element 1 and 2, is only slightly with matrix dependence. Therefore, with the RSFs of compounds, the corrections related to the mean free path which largely influenced the number of photoelectron (signal intensity) are not needed for the quantitative analysis. For HAXPES, the core level peaks can be measured in a wide kinetic energy. Thus, it is suggested that the RSFs obtained by the compound is suitable for HAXPES measurement. In this study, the empirical sensitivity factors for the 1s, 2s, $2p_{3/2}$, $3d_{5/2}$ and 4f levels relative to O 1s were derived from HAXPES measurements with the photon energy of 6, 8, 10 keV. Comparing with the theoretical RSFs calculated from Hartee-Slater cross sections reported by Scofield with combined energy dependence on the spectrometer function and the inelastic mean free path, the good agreement between the empirical and the theoretical RSF values were observed with several notable exceptions, while the discrepancies were observed in several energy regions.

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SA-ThP-2 In Situ Characterization of Freeze-Cast Metal Nanowire Aerogels, *Tyler Fears*, J Hammons, F Qian, T Braun, A Troksa, M Nielsen, J Forien, T Baumann, Y Han, S Kucheyev, M Bagge-Hansen, Lawrence Livermore National Laboratory

Metal nanowire aerogels are a new class of nanoporous materials desirable for a number of applications in energy storage, generation, and utilization. These materials are made by freezing suspensions of high-aspect-ratio (a ≈ 1000) metal nanowires and gently removing the solidified matrix, e.g., via freeze-drying, to prevent collapse of the porous nanowire network. As such, the porosity in the final aerogel is intrinsically linked to solvent phase separation and crystallization during freezing which is highly sensitive to the conditions under which it takes place, e.g., temperature, solvent composition, and sample geometry.

Herein will be discussed recent developments at Lawrence Livermore National Laboratory to produce high-quality ultra-low-density (1-30 mg/cm³) metal aerogels via a facile freeze-casting approach. Due to the hierarchical structure of the aerogels (1-100 μm micropores in a nanoporous matrix of 3-30 nm diameter nanowires) it was necessary to use a wide variety of complementary in situ/ex situ analysis techniques to ascertain the structure and origin of these hierarchical features. This presentation will discuss the unique properties of these aerogels and the advanced analysis techniques used in their characterization, e.g., USAXS/SAXS/WAXS, X-ray tomography, XPS, optical microscopy, and electron microscopy. This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

SA-ThP-3 In situ Probing of the Potential Distribution in a Thin Film All-solid-state Li-ion Battery, *Evgheni Strelcov,* National Institute of Standards and Technology (NIST)/University of Maryland*; E Fuller,* Sandia National Laboratories*; W McGehee, N Zhitenev, J McClelland,* National Institute of Standards and Technology (NIST)*; A Talin,* Sandia National Laboratories

The next generation of portable electronic devices, electric vehicles, power grids, and robots require safer, smaller, lighter, cheaper, and more stable batteries. Of special importance are all-solid-state power sources that do not use conventional, flammable electrolytes and are intrinsically safer. Rational design of such batteries is challenging without in-depth understanding of the chemical and physical processes in electrochemical cells at the microscopic, nanoscopic, and eventually, atomic levels. Particularly important structural elements of solid-state Li-ion batteries (SSLIBs) that control the overall device performance are the interfaces that form between the electrodes and the cathode/anode materials and solid electrolyte. Despite decades of studies with classical electrochemical techniques, spectroscopic and microscopic tools, the interfacial characteristics of batteries, including the origins of high impedance often observed at solid state interfaces, are still poorly understood. Here, we employ in situ Kelvin Probe Force Microscopy (KPFM) to probe the potential distribution in a SSLIB as a function of its charge state. The battery was fabricated by sequentially depositing thin layers of Pt (110-130 nm), $LiCoO_2$ (280-420 nm), LIPON (1100-1200 nm), Si (50-240 nm) Cu or Pt (150-200 nm) onto a Si/SiO_2 wafer (oxide thickness 100 nm). The fabricated battery was cleaved in an Ar atmosphere to expose the stacked layers, mounted on a holder, wired, and safely transferred without exposing to air into a dual-beam instrument that combines a scanning electron microscope (SEM), a Ga-ion focused ion beam (FIB) and an atomic force microscope (AFM) in one vacuum chamber (residual pressure of 10^{-4} Pa). The stacked battery was milled to expose a cross-section of the layers, and imaged using SEM and KPFM, while cycling the battery. The acquired potential maps reveal a highly non-uniform interelectrode potential distribution, with most of the potential drop occurring at the electrolyte-Si anode interface in the pristine battery. During the first charge, the potential distribution gradually changes, revealing complex polarization within the LIPON layer due to Li-ion redistribution. The acquired data shed light onto the interfacial Li-ion transport in SSLIBs and its reversibility.

SA-ThP-4 A New Route for the Determination of Protein Structure in Physiological Environment through Coherent Diffraction Imaging., *Danny Fainozzi*, university of Trieste / Elettra Synchrotron, Italy

Revealing the structure of complex biological macromolecules, such as proteins, is an essential step for understanding the chemical mechanisms that determine the diversity of their functions. Synchrotron based x-ray crystallography and cryo-electron microscopy have made major contributions in determining thousands of protein structures even from micro-sized crystals. They suffer from some limitations that have not been overcome, such as radiation damage, the natural inability to crystallize of a number of proteins and experimental conditions for structure determination that are incompatible with the physiological environment. Today the ultrashort and ultra-bright pulses of X-ray free-electron lasers (XFELs) have made attainable the dream to determine protein structure before radiation damage starts to destroy the samples. However, the signal-to-noise ratio remains a great challenge to obtain usable diffraction patterns from a single protein molecule. We describe here a new methodology that should overcome the signal and protein crystallization limits. Using a multidisciplinary approach, we propose to create a two dimensional protein array with defined orientation attached on a self-assembled-monolayer . We develop a literature-based, flexible toolbox capable of assembling different proteins on a functionalized surface while keeping them under physiological conditions during the experiment, using a water-confining graphene cover.

SA-ThP-5 The League of European Accelerator-Based Photon Sources: New strategic partnerships in Europe and beyond, *Maya Kiskinova*, Elettra-Sincrotrone Trieste, Italy

The grand challenges of our century to evolve from extensive wasteful development to sustainable economies is full understanding of the mechanisms which control the behavior of complex natural and man-made systems. This can be attained only through development of an integrated multidisciplinary approach. Many of the breakthroughs in investigations of a broad range of complex functional material systems have been made using the state-of-the art experimental techniques undergoing continuous developments at the synchrotron and free electron laser large scale facilities.

Recognizing the leading roles of these large scale research centers in paving the road to discoveries and further technological advancements, the recently established new research consortium in Europe called "*The League of European Accelerator-Based Photon Sources (LEAPS)"* is aiming at reaching a new level of cooperation, coordination and integration to better cope with cross-cutting scientific and technological challenges for knowledge-based design of advanced materials and better drugs. The poster will present an overview of the LEAPS strategy, goals and expected impacts in science and innovation.

Actinides and Rare Earths Focus Topic
Room 202C - Session AC+MI+SA-FrM

Actinide and Rare Earth Theory and Related Measurements

Moderators: Paul S. Bagus, University of North Texas, David Shuh, Lawrence Berkeley National Laboratory

8:20am AC+MI+SA-FrM-1 Periodic Boundary Condition and Embedded Cluster DFT Calculations of Water Adsorption on AnO₂ (An = U, Pu) Surfaces, *Nikolas Kaltsoyannis,* University of Manchester, UK, United Kingdom of Great Britain and Northern Ireland **INVITED**

Over half of the World's stockpile of civil plutonium (c. 126 tonnes) is stored at Sellafield in the UK as PuO_2 powder in sealed steel cans. There is evidence of gas generation in some of these cans. Many routes to gas production have been suggested, several of which involve complex, inter-connected and poorly understood PuO_2/H_2O interactions.

We have an ongoing project to study computationally the interaction of AnO_2 (An = U, Pu) surfaces with water. Standard periodic boundary condition (PBC) implementations of DFT using generalized gradient approximation (GGA) functionals can fail to reproduce key features of actinide solids, *e.g.* predicting metallic properties in systems known to be insulating. This failure stems from incorrect description of the strongly correlated 5f electrons, which are overly delocalized by the GGA, and the standard solution to this problem is to correct the GGA functionals with an onsite Coulomb repulsion term known as the Hubbard U. An alternative solution is to employ hybrid DFT, in which some of the exact exchange energy of Hartree–Fock theory is incorporated into the Hamiltonian. Such functionals typically produce more localized 5f electrons, and recover insulator behavior. They are, however, extremely expensive to employ in PBC calculations, and hence are rarely used. We have therefore sought a model which allows the routine use of hybrid DFT in AnO_2/water systems, and have adopted the periodic electrostatic embedded cluster method (PEECM), in which a quantum mechanically treated cluster is embedded in an infinite array of point charges. We treat a cluster of AnO_2 and adsorbing water molecules using hybrid DFT (PBE0) whilst the long-range electrostatic interactions with the bulk are modelled *via* embedding in point charges.

In this presentation, I shall describe the results of both PBC and PEECM studies of the interactions of water with both stoichiometric and reduced (oxygen vacancy) {111}, {110} and {100} surfaces of UO_2 and PuO_2. The geometries and energetics of single and multiple layers of water will be presented, together with our calculations of water desorption temperatures, from which we propose an alternative interpretation of experimental data.

[1] J.P.W. Wellington, A. Kerridge, J.P. Austin and N. Kaltsoyannis *J. Nuc. Mat.* **482** (2016) 124

[2] B.E. Tegner, M. Molinari, A. Kerridge, S.C. Parker and N.Kaltsoyannis *J. Phys. Chem. C* **121** (2017) 1675

9:00am AC+MI+SA-FrM-3 Understanding the Role of Oxidation States on the Chemistry of Actinides through Integration of Theory and Experiment, *Wibe de Jong, J Gibson,* Lawrence Berkeley National Laboratory*; R Abergel,* Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

Fundamental insights into the role of 5f electrons in the redox chemistry of actinides is essential for predicting the fate and controlling the behaviour of nuclear materials in the ecosystem, as well as for developing new advanced applications in energy, medicine and forensics. In recent years computational chemistry has become a key pillar of multidisciplinary actinide research, advancing the fundamental understanding of actinide chemistry through strong synergies between experiment and simulations. We will present some recent multidisciplinary gas-phase thermochemistry and spectroscopy efforts focused on understanding the role of metal-ligand interactions on the oxidation states of actinides across the series.

9:40am AC+MI+SA-FrM-5 An Experimentalist's Viewpoint: The Tremendous Strengths and Occasional Weaknesses of Actinide Cluster Calculations, *James G. Tobin,* University of Wisconsin-Oshkosh

Over the course of the last several years, cluster calculations have been used in a myriad of ways to analyze spectroscopic results from actinide systems and gain insight into the electronic structure of these actinide systems. For example, the calculated 6d Unoccupied Density of States (UDOS) in Uranium Tetrafluoride and Uranium Diode were probed using U L3 (2p) X-ray Absorption Near Edge Structure (XANES) as well as U N7 (4d) X-ray Absorption Spectroscopy (XAS). [1-3] Cluster calculations have also been used successfully to study the development from atomic to bulk electronic structure in Pu [4,5] and issues associated with the 2p Occupied Density of States (ODOS) in Uranium Tetrafluoride. [6, 7] However, there now appear to be some interesting discrepancies between what has been observed experimentally and the predictions of cluster theory. In particular, the F 1s XAS of Uranium Tetrafluoride [8] and the U 4d XAS branching ratio (BR) predictions for oxidized uranium. [1] These issues will be addressed in the talk.

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[6] J.G. Tobin, S.-W. Yu, R. Qiao, W.L. Yang, and D.K. Shuh, "F1s X-ray Emission Spectroscopy of UF4," Progress in Nuclear Science and Technology, submitted 2017.

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10:00am AC+MI+SA-FrM-6 Ligand and Metal XAS Edges In Heavy Metal Compounds, *Paul S. Bagus,* University of North Texas*; C Nelin,* Consultant

In previous work, [1] it has been shown that the magnitude and character of the covalent mixing in representative lanthanide and actinide oxides depends strongly on the nominal oxidation state of the oxide. In the present work, ab initio theoretical wavefunctions, WF, have been determined and have been used to obtain the energies and dipole intensities for different Near Edge X-Ray Absorption (XAS) Fine Structure, NEXAFS edges. The theoretical NEXAFS spectra have been examined in order to determine the extent to which the features of these edges can be used to infer the character and extent of the covalent bonding. An important and novel feature of the theory is that the angular momentum coupling of the open shell electrons is taken into account and the multiplets, both resolved and unresolved, associated with the various NEXAFS features are identified. Furthermore, different sets of variationally optimized orbitals are used for the initial, ground state, and the final, excited state, configurations. Thus, the relaxation and screening in response to the core-hole are taken into account. The systems examined are Ce(III) and Ce(IV) in CeO_2 and U(IV), U((V), and U(VI) in UO_x. For these systems, cation p and d edges are used to distinguish excitations to the frontier nf and (n+1)d orbitals, especially since it has been shown that both of these cation orbitals have significant covalent mixing with the ligands. The O K-edge NEXAFS is presented and the relative excitation energies and intensities into the cation nf and (n+1)d orbitals are compared to the covalent character of the different systems. The WFs are solutions of the Dirac-Coulomb Hamiltonian. [2] Comparisons are made with experiment to demonstrate the accuracy of the theoretical treatments used.

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10:20am AC+MI+SA-FrM-7 Thermal Expansion and Conductivity of Th and Ac from First Principles Calculations, *Dominik Legut, L Kyvala,* VSB-Technical University of Ostrava, Czech Republic*; U Wdowik,* Pedagogical University, Poland

We investigate electronic structure, lattice dynamics, and thermophysical properties of elemental thorium and made a prediction for actinium as

here the experimental data are scare. The results were obtained within density function calculations. Recently, Actinium (Ac) shows excellent potential in radiotherapy and Thorium (Th) appears to be a suitable substitution for uranium in novel nuclear fuels. Therefore, we determined the effect of spin-orbit interaction (SOI) for the electronic, elastic, phonon and thermodynamic properties of number of Ac phases (hcp, bcc, fcc, and sc). Similarly, in the case of Th in addition to SOI we investigated also localized versus itinerant behavior of the f electrons. Therefore we applied so-called Hubbard parameter U in the range of 0.5-2 eV for the Th 5f electrons. Next, we calculated the elastic tensor by the linear-response method as implemented in VASP code [1] to determine elastic constants (C_{ij}). Subsequently, the criteria of stability based on C_{ij} were evaluated. Next, we calculated vibrational properties using the direct force-constant method as implemented in the PHONOPY code [2]. Actinium phase transition is discussed within the quasi-harmonic approximation under temperature and pressure to draw different conclusion than in Ref. [3]. We advance our knowledge to predict the thermal conductivity Using the Boltzman transport code [4] we address contribution to the thermal conductivity not only from phonons but also from free electrons. Our determined mechanical and thermodynamical properties of Th show very good agreement with experimental data and give us a high confidence to be able to predict similar properties of Ac and to explain the highest know thermal conductivity of Th among actinides.

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Acknowledgement

10:40am AC+MI+SA-FrM-8 XANES Investigation into the Electronic Structure of Ce Coordination Complexes, *Liane Moreau, C Booth,* Lawrence Berkeley National Laboratory; *Y Qiao, E Schelter,* University of Pennsylvania

Cerium is of particular interest among the lanthanide elements for its stability in both the Ce(III) and Ce(IV) oxidation states. This provides unique redox properties, making Ce a promising candidate for advanced energy materials. To this end, chemistries to control the Ce oxidation state have been widely developed. More interestingly, Ce-ligand bonding has in some cases shown intermediate behavior between Ce(III) and Ce(IV), which is indicative of a multiconfigurational ground state. This phenomenon results in low-energy ligand-to-metal charge transfer in addition to its magnetic behavior, such as temperature independent paramagnetism. In order to understand the effects of Ce electronic structure on compound chemical and physical properties, it is imperative to develop methods to accurately probe the fractional occupancy between $4f^1$ and $4f^0$ configurations.

Ce L_3 edge X-ray absorption near edge structure (XANES) measurements provide detailed information concerning the density of states from varying Ce-ligand bonding configurations. In particular, XANES spectra of Ce(IV) imido, Ce(III/IV) guanidinate-amide and Ce(IV) anilide complexes are presented and related to their specific coordination chemistry. From XANES, lanthanide-ligand bonding covalency is explored. We also consider the effects of varying the alkali metal species in metal-capped Ce(IV) imido. Results from the Ce(IV) complexes exhibit characteristic double white line absorption, indicative of significant 4f orbital participation in metal-ligand bonding. The extent to which covalency is observed is highly dependent on the specific ligand chemistry. In combination with DFT and magnetism results, XANES is used to study the effects of such chemistries on the orbital configurations and relate them to the observed novel properties of Ce coordination complexes.

11:00am AC+MI+SA-FrM-9 Structure and Properties of Reactively Deposited Uranium Hydride Coatings Studied by the X-ray Scattering Methods, *Milan Dopita,* L Havela, L Horák, E Chitrova, Charles University, Prague, Czech Republic; *D Legut,* VSB-Technical University of Ostrava, Czech Republic; *M Cieslar,* Charles University, Prague, Czech Republic; *Z Matěj,* MAX-IV, Lund, Sweden

A series of Uranium hydride coatings was prepared using a reactive sputtering method. The samples were sputtered with different Mo doping levels as well as at different hydrogen pressure and various substrate temperature. Fused silica and Si single-crystals were used as substrates for deposited coatings. The structure and the real structure (i.e. the deviations of the structure from the ideal 3D crystal periodicity) of the samples were investigated using the x-ray scattering methods. The x-ray reflectivity yielded the information on the coatings thickness, roughness and electron density. The key results of our work were the determination of the phase composition and its evolution, the description of the coherently diffracting domains - crystallite size and defects distributions, the description of the residual stress, strains and preferred orientation of crystallites - textures and its depth profiles in the coatings.

The sample sputtered on the fused silica substrates crystallized in the β-UH_3 structure (stable uranium hydride phase) with the stress free lattice parameter a = 0.6703 ± 0.0004 nm. The coating exhibited strong *00l* preferred orientation of crystallites and compressive residual stress σ = -5.1 ± 0.1 GPa. Additionally, the coating revealed a bimodal distribution of crystallite sizes with two components having the mean crystallite size D_1 = 200 nm and D_2 = 3.6 nm with volume fractions of 60:40, respectively, and huge microstrain in both components. Contrary, the coating sputtered on cooled Si single-crystal substrate showed totally different behavior. It did not form nor the stable β-UH_3 neither the meta-stable α-UH_3 structure. The measured diffraction pattern revealed the fluorite fcc structure, analogous to e.g. PuH_2. This is highly interesting result, since to our best knowledge such form of uranium hydride has not been so far reported in the literature. The polycrystalline coating exhibited tilted *hhh* texture, stress free lattice parameter a = 0.53598 ± 0.00014 nm, compressive residual stress σ = -1.54 ± 0.09 GPa and mean crystallite size of 82 nm. Besides, the coating contains pronounced microstrain caused by the crystal lattice defects and significant fraction of the stacking faults. The results of the x-ray scattering studies were correlated with data obtained from HRTEM. Additionally, the possibility of formation of uranium hydride with fcc fluorite structure was confirmed by the ab-initio theoretical calculations (LDA+U).

11:20am AC+MI+SA-FrM-10 Ligand Induced Shape Transformation of Thorium Dioxide Nanocrystals, *Gaoxue Wang, E Batista, P Yang,* Los Alamos National Laboratory

Nanocrystals (NCs) with size and shape dependent properties are a thriving research field. Remarkable progress has been made in the controlled synthesis of NCs of stable elements in the past two decades; however, the knowledge of the NCs of actinide compounds has been considerably limited due the difficulties in handling them both experimentally and theoretically. Actinide compounds, especially actinide oxides, play a critical role in many stages of the nuclear fuel cycle. Recently, a non-aqueous surfactant assisted approach has been developed for the synthesis of actinide oxide NCs with different morphologies, but an understanding of its control factors is still missing to date. Herein we present a comprehensive study on the low index surfaces of thorium dioxide (ThO_2) and their interactions with relevant surfactant ligands using density functional calculations. A systematic picture on the thermodynamic stability of ThO_2 NCs of different sizes and shapes is obtained employing empirical models based on the calculated surface energies. It is found that bare ThO_2 NCs prefer the octahedral shape terminated by (111) surfaces. Oleic acid displays selective adsorption on the (110) surface, leading to the shape transformation from octahedrons to nanorods. Other ligands such as acetylacetone, oleylamine, and trioctylphosphine oxide do not modify the equilibrium shape of ThO_2 NCs. This work provides atomic level insights into the anisotropic growth of ThO_2 NCs that was recently observed in experiments, and thus may contribute to the controlled synthesis of actinide oxide NCs with well-defined size and shape for future applications.

11:40am AC+MI+SA-FrM-11 Perspectives on the Synthesis, Characterization and Applications of Upconversion and Downconversion Nanomaterials, *Martin Ntwaeaborwa*, University of the Witwatersrand, South Africa

Luminescent nanomaterials incorporating one or more active ions (usually lanthanides) have many uses today in applications such as information displays, light emitting diodes, theft prevention, advertising, medical imaging, photodynamic therapy and photovoltaic cells. In the past few decades, there has been an upsurge of research interest in the synthesis of luminescence down-conversion and up-conversion nanomaterials with different particle morphologies, and their characterization using different optical techniques. The use of lanthanide ions to convert photons either by down-conversion or up-conversion process to different and more useful wavelengths is an interesting research phenomenon for a wide range of applications. For example, the use of down-conversion and up-conversion nanomaterials to improve the power conversion efficiency of crystalline silicon solar cells and for treatment of tumour cells, respectively, have been demonstrated. While efficient down-conversion has been demonstrated from a combination of many rare-earths ions, the most efficient up-conversion has been demonstrated from only a few combination of rare-earths ions such as erbium (Er^{3+}) – ytterbium (Yb^{3+}), thulium (Tm^{3+}) – Yb^{3+}, and holium(Ho^{3+}) – Yb^{3+} incorporated in different host lattices with low phonon energies. Different mechanisms of luminescence down-conversion and up-conversion will be discussed. In addition, a few selected methods used to synthesise luminescence down-conversion and up-conversion nanomaterials will be discussed.

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Rodriguez-Lamas, R: SA+AS+MI-WeA-9, 8
Romero, A: AC+MI+SA-WeM-13, 2
Rubio Zuazo, J: SA+AS+HC+SS-ThA-10, 13
Rueff, J: AS+NS+SA-WeM-2, 3; SA+AS+MI-WeA-9, 8
Rumaiz, A: SA+AS+MI-WeA-12, 8
Rundberg, R: AC+AS+SA-ThM-5, 9
— S —
Samuha, S: AC+AS+SA-ThM-3, 9
Sangely, L: AC+AS+SA-ThM-12, 10
Schelter, E: AC+AS+SA-WeA-1, **6**; AC+MI+SA-FrM-8, 17
Schmitz, C: SA+AS+HC+SS-ThA-7, 12
Schneider, C: SA+AS+HC+SS-ThA-7, **12**; SA+AS+MI-WeA-1, 7
Schöllkopf, W: SA+AS+HC+SS-ThA-6, 12
Schwantes, J: AC+AS+SA-ThM-1, 9
Seehra, M: AC+MI+SA-WeM-13, 2
Seibert, A: AC+MI+SA-WeM-10, 1
Seibert, R: AC+AS+SA-ThM-13, 10
Serrano Rubio, A: SA+AS+HC+SS-ThA-10, 13
Servis, M: AC+AS+SA-ThM-5, 9
Shafer, J: AC+AS+SA-ThM-5, **9**

Shaw, W: SA+AS+HC+SS-ThA-11, 13
Shiwaku, H: AC+AS+SA-WeA-3, 6
Shuh, D: AC+AS+SA-ThM-10, **9**
Simoncig, A: SA+MI-ThM-5, 11
Sinclair, N: SA+AS+HC+SS-ThA-11, 13
Smiles, D: AC+AS+SA-ThM-10, 9
Smith, J: AC+AS+SA-WeA-10, 6
Snow, C: AS+NS+SA-WeM-13, 4
Soltis, J: AC+AS+SA-ThM-1, 9
Stacchiola, D: SA+AS+HC+SS-ThA-1, 12
Stavitski, E: SA+AS+HC+SS-ThA-1, 12
Stein, B: AC+AS+SA-WeA-7, **6**
Sterbinsky, G: SA+AS+MI-WeA-12, 8
Strelcov, E: SA-ThP-3, **14**
Su, J: AC+AS+SA-WeA-1, 6
Sulyok, A: AS+NS+SA-WeM-10, 4
Suzer, S: AS+NS+SA-WeM-11, 4
Suzuki, S: AC+AS+SA-WeA-3, 6
— T —
Taguchi, M: SA+AS+HC+SS-ThA-10, 13
Takagi, Y: SA+AS+MI-WeA-7, **7**
Talin, A: SA-ThP-3, 14
Tereshina-Chitrova, E: AC+MI+SA-WeM-10, 1; AC+MI+SA-WeM-3, **1**
Terry, J: AC+AS+SA-ThM-13, **10**
Tobin, J: AC+MI+SA-FrM-5, **16**
Tokesi, K: AS+NS+SA-WeM-10, 4
Topsakal, M: SA+AS+HC+SS-ThA-1, 12
Tougaard, S: AS+NS+SA-WeM-2, 3
Trappen, R: AC+MI+SA-WeM-13, 2; SA+MI-ThM-2, 10
Troksa, A: SA-ThP-2, 14
Turek, I: AC+MI+SA-WeM-10, 1
Tyliszczak, T: AC+AS+SA-ThM-10, 9
— U —
Ueda, S: AS+NS+SA-WeM-2, 3; SA+AS+MI-WeA-2, **7**; SA+AS+MI-WeA-9, 8
Ulgut, B: AS+NS+SA-WeM-11, 4

— V —
Velasco, C: AS+NS+SA-WeM-6, **3**
Vine, D: AC+AS+SA-ThM-10, 9
— W —
Wang, G: AC+MI+SA-FrM-10, **17**
Warren, M: AC+AS+SA-ThM-13, 10
Waser, R: SA+AS+HC+SS-ThA-7, 12
Wdowik, U: AC+MI+SA-FrM-7, 16
Weiland, C: SA+AS+MI-WeA-12, **8**
Weiss, A: AC+AS+SA-ThM-3, 9
Weisz, D: AC+AS+SA-ThM-12, 10
Willey, T: SA+AS+HC+SS-ThA-11, **13**
Willingham, D: AC+AS+SA-ThM-12, **10**
Winters, C: AS+NS+SA-WeM-13, 4
Woicik, J: SA+AS+MI-WeA-12, 8
Wu, D: AC+AS+SA-ThM-5, 9
Wu, Z: SA+AS+HC+SS-ThA-6, **12**
— X —
Xu, H: AS+NS+SA-WeM-10, 4
— Y —
Yaita, T: AC+AS+SA-WeA-3, **6**
Yamashita, Y: AS+NS+SA-WeM-2, 3; SA+AS+MI-WeA-9, 8
Yang, L: AS+NS+SA-WeM-10, **4**
Yang, P: AC+AS+SA-WeA-1, 6; AC+AS+SA-WeA-7, 6; AC+MI+SA-FrM-10, 17
Yasuno, S: SA-ThP-1, **14**
Yoon, R: AC+AS+SA-WeA-9, 6
Yousefi Sarraf, S: SA+MI-ThM-2, **10**
Yousefi, S: AC+MI+SA-WeM-13, 2
— Z —
Zangrando, M: SA+MI-ThM-5, 11
Zborowski, C: AS+NS+SA-WeM-2, 3
Zhitenev, N: SA-ThP-3, 14