

## Actinides and Rare Earths Focus Topic Room: 22 - Session AC+MI+SA+SU-MoM

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

**Moderator:** Tomasz Durakiewicz, Los Alamos National Laboratory

8:20am **AC+MI+SA+SU-MoM1** **Magnetic and Transport Characteristics in the Uranium Intermetallic Compounds with the HoCoGa<sub>5</sub>-type Structure, Yoshinori Haga**, Japan Atomic Energy Agency, Japan **INVITED**

Physical properties of actinides compounds are mainly dominated by the 5f electrons behavior. The spatial extent of the 5f wave function and resulting hybridization with the neighboring atoms lead to itinerant characters. On the other hand, well isolated 5f electrons carry magnetic moment. Competition between those two characteristics often bring about peculiar electronic properties. Among a series of actinides compounds, so-called 115 compounds crystallizing in the tetragonal HoCoGa<sub>5</sub>-type structure have extensively been studied because of unusual correlated electronic states, including heavy effective mass of conduction electrons, magnetic orderings and heavy fermion superconductivity. Those compounds are also good cases to study electronic transport properties in detail because of availability of extremely high quality samples. Among them, we discuss electronic properties of URhX<sub>5</sub> (X = Ga and In). While URhIn<sub>5</sub> orders antiferromagnetically at fairly high temperature 98 K, isostructural and formally isoelectronic analogue URhGa<sub>5</sub> is a nonmagnetic semimetal [1,2,3]. Detailed transport measurements as well as the de Haas-van Alphen experiment revealed Fermi surface characteristics. We discuss origin of magnetism of uranium 5f electrons and its relationship between superconductivity realized in Pu-analogues.

[1] Y. Matsumoto et al., Phys. Rev. B 88, 045120 (2013).

[2] S. Ikeda et al., Physica B 359-361, 1039 (2005).

[3] Y. Matsumoto et al., JPS Conf. Proc. 3, 011097 (2014).

9:00am **AC+MI+SA+SU-MoM3** **Magnetic Structures of Layered U<sub>n</sub>RhIn<sub>3n+2</sub> Materials, Attila Bartha, M. Klicpera**, Charles University, Prague, Czech Republic, P. Čermák, Forschungszentrum Juelich GmbH, Germany, B. Ouladdiaf, Institut Laue Langevin, France, P. Javorský, J. Custers, Charles University, Prague, Czech Republic

Materials of reduced dimensionality appear in many contemporary fields of research and technology, because they encompass a wide variety of interesting electronic phenomena. For instance carbon can be prepared in 3D (diamond), quasi-2D (graphite), 2D (graphene) or 1D (carbon nanotubes). All of these structures have distinct electronics. Diamond is an insulator. Graphene is semimetal. However, when the dimensionality is increased by putting several graphene layers together (eventually making graphite), the resulting band structure moves to that of a more trivial metal. Another example is high temperature superconductors being quasi-2D materials as well.

The role of dimensionality in *f*-electron systems has been mainly discussed in the context of quantum phase transitions and related phenomena. The series Ce<sub>n</sub>T<sub>m</sub>In<sub>3n+2m</sub> (*n*=1, 2; *m*=0, 1, 2; *T*=transition metal) of layered compounds, which can be viewed as *m* TIn<sub>2</sub>-layers alternating with *n*-layers of CeIn<sub>3</sub> along the *c*-axis, has been extensively investigated. CeIn<sub>3</sub> is cubic (3D) and orders antiferromagnetically (AFM) at *T<sub>N</sub>* = 10.2 K [1] with a propagation vector *k* = (0.5, 0.5, 0.5) [2]. Under hydrostatic pressure superconductivity appears with highest *T<sub>c</sub>* = 0.3 K at *p* = 2.5 GPa. In CeRhIn<sub>5</sub>, the anisotropic crystal structure leads to an incommensurate magnetic structure described with *k* = (0.5, 0.5, 0.297). The AFM order is reduced (*T<sub>N</sub>* = 3.8 K) while superconductivity is supported, *T<sub>c</sub>* increases to 1.9 K at *p* = 1.77 GPa [3-4].

We report on the magnetic structures of URhIn<sub>5</sub> and U<sub>2</sub>RhIn<sub>8</sub>, two new members of this intriguing R<sub>n</sub>T<sub>m</sub>X<sub>3n+2m</sub> (*R*= Lanthanide, Actinide, *X* = In, Ga) family of compounds. Neutron diffraction measurements were performed on structurally well-defined single crystals. Both, URhIn<sub>5</sub> and U<sub>2</sub>RhIn<sub>8</sub>, adopt the tetragonal Ho<sub>n</sub>CoGa<sub>3n+2</sub>-type structure (*P4/mmm*) typical for this group of compounds. URhIn<sub>5</sub> orders antiferromagnetically below *T<sub>N</sub>* = 98 K. The propagation vector equals *k* = (0.5, 0.5, 0.5) and we obtained a value of 1.65 μ<sub>B</sub>/U<sup>3+</sup> for the size of the ordered magnetic moment. The antiferromagnetic transition temperature of U<sub>2</sub>RhIn<sub>8</sub> is higher yielding 117 K. We found that the magnetic structure can be described by propagation vector *k* = (0.5, 0.5, 0). The respective ordered magnetic moment amounts 1.7 μ<sub>B</sub>/U<sup>3+</sup>. In both

materials the ordered magnetic moments are aligned along the tetragonal *c*-axis. Comparison with isostructural compounds and general conclusions for the series will be presented.

[1] C. Pfleiderer, Rev. Mod. Phys. 81 (2009) 1551

[2] A Benoit et al., Solid State Commun. 34 (1980) 39

[3] H. Shishido et al. J. Phys. Soc. Jpn. Vol. 71 Suppl. (2002) 276

[4] H. Hegger et al., Phys. Rev. Lett. 84 (2000) 4986

9:20am **AC+MI+SA+SU-MoM4** **U<sub>3</sub>Si<sub>2</sub> – Physical Properties and Resistance to Hydrogen, Silvie Maskova**, Charles University, Prague, Czech Republic, K. Miliyanchuk, Ivan Franko National University of Lviv, Lviv, Ukraine, S. Middleburgh, Westinghouse Electric Sweden AB, Vasteras, Sweden, L. Havela, Charles University, Prague, Czech Republic U<sub>3</sub>Si<sub>2</sub> (tetragonal structure with the space group of *P4/mbm* and two different U-positions, U1 and U2, in the unit cell) is considered to be promising material (due to its high density of uranium) as an accident-tolerant nuclear fuel [1] with rather high melting point (1938 K) indicating a high thermodynamic stability. From this point of view, it is very important to study its resistance to oxygen or hydrogen, as it can significantly influence the integrity of the material. U<sub>3</sub>Si<sub>2</sub> was reported to oxidize at elevated temperatures [2].

We studied the H absorption and concomitant changes of basic electronic properties. We found that U<sub>3</sub>Si<sub>2</sub> reversibly absorbs hydrogen (H can be released again by heating up to approx. 700 K) to the level of approximately 1.8 H/f.u., i.e. yielding U<sub>3</sub>Si<sub>2</sub>H<sub>1.8</sub>. The H absorption proceeds at very low H pressures (kPa range) already, resulting in 10 % volume expansion. The temperature-induced desorption experiment showed that the hydrogen atoms are located in one specific position only. The crystal structure arrangement suggests that two different positions should be considered - U<sub>3</sub>Si tetrahedra (similar to U<sub>3</sub>T tetrahedra in U<sub>3</sub>T<sub>2</sub>X compounds [3] crystallizing in an ordered ternary derivative of the U<sub>3</sub>Si<sub>2</sub> structure) and a split position in the U<sub>6</sub> octahedra consisting of 4 U1 and 2 U2 atoms (H atom shifts from the central position into the tetrahedra formed by 2 U1 and 2 U2 atoms. As H generally does not occupy two adjacent tetrahedra, we can assume only two from the 4 tetrahedra occupied). The later was confirmed as more plausible option by ab-initio calculations using Vienna Ab-initio Simulation Package (VASP) with the PBE-GGA exchange correlation.

Magnetic studies of U<sub>3</sub>Si<sub>2</sub> confirmed that it is a Pauli paramagnet, as reported previously [4]. The volume expanded hydride reveals a Curie-Weiss behavior and a weak and inhomogeneous ferromagnetism arising gradually below *T* = 100 K. The low-temperature specific heat of U<sub>3</sub>Si<sub>2</sub>H<sub>1.8</sub> shows an upturn and a dramatic enhancement of the Sommerfeld coefficient of electronic specific heat γ, which reaches 440 mJ/mol f.u. K<sup>2</sup> (γ = 88 mJ/mol f.u. K<sup>2</sup> for U<sub>3</sub>Si<sub>2</sub>).

This work was supported by The Czech Science Foundation under the Grant No. 15-01100S.

[1] K.D. Johnson, A.M. Rafferty, D.A. Lopes, J. Wallenius, J. Nucl. Mater. 477 (2016) 18-23.

[2] E. Sooby Wood, J.T. White, A.T. Nelson, J. Nucl. Mater. 484 (2017) 245-257.

[3] K. Miliyanchuk, L. Havela, A.V. Kolomiets, A.V. Andreev, Physica B 359-361 (2005) 1042-1044.

[4] T. Miyadai, H. Mori, T. Oguchi, Y. Tazuke, H. Amitsuka, T. Kuwai and Y. Miyako, J. Magn. Magn. Mater. 104-107 (1992) 47-48.

9:40am **AC+MI+SA+SU-MoM5** **Understanding Surface Chemistry of f-element Oxides using First-principle Methods, Ping Yang**, Los Alamos National Laboratory **INVITED**

Interfacial chemistry for f-element materials is critical for nuclear waste management and to address the environmental concerns associated with actinides. Cerium is often used as a surrogate for more radioactive actinide elements for thorough characterization using advanced spectroscopic techniques. Herein, we will present recent progress in characterizing interfacial interactions of ligands with CeO<sub>2</sub> and ThO<sub>2</sub> in both surface and nanoparticle forms. We will demonstrate how the synergy between theory and experiment has accelerated the progress in this field. The theoretical results are validated by spectroscopic characterizations. A better molecular-level understanding of the interfacial chemistry including coordination, energetics and reaction mechanisms will pave the way to a better strategy for waste management and environment remediation.

10:40am **AC+MI+SA+SU-MoM8 Inelastic X-ray Scattering Study of the Crystal Dynamics of Neptunium and Uranium Dioxide, Roberto Caciuffo**, European Commission, Joint Research Centre, Karlsruhe, Germany, *P. Maldonado*, Uppsala University, Sweden, *L. Paolasini*, European Synchrotron Radiation Facility, France, *P.M. Oppeneer*, Uppsala University, Sweden, *T.R. Forrest*, European Synchrotron Radiation Facility, France, *A. Prodi*, Consiglio Nazionale delle Ricerche, Italy, *N. Magnani*, European Commission, Joint Research Centre, Karlsruhe, Germany, *A. Bosak*, European Synchrotron Radiation Facility, France, *G.H. Lander*, European Commission, Joint Research Centre, Karlsruhe, Germany

**INVITED**

The energy-wavevector dispersion relations for normal modes of vibration propagating along high-symmetry lines in  $\text{NpO}_2$  and  $\text{UO}_2$  have been determined by measuring the coherent one-phonon scattering of X-rays from single-crystal specimens with mass varying from a few  $\mu\text{g}$  to  $\sim 1$  mg. The inelastic X-ray scattering (IXS) experiments were carried out using the ID28 beamline at ESRF with an incident energy  $E=17.794$  keV. The results are compared against *ab initio* phonon dispersion simulations computed within the first-principles density functional theory in the generalized gradient approximation plus Hubbard U correlation (GGA+U) approach, taking into account third-order anharmonicity effects in the quasiharmonic approximation.

In the case of  $\text{NpO}_2$ , the sample of dimension of  $0.4 \times 0.3 \times 0.3 \text{ mm}^3$  was oriented with the specular direction along the (100) crystal axis and the (011) axis in the scattering plane. We have investigated different Brillouin zones in order to optimize the inelastic structure factor for the different optic branches. Optic phonons arise mainly from oxygen vibration modes and are very weak. Thermal expansion, heat capacity, thermal conductivity, phonon linewidth, and thermal phonon softening are calculated and compared with experimental data available for both  $\text{NpO}_2$  and  $\text{UO}_2$  [1]. We show that optical phonons contribute significantly to the heat transport due mainly to their large velocities and short lifetimes. Compared with  $\text{UO}_2$ , the main differences in the phonon density of states of  $\text{NpO}_2$  are a softening of the optical modes and an increase of the peak centred around 55 meV, whereas the acoustic modes in  $\text{NpO}_2$  are shifted to higher frequencies. The calculated value at 0 K of the bulk modulus in  $\text{NpO}_2$  is in agreement with the experimental value and slightly smaller than the one determined by high-pressure X-ray diffraction for  $\text{UO}_2$ .  $\text{NpO}_2$  has a smaller thermal conductivity than  $\text{UO}_2$ , at least in the temperature range 600 to 1000 K for which experimental values are available.

The lattice dynamics of  $\text{UO}_2$  have been extensively investigated by neutron scattering both at low and high temperature. In this study we focussed our attention to the low temperature region, searching for vibronic contributions to the vibrational-magnetic-quadrupolar mixed modes that appear in  $\text{UO}_2$  because of magnetoelastic and multipolar superexchange interactions. The situation is cleaner than with neutrons, as the latter see both magnons and phonons – the IXS spectra just the phonons. This observation opens a new window on these “hidden excitations”, which drive much of the physics of  $\text{UO}_2$ .

[1] P. Maldonado *et al.*, Phys Rev B **93**, 144301 (2016)

11:20am **AC+MI+SA+SU-MoM10 Emergent Phenomena in 4f Heavy-Fermion Systems: from Bulk to Thin-Films, Priscila Rosa**, Los Alamos National Laboratory

**INVITED**

The interplay between magnetism and unconventional superconductivity in bulk materials has been one of the central topics in condensed matter physics for the past 40 years. In particular, the family of compounds  $\text{CeMIn}_5$  ( $M = \text{Co, Rh, Ir}$ ) provides an ideal platform for such investigation due to the small energy scales involved, and the high sample quality. In this talk, I will first discuss novel insights provided by substitution studies in bulk  $\text{CeRhIn}_5$  under pressure. I will then present recent efforts to fabricate hybrid superlattices consisting of alternating superconducting  $\text{CeCoIn}_5$  and antiferromagnetic  $\text{CeRhIn}_5$ .

## Actinides and Rare Earths Focus Topic Room: 22 - Session AC+AS+SA+SU-MoA

### Chemistry and Physics of the Actinides and Rare Earths Moderator: David Shuh, Lawrence Berkeley National Laboratory

1:40pm **AC+AS+SA+SU-MoA1 Oxidation and Crystal Field Effects in Uranium**, *James G. Tobin*, University of Wisconsin-Oshkosh, *S.W. Yu*, Lawrence Livermore National Laboratory, *C.H. Booth*, Lawrence Berkeley National Laboratory, *T. Tylliszczak*, Lawrence Berkeley Lab, University of California, Berkeley, *D.K. Shuh*, Lawrence Berkeley National Laboratory, *G. van der Laan*, Diamond Light Source, UK, *D. Sokaras*, *D. Nordlund*, *T.C. Weng*, Stanford Synchrotron Radiation Lightsource, *P.S. Bagus*, University of North Texas

An extensive investigation of oxidation in uranium has been pursued. [1] This includes the utilization of soft x-ray absorption spectroscopy, hard x-ray absorption near-edge structure, resonant (hard) x-ray emission spectroscopy, cluster calculations, and a branching ratio analysis founded on atomic theory. The samples utilized were uranium dioxide ( $\text{UO}_2$ ), uranium trioxide ( $\text{UO}_3$ ), and uranium tetrafluoride ( $\text{UF}_4$ ). A discussion of the role of nonspherical perturbations, i.e., crystal or ligand field effects, will be presented. The conclusions are as follows. (1) The hypothesis of the potential importance of CF effects in the XAS branching ratio (BR) analysis of 5f states was incorrect. (2) Both  $\text{UO}_2$  and  $\text{UF}_4$  are  $n_{5f} = 2$  materials. The combination of the 4d XAS BR and RXES analyses is particularly powerful. (3) CF broadening in the  $L_3$  RXES spectroscopy does not preclude a successful analysis. (4) The prior experimental result that  $n_{5f}(\text{UO}_2) = 3$  and the proposed causation by covalent bonding was incorrect.  $\text{UO}_2$  is an  $n_{5f} = 2$  material and analysis within a simple, ionically localized picture provides the correct result. (5)  $\text{UO}_3$  appears to be an  $n_{5f} = 1$  material. (6) While the 4d XAS BR analysis is blind to CF effects, crystal field and covalence remain important. (7) For localized actinide systems, the 4d XAS BR analysis founded upon the utilization of the intermediate coupling scheme remains a powerful tool. (8) For delocalized actinide systems, the BR analysis is problematic.

[1] J. G. Tobin, S.-W. Yu, C. H. Booth, T. Tylliszczak, D. K. Shuh, G. van der Laan, D. Sokaras, D. Nordlund, T.-C. Weng, and P. S. Bagus, *Phys. Rev. B* **92**, 035111 (2015)

2:00pm **AC+AS+SA+SU-MoA2 Electron Spectroscopy Studies of U and U-Mo Hydrides**, *Ladislav Havela*, *M. Paukov*, *M. Dopita*, *L. Horak*, *M. Divis*, *I. Turek*, Charles University, Prague, Czech Republic, *T. Gouder*, *A. Seibert*, *F. Huber*, European Commission, Joint Research Centre, Karlsruhe, Germany, *D. Legut*, VSB - Technical University of Ostrava

U hydride was the first material indicating that 5f states can yield ferromagnetism analogous to 3d metals. However, the electronic structure of  $\text{UH}_3$  is not yet well understood, and it is not clear to which extent it can be described by conventional band structure calculations. We have been studying structure and electronic properties of  $\text{UH}_3$  and  $(\text{UH}_3)_{1-x}\text{Mo}_x$  films synthesized by reactive sputtering. Primary diagnostics was performed by in-situ XPS. The U-4f core level spectra exhibit a development as a function of partial pressure of  $\text{H}_2$  in Ar ( $p_{\text{Ar}} = 8 \times 10^{-3}$  mbar). Their intensity gradually decreases, they shift by 0.2 eV towards higher binding energies (BE) and an extended (9 eV wide) satellite structure develops on the high BE side of both 4f peaks. This tendency saturates at 5%  $\text{H}_2$  concentration, and we assume that this pressure is sufficient to form  $\text{UH}_3$ . XRD and X-ray reflectivity proved indeed the  $\beta\text{-UH}_3$  structure of deposited films, which were polycrystalline, but highly textured. Ferromagnetism of the  $\text{UH}_3$  films has the correct Curie temperature  $T_C \approx 165$  K. Magnetic coercivity of the films is enormous, the width of hysteresis loop exceeds 10 T at low temperatures. Details of the valence band observed in UPS reveal a transformation of the triangular emission of the U metal into a sharp feature at the Fermi level accompanied by a broad shoulder around 0.5 eV for the hydride. A distinct development was noticed also for the U-6p states, which become narrower and shift by 1.2 eV to higher BE in the hydride, which can be interpreted as an impact charge transfer from U towards H. Besides photoelectron spectroscopy, the variations of electronic states were monitored also by BIS spectra collected for the 1486.6 eV photon energy. The spectroscopy results are confronted with different types of in-initio calculations.

As U-Mo alloys tend to form nanocrystalline  $\beta\text{-UH}_3$  based hydrides, we were curious about reactive sputter deposition of the U-Mo alloys. We found that the tendency to form hydrides is fast suppressed by Mo for room temperature sputtering ( $\gamma\text{-U}$  alloy without H is the product), but cooling the substrate to 77 K helps to maintain the hydride phase even for even higher Mo concentrations.

This work was supported by the Czech Science Foundation under the grant No. 15-01100S.

2:20pm **AC+AS+SA+SU-MoA3 Comparative Structural Studies of Tetravalent f ions in Solids and in Aqueous Solutions**, *Lynda Soderholm*, Argonne National Laboratory

**INVITED**  
Predicting a metal ion's aqueous chemistry – including its stability, reactivity, and solubility – requires molecular-level knowledge of the various factors influencing speciation and complex formation. This chemistry is particularly complicated for f-ions, where the electrostatic, non-directional bonding provides flexibility to their coordination environments, which can vary widely depending on the ligating species. This presentation will focus on our efforts to establish trends in f-ion solution behavior and to provide a direct link between metal correlations in solution and the thermodynamic stability constants that are used to derive relative free energies of available metal-ligand complexes. Although several examples will be provided, the discussion will center on a comparison between the behaviors of tetravalent Th, Pu, and Ce and how differences in the complexes formed in solution impact the composition and structure of precipitates that form. High-energy X-ray scattering (HEXS) experimental results will be used to demonstrate how changing conditions can influence solution chemistry, with a specific emphasis on the role of the anion. X-ray surface-based techniques will be used to provide a link between solution speciation and the complexes that form on mineral surfaces. The structures of molecular species isolated as single-crystals from these solutions will be directly compared with the solution and surface-adsorbed species. This work is supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Biosciences and Geosciences, Heavy Element Chemistry, under contract No. DE-AC02-06CH11357.

4:00pm **AC+AS+SA+SU-MoA8 Interfacial Dynamics in Radiation Environments and Materials: An Energy Frontier Research Center**, *Sue Clark*, Pacific Northwest National Laboratory

**INVITED**  
The US Department of Energy's Office of Environmental Management (EM) is faced with remediating millions of liters of highly radioactive wastes that resulted from the production of nuclear weapons during the Cold War. These legacy wastes are stored in large, underground tanks at former nuclear weapons production sites in the US. Not only are these wastes radioactive, but they are also highly alkaline and concentrated in electrolytes. Using currently available technologies and approaches, EM estimates that processing these wastes into waste forms for disposal in a geologic repository will take at least 5 decades and over \$300 billion dollars. Basic research on the chemical and physical behavior of these materials in such extreme conditions is needed to provide a foundation of innovation to accelerate processing and reduce aggregate costs.

IDREAM is an Energy Frontier Research Center (EFRC) conducting fundamental research to support innovations in processing high-level radioactive wastes (HLW). Activities in IDREAM are designed to support the transformation of HLW processing by elucidating the basic chemistry and physics required to control and manipulate interfacial phenomena in extreme HLW environments (e.g., non-equilibrium, heterogeneous, and chemically complex). This foundational knowledge is required to achieve IDREAM's vision to master molecular-to-mesoscale chemical and physical phenomena at interfaces in complex environments characterized by extremes in alkalinity and low-water activity, and driven far from equilibrium by ionizing (g,b) radiation. Further, understanding these processes will enable prediction of waste aging over the many decades required to complete this difficult cleanup task.

Currently, IDREAM activities focus on the aluminate anion in alkaline solutions, and its nucleation into boehmite (aluminum (oxy)hydroxide,  $\text{AlO}(\text{OH})$ ) and gibbsite (aluminum hydroxide,  $\text{Al}(\text{OH})_3$ ), as they are key principal components of bulk waste materials to which a variety of other metal ions and radionuclides partition. In this presentation, initial results on interfacial reactivity between aluminate, boehmite, and gibbsite will be discussed. The impact of g and b radiation on boehmite and gibbsite will also be presented.

4:40pm **AC+AS+SA+SU-MoA10 Real Structure of Nanocrystalline Uranium based Hydrides Studied By the X-ray Scattering Methods**, *Milan Dopita*, *L. Havela*, *L. Horak*, *M. Paukov*, Charles University, Prague, Czech Republic, *Z. Matej*, MAX-IV, Lund, Sweden

Interaction of hydrogen with uranium is not only an important issue for its nuclear and military applications but also contributes to understanding of the 5f magnetism. Uranium hydrides provide a unique tool to observe an impact of expansion of the U lattice, allowing formation of U moments and their ferromagnetic ordering. However, the electronic structure of uranium

hydrides is not fully understood yet. Especially, the role of the real structure, i.e. the influence of the lattice defects, particle size in the nanocrystalline bulk materials and the preferred orientation of crystallites – the texture, the strains and stresses in the case of films is not well described, but can significantly influence electronic and magnetic properties of materials.

In our contribution we report the real structure of bulk and powder Mo- and Zr-alloyed uranium hydrides, prepared by rapid (splat) cooling and high pressure synthesis, and Mo alloyed uranium hydride films synthesized by reactive sputtering, using X-ray scattering methods. The sample series with different alloying element concentration as well as at different hydrogen pressure were prepared. Since the classical powder diffraction methods, as the profile analysis and/or Rietveld method, reach the limits of their applicability for the nanocrystalline uranium hydrides alloys in terms of the real structure description, the use of more advanced methods is necessary. Here we describe the total scattering method – pair distribution function analysis, and Debye equation calculation for simulations of the intensity scattered from nanocrystalline clusters.

The key results of our study were the determination of the phase composition and its evolution, as well as detailed atomic positions, which can influence the U-U spacings in individual phases, tuning the 5f magnetism. The methods are able to describe the particle size and defect distributions, the stress, strains, and textures in the films. In addition, the depth profiles and evolution of above mentioned parameters can be determined. Such X-ray analysis provides useful characterization of the sputter-deposited films, which are also used for fundamental electron spectroscopy studies of UH<sub>3</sub>-based films, exhibiting much lower surface contamination by oxygen than comparable bulk material.

This work was supported by the project “Nanomaterials centre for advanced applications”, Project No. CZ.02.1.01/0.0/0.0/15\_003/0000485, financed by ERDF.

# Tuesday Morning, October 31, 2017

## Actinides and Rare Earths Focus Topic

Room: 22 - Session AC+AS+SA-TuM

## Nuclear Power, Forensics, and Other Applications

**Moderator:** James G. Tobin, University of Wisconsin-Oshkosh

8:00am **AC+AS+SA-TuM1 Design of Synergistic Protein-ligand Systems for f-element Coordination, where Separation, Decontamination and Nuclear Medicine Meet, Rebecca Abergel, Lawrence Berkeley National Laboratory** **INVITED**

Separation of elements from the 4f- and 5f- series is a challenging task due to the similarities in their ionic radii and the existence of most of these metal ions in the trivalent oxidation state. Understanding the fundamental bonding interactions between those metal centers and selective ligands presents a rich set of scientific challenges and is critical to the development of new separation strategies as well as to a number of applied problems such as the need for decontamination after a nuclear accident or the use of radio-isotopes for new cancer treatments. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques to investigate specific lanthanide and actinide coordination features by bio-inspired catecholamide and hydroxypyridinone hard oxygen-donor ligands. Using such ligands allows the solution differentiation of different metals through stabilization in specific oxidation states and provides information on their respective electronic structures. In addition, X-ray diffraction analyses using the mammalian iron transport protein siderocalin as a crystallization matrix revealed remarkable aspects of the protein's interactions with chelated metals, establishing series of isostructural systems that can be used to derive trends in the later 5f-element sequence, when combined with theoretical predictions. These results will be discussed with a perspective on how such studies have important implications for the use of spectroscopic and thermodynamic methods to exploit the fundamental knowledge of the role of f-electrons in actinide bonding for the development of new transport, separation, luminescence, and therapeutic applications.

8:40am **AC+AS+SA-TuM3 Image Processing And Particle Analysis Of Fission-Truck-Analysis In Nuclear Forensic, Itzhak Halevy, Department of Physics, NRCN, Israel, U. Admon, (Retiree), IAEC-NRCN, Department of Materials, Beer-Sheva Israel, E. Chinea-Cano, Office of Safeguards Analytical Services (SGAS), International Atomic Energy Agency (IAEA), Austria, A.M. Weiss, Faculty of Engineering, Bar-Ilan University, Israel, N. Dzigal, Office of Safeguards Analytical Services (SGAS), Austria, E. Boblit, Department of Physics, IAEC-NRCN, Israel**

Particle analysis is a key discipline in safeguards and nuclear forensic investigations, as well as in environmental research. The radioactive particles are usually in the micrometric size range, and intermixed within huge populations of other particles, like air-borne dust, soil, industrial exhaust pollutants or estuary sediments.

We are using the Fission Truck Analysis (FTA) technique. In that technique plastic detectors used for rapping a Lexan catcher with the particles and together are radiated in nuclear reactor with thermal neutrons. The Fission Truck are trucks done by the fission products. The fission material is dominant in producing the trucks, namely the  $^{235}\text{U}$  isotope. The Fission Truck could be more visible by special etching and can be used to locate the particles.

From that point, the analysis of Fission Truck is an image processing. Scanning the detectors is a time-consuming procedure. Automated scanning and fission star recognition will make all the Analysis easier to quantify

The challenge, therefore, consists in scanning and imaging a relatively large area detector, at a resolution of about  $1\mu\text{m}$ , and locating the FT clusters while rejecting the artefacts.

Image processing was done using the Fiji distribution of ImageJ. The algorithms shown in this report were implemented using either the ImageJ macro language or the ImageJ Python scripting engine. Basic noise removal, Illumination correction and Segmentation are the basic of the imaging analysis.

I cass of large area detector a set of picture will be taken and by stitching a larg picture will be composed.

Roundness and endpoint thresholds can be adjusted to obtain fewer false negatives at the expense of more false positives. A receiver operation characteristic (ROC) can be used to characterise this.

The high and low threshold determination in the hysteresis thresholding step should be improved.

After the automated procedure the operator can go over the FT and decide if to add stars that were not found by the software or to cancel stars that are artifact.

Correlation between forensic and image processing parameters will be defined. Even that stars are coming from  $^{235}\text{U}$  only and it is no one to one connected only to enrichment we still think that the shape, color, number of end points and roundness can be parameters to indicates different forensic properties.

9:00am **AC+AS+SA-TuM4 Application of Linear Least Squares to the Analysis of AES Depth Profiles of Plutonium Oxides, Scott Donald, A.J. Nelson, Lawrence Livermore National Laboratory**

Application of the linear least squares (LLS) methodology allows for quantitative determination of variation in material composition with depth, as well as permitting an understanding of differences resulting from changes in the method of preparation. LLS fits were applied to decompose and enhance the interpretation of spectra obtained by Auger electron spectroscopy (AES) during depth profiles of oxidized plutonium surfaces. By means of the LLS algorithm, chemical state assignments of the  $\text{Pu P}_{1/2}\text{VV}/\text{O}_{45}\text{VV}$ ,  $\text{O KLL}$ , and  $\text{C KLL}$  Auger transitions were determined and the existence of a subsurface oxy-carbide layer was identified, with confirmation provided from comparison to previous measurements of standard samples.

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

9:20am **AC+AS+SA-TuM5 Physical and Chemical Characterization of Solid Pu and Np Sources after Multi-year Exposure to Environmental Conditions, Brian Powell, Clemson University** **INVITED**

A field scale radionuclide vadose zone transport experiment at the United States Department of Energy Savannah River Site is being operated by Savannah River National Laboratory and Clemson University scientists. In this experiment, plutonium and neptunium solid sources are buried in 61 cm long x 10 cm diameter lysimeters which are open to precipitation. Such experiments provide the opportunity to observe changes in the microcrystalline structure of plutonium and neptunium solid phases under various environmental conditions. In the current experiments, sources of neptunium and plutonium in multiple initial oxidation states and chemical forms have been deployed for 2-5 years of field exposure. These sources include  $\text{Pu(V)NH}_4\text{CO}_3(\text{s})$ ,  $\text{Pu(IV)}(\text{C}_2\text{O}_4)_2(\text{s})$ ,  $\text{Pu(III)}_2(\text{C}_2\text{O}_4)_3(\text{s})$ ,  $\text{Pu(IV)O}_2(\text{s})$ ,  $\text{Np(IV)O}_2(\text{s})$  and  $\text{NpO}_2\text{NO}_3(\text{s})$ . X-ray absorption spectroscopy (XAS) analysis of initially  $\text{Pu(V)NH}_4(\text{CO}_3)$  sources archived in an inert atmosphere and sources exposed to lysimeters indicate some reduction to  $\text{Pu(IV)}$  within the sources leading to the formation of  $\text{Pu(IV)O}_2(\text{s})$ . Thus, there appears to be an auto-reduction of  $\text{NH}_4\text{Pu(V)CO}_3(\text{s})$  to  $\text{Pu(IV)O}_2(\text{s})$  even under inert conditions. However, solvent extraction on archived and field-deployed sources show the archived source still contains around 40%  $\text{Pu(V)}$  whereas the same source from a field lysimeter deployed for 2.5 years contained less than 10% of  $\text{Pu(V)}$ . XAS and electron microscopy studies have demonstrated differences between  $\text{Pu(IV)O}_2(\text{s})$  formed via reduction of  $\text{Pu(V)O}_2\text{NH}_4\text{CO}_3$  and initially  $\text{Pu(IV)O}_2$  formed from precipitation of a  $\text{Pu(IV)}$  solution. The behavior of initially  $\text{Np(IV)O}_2$  sources was quite different showing oxidation to  $\text{Np(V)}$  and subsequent downward transport of more soluble  $\text{Np(V)O}_2^+$ . The oxidation of  $\text{Np(IV)O}_2(\text{s})$  leads to formation of a much more disordered solid phase with a significantly altered morphology than the initial  $\text{Np(IV)O}_2(\text{s})$ . The results of these experiments will be discussed in terms of evaluating the history of the sample through analysis of the microcrystalline structure and the influences of aging under various environments.

11:00am **AC+AS+SA-TuM10 Synchrotron Radiation Investigation of f-element Extraction from a Carboxylic Acid Functionalized Porous Aromatic Framework, David Shuh, Lawrence Berkeley National Laboratory, S. Demir, N.K. Brune, University of California Berkeley, LBNL, J.F. Van Humbeck, J.A. Mason, University of California Berkeley, T.V. Plakhova, Lomonosov Moscow State University, Russia, S. Wang, University of California Berkeley, LBNL, G. Tian, S.G. Minasian, T. Tysliszczak, Lawrence Berkeley National Laboratory, T. Yaita, T. Kobayashi, Japan Atomic Energy Agency, S. Kalmykov, Lomonosov Moscow State University, Russia, H. Shiwaku, Japan Atomic Energy Agency, J.R. Long, University of California Berkeley**

Porous aromatic frameworks (PAFs) incorporating a high concentration of acid functional groups possess characteristics that are promising for use in separating lanthanide and actinide metal ions, as required in the treatment of radioactive waste. These materials have been shown to be indefinitely stable to concentrated acids and bases, potentially allowing for multiple

adsorption/stripping cycles. Additionally, the PAFs combine exceptional features from metal organic frameworks (MOFs) and inorganic/ activated carbons giving rise to tunable pore surfaces and maximum chemical stability. The adsorption of selected metal ions,  $\text{Sr}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Am}^{3+}$ , from aqueous solutions employing a carbon-based PAF, BPP-7 (Berkeley Porous Polymer-7) has been investigated. This material displays high metal loading capacities together with excellent adsorption selectivity for neodymium over strontium. X-ray absorption spectroscopy studies show that the stronger adsorption of neodymium is attributed to multiple metal ion and binding site interactions resulting from the densely functionalized and highly interpenetrated structure of BPP-7. Recyclability and combustibility experiments demonstrate that multiple adsorption/stripping cycles can be completed with minimal degradation of the polymer adsorption capacity.

11:20am **AC+AS+SA-TuM11 The Effect of  $\text{Al}_2\text{O}_3$  Encapsulation Using Atomic Layer Deposition on the Photoluminescent, Water and Thermostability Properties of  $\text{SrAl}_2\text{O}_4$  Based Phosphors, Erkul Karacaoğlu, E. Öztürk, Karamanoglu Mehmetbey University, Turkey, M. Uyaner, Selcuk University, Turkey**

Aluminate based phosphors ( $\text{MAl}_2\text{O}_4$ ,  $\text{M}_4\text{Al}_{14}\text{O}_{25}$ ,  $\text{M} = \text{Sr, Ba, Ca, etc.}$ ) are chemically unstable against water and even moisture. Moreover, some of phosphors, like green emitting phosphorescent materials' luminescence properties, but not their structural properties, are affected negatively during reheating applications because the  $2+$  ionic state of europium is oxidized to  $3+$  in open atmosphere low temperature heating process thus limiting their applications. Their hydrolysis process were studied and analyzed intensively by researchers. Changes of pH value of suspensions, the structures and optical properties of the hydrolysis of phosphor structures had been investigated. In this research, to prevent or minimize this degradation, to enhance the water resistance and to maintain the phosphorescence properties, an  $\text{Al}_2\text{O}_3$  coating on the surface of  $\text{SrAl}_2\text{O}_4$  based phosphor pellets (1 mm thickness) were prepared using Atomic Layer Deposition (ALD) method with Trimethylaluminum (TMA) precursor. The investigation of phase formation of strontium aluminate was analyzed by thermal analysis (DTA/TG) until  $1500^\circ\text{C}$ . The  $\text{SrAl}_2\text{O}_4$  with Monoclinic structure in single phase having lattice parameters  $a=8.44365\text{Å}$ ,  $b=8.82245\text{Å}$ ,  $c=5.15964\text{Å}$  and  $\alpha=90^\circ$   $\beta=90^\circ$   $\gamma=90^\circ$  were obtained according to XRD analysis. The photoluminescence (PL) results of both open and reduced atmosphere synthesized phosphors with excitation and emission wavelengths and decay time were determined by a PL spectrometer at room temperature. The reduced and open atmosphere synthesized samples have different photoluminescent characteristics because of ionic state of europium in  $2+$  and  $3+$  at reduced atmosphere and open atmosphere, respectively. Moreover, it was obtained that the main crystal,  $\text{SrAl}_2\text{O}_4$ , had photoluminescent properties. The surface analysis of phosphors as morphology and elemental analysis (SEM/EDX), X-ray diffraction (XRD), water and heat resistance (thermostability), photoluminescence (PL) of the phosphors before and after encapsulation were discussed in detail.

## Magnetic Interfaces and Nanostructures Division

### Room: 11 - Session MI+2D+AC+SA+SS-TuM

#### Novel Magnetic Order at Interfaces

**Moderators:** Axel Enders, University of Bayreuth, Germany, Valeria Lauter, Oak Ridge National Laboratory

8:20am **MI+2D+AC+SA+SS-TuM2 Transition from Spatial to Magnetic Confinement in Graphene Quantum Dots, Fereshte Ghahari, D. Walkup, C. Gutierrez, NIST; Maryland NanoCenter UMD, J.R. Rodriguez-Nieva, Harvard University, K.G. Watanabe, T. Taniguchi, National Institute for Materials Science, Japan, L.S. Levitov, MIT, N.B. Zhitenov, J.A. Stroscio, NIST**

Recent progress in creating and probing graphene quantum dots has offered a new platform to investigate Klein tunneling related phenomena. The quasi-bound resonances in these circular resonators can be confined even further by the application of a perpendicular magnetic field where they condense into highly degenerate Landau levels. Here, we use scanning tunneling spectroscopy to visualize the transition from spatial to magnetic confinement in quantum dots created in graphene/boron nitride heterostructures. In high magnetic fields, electrons redistribute themselves due to coulomb interactions leading to compressible regions separated by incompressible strips.

8:40am **MI+2D+AC+SA+SS-TuM3 Chiral and Proximity Induced Magnetism in Magnetic Multilayers and 2D Heterostructures, Hyunsoo Yang, National University of Singapore, Singapore INVITED**

Topologically non-trivial chiral spin textures are present in systems with a strong Dzyaloshinskii-Moriya interaction (DMI) with a spatial extent of only

tens to a few hundred nanometers. Thin film heavy metal/ferromagnetic bi- and multilayers have emerged as an ideal candidate for the development of such devices due to their tunability through a variation of the constituent components and relative layer thicknesses. However, to date, no chiral spin textures have been observed in thick ferromagnetic multilayers in which the disparate magnetic layers are exchange coupled. Furthermore, previous observations required either the presence of an out-of-plane bias field or careful tuning of a geometric confining potential to stabilize the skyrmion structure. In this work, we have imaged the formation of room temperature Néel skyrmions in a symmetric Co/Pd multilayer with Lorentz transmission electron microscopy for the first time [1]. Importantly, the size of the observed skyrmions is significantly smaller than previously reported systems in which non-multilayer films are used. The formation and resolution of the internal spin structure of room temperature skyrmions without a stabilizing out-of-plane field in thick magnetic multilayers opens up a new set of tools and materials to study the physics and device applications associated with magnetic chiral ordering.

Due to the unique topology associated with their band structure, two-dimensional (2D) transition metal dichalcogenides (TMDs) such as  $\text{WSe}_2$ ,  $\text{MoS}_2$  and  $\text{WTe}_2$  provide a unique platform to develop novel electronics using the spin-valley degree of freedom. The incorporation of the heavy metal in the TMD suggests strong intrinsic spin orbit interactions, and could further result in a chiral DMI. However, confirmation of the DMI in such films and its effects on the spin ordering in the overlaying magnetic layer is lacking. Further, it has recently been predicted that orbital hybridization at the TMD/FM interface may occur and result in generation of a non-negligible magnetic moment in the TMD layer. In the present study we explore the interface induced magnetism in TMD/FM films. Finally, we also explore the effects of DMI and generation of chiral spin textures that result from it by measuring the imbalance between left and right-handed domains within the ferromagnetic layer. As the polarized neutron scattering is strongly dependent on spin chirality, this method has been utilized to study chiral magnetism in multilayer structures with strong DMI.

[1] S. Pollard et al. "Observation of stable Néel skyrmions in cobalt/palladium multilayers with Lorentz transmission electron microscopy" Nat. Comm. 8, 14761 (2017).

9:20am **MI+2D+AC+SA+SS-TuM5 Surface Magnetism Induced by Interstitial Defects in PbO, Elvis Arguelles, Osaka University, Japan, S. Amino, A.L.M.T. Corp, Japan, H. Nakanishi, S. Aspera, H. Kasai, National Institute of Technology, Akashi College, Japan, W.A. Dino, Osaka University, Japan**

We investigated the possibility of employing the polycrystalline  $\alpha\text{PbO}$  as a spintronics device by *first principles* calculations based on the density functional theory (DFT). In particular, we explored the effects of  $3d$  transition metal atom, Fe on the structural and electronic properties of the layered  $\alpha\text{PbO}$  (001) surface. Since it has been proven that ferromagnetic signals in experiments are often detected in thin films[1] we used a  $2\times 2$ , 3-layered surface slab model of  $\alpha\text{PbO}$  with  $20\text{Å}$  of vacuum space to simulate this environment in this study. The impurity atoms are placed in between the surface and subsurface of the crystal. The results show that the interstitial Fe interstitial forms shorter bonds with the oxygen atoms located at the surface and second layers. Also, this impurity is found to induce magnetism in the host crystal with magnetic moment value of  $2.25\mu_B$ , which is highly localised on the transition metal.

In the bonding process, the Fe's lower energy lying  $d$  states form overlaps with nearest neighbour oxygen atoms with non-bonding  $d$  states situated near or at the Fermi level and are spin split. These spin split orbitals induce spin polarisation of  $p$  impurity states of oxygen atoms in the subsurface. Moreover, the magnetic order is determined using the energy difference between the antiferromagnetic and ferromagnetic states. The energy difference is  $0.068\text{ eV}$ , suggesting that Fe interstitial impurities induce ferromagnetism in  $\alpha\text{PbO}$  [2]. In this workshop, the effects of charge carriers to the magnetic properties will be briefly discussed. Finally, the position of the Fermi level in the density of states (DOS) suggests that in the case of  $\alpha\text{PbO}$  with Fe interstitials where the minority non-bonding  $d$  states are partially filled, the Zener's ferromagnetic double exchange mechanism may be dominant and stabilizing the ferromagnetic state.

#### References:

- [1] M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, Phys. Rev. Lett. 93, 177296 (2007)
- [2] E. F. Arguelles, S. Amino, S. Aspera, H. Nakanishi, and H. Kasai, J. Phys. Soc. Jpn. 84, 045002 (2015)

9:40am **MI+2D+AC+SA+SS-TuM6 XMCD Quest for Magnetic Proximity Effect in Ferromagnetic Insulator/Non-Magnetic Metal Interfaces**, *Andrei Rogalev, F. Wilhelm*, European Synchrotron Radiation Facility, France

The rise of spin current physics together with enormous technological advances to engineer layered structures with tailored spin-orbit interactions have placed 4d and 5d transition metals at the heart of the emerging fields of spinorbitronics, magnonics and caloritronics. In this context, magnetic properties at the interfaces between a ferromagnetic materials and non magnetic metals with large spin-orbit coupling play a central role. Some of those heavy metals like Pt or Pd are known to exhibit so-called magnetic proximity effect, i.e. they acquire interfacial induced magnetic moments whenever they are in contact with 3d metallic ferromagnets. However, when they are grown on magnetic insulators, e.g. yttrium iron garnet (YIG), whether induced magnetic moments are indeed ubiquitous is still an open question as contradictory reports have been published. This is indeed the key question for correct interpretation of the spin Hall magnetoresistance or the newly discovered unidirectional magnetoresistance phenomena and, in more general, to understand mechanisms of pure spin currents generation. To answer this question and to unravel a possible role of magnetic proximity effects at ferromagnetic/non-magnetic interfaces, X-ray magnetic circular dichroism (XMCD) spectroscopy appears to be the method of choice due to its element selectivity and high sensitivity. In this talk, we present a thorough review of XMCD experiments aimed at detection of magnetic proximity effect in a variety of ferromagnetic insulator/non-magnetic metal interfaces.

11:40am **MI+2D+AC+SA+SS-TuM12 Depth-Dependent Measurement of Atomic Valence and Magnetization in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  Magnetic Thin Films**, *Mikel Holcomb, R. Trappen, S. Kumari, N. Mottaghi, S. Yousefi Sarraf, C.-Y. Huang, G. Cabrera*, West Virginia University

Magnetic thin films often lose their magnetic order and even bulk materials can have significant deviations of the magnetic order and other properties near surfaces and interfaces. In strongly correlated oxides, there are many competing parameters affecting the material properties, complicating the understanding of these systems. We utilize a combined approach of bulk and surface sensitive techniques measuring many film thicknesses to back out layer-by-layer properties in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO) thin films. Strong changes from the bulk are observed for surfaces and interfaces. We will compare these models with theoretical predictions. LSMO has been widely proposed for diverse applications such as tunnel junctions and solid oxide fuel cells. Experimental support is provided by NSF (DMR-1608656). Theoretical support is provided by DoE (DE- SC0016176).

12:00pm **MI+2D+AC+SA+SS-TuM13 Coherent Magnetization Rotation of FeGa/NiFe Multilayers via Strain-Inducing Electric Field**, *Colin Rementer*, University of California at Los Angeles, *M.E. Jamer*, NIST, *A. Barra*, University of California at Los Angeles, *J. Borchers, A.J. Grutter, B.J. Kirby*, NIST, *G.P. Carman, J.P. Chang*, University of California at Los Angeles

The ability to reduce the size of antennae would enable a revolution in wearable electronics, extendable to implantable electronic devices. Antenna miniaturization could be enabled by multiferroic materials, which enable the efficient control of magnetic via electricity. Multiferroic antennae, composed of coupled ferromagnetic and piezoelectric phases, could reduce antenna size by up to five orders of magnitude. This requires a magnetic material that is low loss, has an easily rotatable magnetization and is able to convert magnetic field to strain via magnetostriction.

Galfenol ( $\text{Fe}_{84}\text{Ga}_{16}$ , or FeGa) is a promising magnetic material due to its large magnetostriction (>200 ppm), high piezomagnetic coefficient (3 ppm/Oe), and high stiffness (70 GPa), but has high loss in the GHz regime. Permalloy ( $\text{Ni}_{81}\text{Fe}_{19}$  or NiFe) is a soft magnetic material that has very low loss in the GHz regime (<20 Oe) but almost no magnetostriction. In this work, multilayer laminates containing alternating FeGa/NiFe layers were fabricated to reduce loss at high frequencies and properties were tuned via layer number and thickness. In this work, optimized multilayer laminates containing alternating FeGa/NiFe layers were shown to exhibit desirable magnetic softness (<20 Oe), narrow FMR line width (<40 Oe), high permeability (>400), and strong magnetostriction (> 70 microstrain). The focus of this work is to determine if the rotation of the magnetization of the individual layers is coherent with applied strain.

Polarized neutron reflectometry was used to determine the depth profiles of the structure and in-plane vector magnetization as functions of applied magnetic field and voltage. Initial studies showed that a FeGa/NiFe superlattice with the structure (20 nm FeGa/7 nm NiFe)/20 nm FeGa demonstrated coherent and linear rotation of magnetization with applied strain. To probe the thickness dependence of this rotation, three single NiFe/FeGa bilayers were fabricated on PMN-PT [011] with 40 nm, 20 nm and 7 nm of NiFe on a base layer of 20 nm FeGa. Application of 400 V results in an enormous increase in spin-flip scattering, unambiguously

demonstrating a substantial rotation of the magnetization perpendicular to the applied magnetic field direction for all samples measured. Micromagnetic and finite element simulations support the experimental results, showing coherent rotation of the magnetization with only small deviations with thicker NiFe layers. These measurements provide direct evidence of a voltage-induced rotation of the both the NiFe and FeGa magnetization as well as a means to separate the response of the magnetostrictive and non-magnetostrictive layer components.

## Sustainability Focus Topic

**Room: 5 & 6 - Session SU+AC+MI+MS-TuM**

## Critical Materials and Energy Sustainability

**Moderators:** Erik B. Svedberg, The National Academies, Robert Lad, University of Maine

8:00am **SU+AC+MI+MS-TuM1 How Critical Materials Affect Emerging Technologies**, *Alexander King*, The Ames Laboratory **INVITED**

We live in a golden age for the development of technologies that have potential for clean and efficient production, storage or use of energy. Many, if not all of these technologies, however, depend on the properties of specific materials that may have low availability, or produce environmental challenges of their own during their production. We will look at the impact of materials supply challenges on the adoption of some recent clean energy technologies, consider possible impacts on some emerging technologies, and describe what efforts must be undertaken to ensure that fragile materials supply-chains do not prevent the adoption of technologies that promote a sustainable energy future.

9:20am **SU+AC+MI+MS-TuM5 The Role of Oxidation and Charging Rates on Li Electrochemical Deposition in Solid State Batteries**, *Alexander Yulav*, University of Maryland, *V. Oleshko*, NIST, *P. Haney*, NIST Center for Nanoscale Science and Technology, *A.A. Talin*, Sandia National Laboratories, *M.S. Leite*, University of Maryland, *A. Kolmakov*, NIST Center for Nanoscale Science and Technology

The recent progress in all-solid-state Li-ion batteries (SSLIBs) allowed a significant reduction of overall dimensions of stand-alone medical and micro-electronic devices. Owing to their compatibility with microfabrication process, high specific power, energy densities, and reduced safety risks of the thermal runaway, SSLIBs are likely to compete with their liquid counterparts in the near future. However, the large-scale implementation of SSLIBs requires further characterization during their fabrication and operation. Particularly, spatially resolved *in-operando* techniques probing electrochemical processes at the interfaces are needed. In the present work, we quantify the effects of oxidizing environment and charging rates on a lithium plating morphology using UHV electron microscopy and spectroscopy in correlation with electrochemical characterization. To conduct these measurements, we fabricate a model thin-film planar battery with  $\text{LiCoO}_2$  cathode, LiPON electrolyte, and an ultra-thin carbon anode. Our experimental data reveal a strong dependence of plated Li morphology on presence of oxidation species at the surface and a gas phase. Under UHV conditions a linear correlation between the nucleation density of lithium clusters and a charging rate is observed. We show that the 2D nucleation model adequately describes the obtained dependence. The plated lithium morphology drastically changes from the in-plane clusters to out-of-plane whisker growth when  $\sim 10^{-7}$  Pa of oxygen is admitted to the UHV chamber. The in-plane cluster growth resumes when oxygen pressure increases from  $10^{-7}$  to  $10^{-5}$  Pa. We envision that our findings will contribute to whisker-free safer SSLIB performance under realistic operating conditions.

9:40am **SU+AC+MI+MS-TuM6 Unique Super-Ionicity Achieved on the Nanoscale with Applications in Next-Generation Lithium Ion Batteries**, *Progn Banerjee*, *D. Dumett Torres*, *P. Jain*, University of Illinois at Urbana-Champaign

Lithium-ion (Li-ion) batteries have been dominating the global market for consumer electronics and power vehicles. However, significant safety concerns arise from degradation reactions (reduction/decomposition) of the electrolyte during cycling, potentially causing dendrite formation resulting in leakage and fires. A potential solution is the replacement of the flammable organic electrolyte with an inorganic solid electrolyte with superior electrochemical, mechanical and thermal stability, absence of leakage, long shelf-life, enhanced electrochemical stability and the possibility of battery miniaturization.

A promising candidate for these solid electrolytes are super-ionic materials which exhibit high ionic conductivities matching those of liquid electrolytes.

In these materials, past a phase transition, one sub-lattice (often the cationic) melts, resulting in a disordered cation network, wherein cations can transport in a manner reminiscent of that of a liquid. Known superionic materials, such as AgI, Cu<sub>2</sub>Se etc. in their bulk form, display this phase transition at high temperatures and/or pressures, making them unsuitable for many applications. In our recent study, we examined Cu<sub>2</sub>Se nanocrystals (NCs) prepared from their magic-sized CdSe counterparts using a synthetic topotactic method called cation exchange. In these NCs, the superionic disordered “liquid-like” behavior was observed under ambient conditions. Larger NCs prepared under similar conditions interestingly display ordered layers of Cu<sup>+</sup> ions and vacancies similar to bulk solid. We investigate the origin of this nanoscale effect using arguments based on lattice strain, cationic occupancies obtained from crystallography, and density functional theory (DFT) calculations.

We are extending this work to investigate the possible mechanism of ionic transport in these NCs using a.c. impedance measurements. We are investigating size and dimensionality effects on the transport behavior of cations and the superionic phase transition. We will also investigate the effect of cation vacancies in terms of their profile and density on the phase transition behavior and ionic conductance. This study will pave the way to fundamental understanding on ion transport behavior in solids, and applications as solid-state electrolytes, thermoelectrics and ultrafast electronic switches.

11:00am **SU+AC+MI+MS-TuM10 Electric Cell Potential Driving Changes in Perovskite Surface Termination and Enabling Catalysis, Monika Backhaus, Corning, L. Gregoratti, M. Amati, Elettra-Sincrotrone Trieste, Italy**

**INVITED**

Dynamic segregation processes in perovskite electrodes have been studied in operando in electrochemical model cells with thin zirconia electrolyte and mixed perovskite catalyst by spatially resolved scanning photoelectron microscopy (SPEM) in combination with impedance spectroscopy and gas analysis in the goal to gain better understanding of electrode surface chemistry and its key drivers. We focused on the oxygen reduction reaction at perovskite electrodes and electrochemically driven reactions, such as redox reactions in chemical reactors or sensors. The current overview summarizes our synchrotron in-operando surface spectroscopy in various technical areas.

Our electrochemical cells are built of a thin zirconia electrolyte and mixed perovskite catalyst. They were studied by SPEM at the Elettra synchrotron. The experimental set up allowed operating temperatures up to 700°C, mixtures of unreactive or reactive gases at chamber pressure up to 10<sup>-5</sup> mbar and local pressure above the sample of 1 mbar (gas jet). Electrochemical measurements, such as monitoring of i-V behavior or impedance were realized simultaneously.

The surface termination of (La,Sr)MnO<sub>3</sub> (LSM) electrodes was studied as a function of cell potential, oxygen partial pressure and temperature. The surface chemistry reversibly changed with applied potential, exhibiting Mn-termination in highly oxygen-rich environment and increasing strontium segregation in oxygen-poor environment and under reducing cell potential. Cathode termination changed not only with applied cell potential, but also with cell current. LSM cathode pump cells operating at high current densities preserved an “oxygen-rich” surface chemistry under high cell potential, while low current cells exhibited large changes in surface chemistry.

The response of perovskite electrodes to reactive gas environment was also investigated. Model cells with LSM electrodes were studied in oxygen-propene gas mixtures at different cell potentials under oxygen flux at 400-600°C. Oxygen ion flux and cell potential, both were found to drive dynamic changes of catalyst and electrolyte surface chemistry, including redox reaction, surface segregation and long range surface diffusion. Strongly positive cell potential drove an interaction of hydrocarbon with the mixed oxide catalyst surface, yielding adsorbed carbonaceous species with epoxy-type bonding at a strongly Sr-enriched surface. The carbonaceous surface complexes reversibly formed and decomposed with cell potential, suggesting it to play the role of an intermediate in an oxide-electro-catalyzed partial oxidation of propene.

11:40am **SU+AC+MI+MS-TuM12 Possibilities of Hydrogen Energy Utilization in Kazakhstan: Preparation of TiCrMn Hydrogen Storage Alloys and Investigation of Their Absorption Properties, Saule Zholdayakova, H.-H. Uchida, Y. Matsumura, Tokai University, Japan**

The society of Kazakhstan has been becoming strongly dependent on fossil fuels, which results in facing serious environmental problems. Kazakhstan is a Central Asian country with rich natural resources, such as Mn, Cr and Ti and energy self-sufficiency is 200% including exportation. Most of the consumption is fossil resources, mainly dependent on coal. The power configuration of Kazakhstan is 70% coal, 19% natural gas, 1% oil, and 10% hydraulic power. With a background of rich production of fossil fuels, Kazakhstan exports most of its oil and domestically dependent on coal. By 2020, Kazakhstan government planning to reduce the amount of green house gas produces by 15% of that in 1992. For these reasons, the development of

renewable energy is significant. In this study we focus on the application of hydrogen as an energy carrier for spreading renewable energy, especially hydrogen energy to solve the environmental problems in Kazakhstan. Hydrogen has more energy per unit of mass, flexible storage options, and it is clean energy. Hydrogen can be stored as a gas, a liquid and as a solid. The other side, for realization hydrogen energy system we need to think more concretely about a manufacture of hydrogen, storage, transportation and utilization. The main manufacture method for hydrogen is electrolysis. The electricity consumption per capita is 5000 kWh/year. If hydrogen energy become a conductor of energy, 1.13m<sup>3</sup>/year of water will necessary to source of hydrogen. After utilizing renewable energy for product hydrogen from water, storage, transport and change to electric power. In the end of consumption, we get the same amount of water. In this study, especially conditions necessary for the renewable energy in Kazakhstan are summarized and trained to preparing hydrogen storage ally using the metals of Mn, Cr and Ti available in Kazakhstan.



# Tuesday Afternoon, October 31, 2017

**Actinides and Rare Earths Focus Topic**  
**Room: 22 - Session AC+MI+SA+SU-TuA**

## Actinide and Rare Earth Theory

**Moderator:** Ladislav Havela, Charles University, Prague, Czech Republic

2:20pm **AC+MI+SA+SU-TuA1 Magnetic Susceptibility, Magnetic Resonance, and Bonding in Actinide Complexes: Ab-initio Calculations, Jochen Autschbach, University of Buffalo, SUNY** **INVITED**

Actinide complexes exhibit fascinating magnetic properties and interesting chemical bonding. An on-going research project in our group is devoted to first-principles calculations of magnetic resonance parameters (NMR, EPR), magnetic susceptibilities, and other spectroscopic parameters of actinide complexes in relation to their chemical bonding, in particular regarding the involvement of the 5f shell in metal-ligand bonding. We will present results from recent computational studies of magnetic resonance parameters and the magnetic susceptibility of f-element complexes utilizing relativistic quantum chemical methods.

References: Gendron, F. et al., 'Puzzling lack of temperature dependence of the PuO<sub>2</sub> magnetic susceptibility explained according to ab-initio wavefunction calculations', J. Phys. Chem. Lett. 2017, 8, 673-678. 'Ligand NMR chemical shift calculations for paramagnetic metal complexes: 5f1 vs. 5f2 actinides', J. Chem. Theory Comput. 2016, 12, 5309-5321. 'Magnetic properties and electronic structure of neptunyl(VI) complexes: Wavefunctions, orbitals, and crystal-field models', Chem. Eur. J. 2014, 20, 7994-8011. Knecht, S. et al., 'A nonorthogonal state-interaction approach for matrix product state wave functions', J. Chem. Theory Comput. 2016, 12, 5881-5894. Silver, M. et al., 'Characterization of berkelium(III) dipicolinate and borate compounds in solution and the solid state', Science 2016, 353, aaf3762.

3:00pm **AC+MI+SA+SU-TuA3 Combining DMRG with Standard Relativistic Multireference Methods to Probe the Properties of Strongly Correlated Systems: Plutonium Oxides, Valérie Vallet, S. Kervazo, CNRS / University of Lille, France, F. Réal, University of Lille, France, A. Severo Pereira Gomes, CNRS / University of Lille, France, F. Viot, IRSN, France** **INVITED**

Actinide-containing complexes present formidable challenges for electronic structure methods due to the large number of degenerate or quasi-degenerate electronic states arising from partially occupied 5f and 6d shells. In particular, we focus our study here on volatile forms of plutonium such as PuO<sub>2</sub>, PuO<sub>3</sub> or PuO<sub>2</sub>(OH)<sub>2</sub>, for which spectroscopic and thermodynamics properties are of interest.

To attain an accuracy comparable to that of experiments, highly accurate calculations including static and dynamic correlation effects as well as relativistic effects are required. Conventional multi-reference methods, however, can treat active spaces that are often at the upper limit of what is required for a proper treatment of species with complex electronic structures and large number of valence orbitals involved in chemical bonds, leaving no room for verifying their suitability.

In this work, we address first the issue of properly defining the active spaces in such calculations, and introduce a protocol to determine optimal active spaces based on the use of the Density Matrix Renormalization Group algorithm and concepts of quantum information theory.<sup>1</sup>

The guidance offered by this protocol allows us to define the suitable active space to compute the electronic structures

and the nature of the ground states with the desired accuracy, i.e. the clear multi-reference character of the wave-function of those compounds requires that the energies of formation to be computed with multi-configurational quantum chemical methods like CASSCF and CASPT2 and with spin-orbit interaction, treated here *a posteriori* with the state-interaction RASSI method. Specifically, our results illustrate the complex multi-configurational character of PuO<sub>3</sub>. The computed thermodynamics quantities reach a high accuracy allowing us to predict the composition of the released volatile products.

5:00pm **AC+MI+SA+SU-TuA9 The Thermal Expansion of UC and UO<sub>2</sub> from First Principles Calculations - The Importance of Correlations Effects and Spin-orbit Coupling, Dominik Legut, IT4Innovations Center, VSB - Technical University of Ostrava, Czech Republic, U.D. Wdowik, Pedagogical University, Poland, P. Piekarczyk, Polish Academy of Sciences, Poland, G. Jaglo, Pedagogical University, Poland, L. Havela, Charles University, Prague, Czech Republic**

Uranium monocarbide, a potential fuel material for the generation IV reactors, is investigated within density functional theory. Its electronic, magnetic, elastic, and phonon properties are analyzed and discussed in terms of spin-orbit interaction and localized versus itinerant behavior of the 5f electrons. We demonstrate that the theoretical electronic structure, elastic constants, phonon dispersions, and their densities of states can reproduce accurately the results of x-ray photoemission and bremsstrahlung isochromat measurements as well as inelastic neutron scattering experiments only when the 5f states experience the spin-orbit interaction and simultaneously remain partially localized [1]. The partial localization of the 5f electrons could be represented by a moderate value of the on-site Coulomb interaction parameter of about 2 eV. The results of the present studies indicate that both strong electron correlations and spin-orbit effects are crucial for realistic theoretical description of the ground-state properties of uranium carbide. This is even more pronounced considering the thermal expansion and thermal conductivity of UC, where for the latter the optical phonon branches may cause a significant contributions [2]. We compare the novel material UC to the experimental data and to the presently used nuclear fuel material, UO<sub>2</sub> oxide. Here our calculations show that considering the exchange and electron correlations effects the generalized gradient approximation was successful in describing the phonon dispersion spectrum, thermal expansion, and heat capacity w.r.t to the recorded data [3]. For both materials the so-called direct method, based on the harmonic and quasi-harmonic approximation, was used [4]. To study the pressure dependence of the phonon frequencies of UO<sub>2</sub> we calculated phonon dispersions for several lattice constants. Our computed phonon spectra demonstrate the opening of a gap between the optical and acoustic modes induced by pressure. Taking into account the phonon contribution to the total free energy of UO<sub>2</sub> its thermal expansion coefficient and heat capacity have been computed from first-principles [3].

1. U. D. Wdowik, P. Piekarczyk, D. Legut, and G. Jaglo, Phys. Rev. B **94**, 054303 (2016).
2. P. Maldonado, L. Paolasini, P. M. Oppeneer, T. R. Forrest, A. Prodi, N. Magnani, A. Bosak, G. H. Lander, and R. Caciuffo, Phys. Rev. B **93**, 144301 (2016).
3. Y. Yun, D. Legut and P. M. Oppeneer, J. Nucl. Mat. **426**, 109 (2012).
4. K. Parlinski, Z.-Q. Li, and Y. Kawazoe, Phys. Rev. Lett. **78**, 4063 (1997); K. Parlinski, Software PHONON, ver. 6.15, Krakow, Poland, (2015).

## Magnetic Interfaces and Nanostructures Division

**Room: 11 - Session MI+2D+AC+NS-TuA**

## Spin-Orbit Phenomena at Surfaces and Interfaces

**Moderators:** Markus Donath, Westfälische Wilhelms-Universität Münster, Germany, Axel Hoffmann, Argonne National Laboratory

2:20pm **MI+2D+AC+NS-TuA1 Coherent Control over Spin-polarized Dirac Surface State in Topological Insulators, Kenta Kuroda, The Institute for Solid State Physics, The University of Tokyo, Japan** **INVITED**

A number of challenging efforts have been recently made for a coherent control of highly spin-polarized Dirac surface states in various topological insulators, suggesting ultrafast optospintronic devices. However, these attempts generally neither realized a selective photoexcitation of the surface state, since the optical response is typically governed by the bulk properties, nor do they exclusively probe the excitation of the surface state, because the applied techniques are not surface sensitive.

In my talk, I will report that the difficulty can be overcome by direct band mapping of a photoexcitation in the Dirac surface state with time-resolved two-photon photoemission spectroscopy combined with ultrashort tunable pump pulses in mid-infrared regime. It is revealed that the mid-infrared excitation permits a direct population of the unoccupied Dirac-cone owing to a novel optical coupling across the Dirac point. In addition, the direct optical transition induces a pronounced asymmetry of the transient surface population in *k*-space which indicates an excitation of a net spin-polarized

photocurrent even with linear pump polarization [Phys. Rev. Lett. **116**, 076801 (2016)]. Moreover, the pump polarization can control the asymmetric population, *i.e.* the surface photocurrent, through the coherent optical transition of the surface Dirac-cone [Phys. Rev. B **95**, 081103(R) (2017)]. By observing the decay of the asymmetric population, the ultrafast dynamics of the photocurrent in the surface Dirac-cone is directly investigated. Our discovery promises important advantages of photoexcitation by mid-infrared pulses for optospintronic applications.

**3:00pm MI+2D+AC+NS-TuA3 Enhancement of Voltage-Controlled Magnetic Anisotropy Through Metallic Insertion at the CoFeB/MgO Interface, Kevin Fitzell, X. Li, C.T. Karaba, A. Buditama, G. Yu, K. Wong, University of California at Los Angeles (UCLA), D. Wu, UCLA; Fudan University, Republic of China, N. Altieri, C. Grezes, UCLA, N. Kiousis, CSU, Northridge, S.H. Tolbert, UCLA, Z. Zhang, Fudan University, Republic of China, J.P. Chang, P.K. Amiri, K.L. Wang, UCLA**

Paramount to the continued scaling of MRAM devices is a comprehensive understanding and control of the factors affecting the interfacial phenomena that occur at the CoFeB/MgO interface, from which the perpendicular magnetic anisotropy (PMA) of the CoFeB originates. Efficient manipulation of this PMA using an applied voltage, known as the voltage-controlled magnetic anisotropy (VCMA) effect, offers significant energy savings over electric-current-controlled alternatives such as STT-RAM. *Ab initio* studies in the literature on Fe/MgO interfaces revealed a dependence of the VCMA effect on the oxidation state of interfacial Fe atoms<sup>1</sup> and on the addition of various heavy metal insertion layers<sup>2</sup> at the CoFeB/MgO interface. While this effect of metallic insertion layers at the CoFeB/MgO interface has not been extensively studied experimentally, inserting a thin Mg layer at the CoFeB/MgO interface has been shown in the literature to improve the (001) texture of the MgO, the tunneling magnetoresistance (TMR) ratio of the MTJ, and the thermal stress stability of the CoFeB layer's PMA.<sup>3,4</sup> What is lacking in the literature, however, is experimental work studying the dependence on the VCMA effect of Mg insertion layers at the CoFeB/MgO interface.

In this work, the impact of several types of metallic insertion layers (Ta, Pt, and Mg) at the CoFeB/MgO interface on the VCMA characteristics and other magnetic properties is studied. For the case of Mg insertion, four different regimes of materials properties were observed, corresponding to the oxidation state at the CoFeB/MgO interface. Inserting an ultrathin Mg layer of 0.1–0.3 nm yielded a VCMA coefficient of ~100 fJ/V $\times$ m, representing more than a factor of 3 improvement over average values of ~30 fJ/V $\times$ m reported in Ta/CoFeB/MgO-based structures. Ultrathin Ta and Pt insertion layers also showed a small improvement, yielding VCMA coefficients around 40 fJ/V $\times$ m. Electrical, magnetic, and synchrotron-based X-ray diffraction results reveal that a 1.1–1.3 nm Mg insertion layer gives rise to the highest perpendicular magnetic anisotropy and saturation magnetization, as well as to the best CoFe and MgO crystallinity; Mg insertion layers thicker or thinner than this give rise to either under- or over-oxidation of the CoFeB/MgO interface. These results demonstrate that precise control over the oxidation level at the CoFeB/MgO interface is crucial for the development of electric-field-controlled perpendicular magnetic tunnel junctions with low write voltage.

**3:20pm MI+2D+AC+NS-TuA4 THz Radiation Generated from Interfacial Rashba Spin-orbit Coupling, M.B. Jungfleisch, Argonne National Laboratory, Q. Zhang, Argonne National Laboratory, W. Zhang, Oakland University, J.E. Pearson, H. Wen, Axel Hoffmann, Argonne National Laboratory**

Electromagnetic terahertz (THz) radiation is a versatile tool for a wide variety of sensing technologies ranging from security systems to medical applications. Commonly THz radiation is generated using semiconducting materials and using their inherent charge dynamics. Recently, it was also demonstrated that optical excitation of fast spin current pulses in magnetic materials may generate strong broadband THz radiation from transverse spin transport phenomena, known as spin Hall effects. These experiments rely on a bulk conversion of spin currents into charge current, which then subsequently generate the THz radiation. Here we investigate whether interfacial spin-orbit coupling phenomena may also be an efficient source for generating THz radiation. For this purpose we combine a bilayer of Ag and Bi, which is known to have strong Rashba-type spin-orbit coupling at its interface with a magnetic CoFeB layer. Upon optical excitation we also observe in this system THz radiation. Additional experiments with individual Ag and Bi layers show that this radiation originates from interfacial spin galvanic effects. Furthermore, we demonstrate that the amplitude of the THz radiation varies with the helicity of the incident optical light pulse. These observations open up new perspectives for the development of ultrafast spintronic devices.

This work was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division. Lithographic patterning was carried out at the Center for Nanoscale Materials, which is supported by DOE, Office of Science, BES (#DE-AC02-06CH11357).

**4:20pm MI+2D+AC+NS-TuA7 Spin-orbit Coupled d-electron Surface States of Delafossite Oxides, Phil King, University of St Andrews, UK INVITED**

The ABO<sub>2</sub> family of delafossite oxide metals has recently found renewed prominence due to their remarkable transport properties. The Pd- and Pt-based cobaltates are the most conductive oxides known, with room-temperature resistivities lower per carrier even than copper metal [1,2]. Meanwhile, giant low-temperature mean-free paths of up to 10<sup>5</sup> lattice spacings make hydrodynamic effects of the electron fluid observable in mesoscopic samples [3] and lead to a curious negative longitudinal magnetoresistance [4]. This is all underpinned by extremely broad bandwidths of the bulk electronic structure around the Fermi level, dominated by Pd/Pt-derived carriers that behave remarkably like free electrons [2], in part mediated by an unusual interplay with correlations which renders the Co block insulating. The crystal structure is polar, however, opening the potential for their surface electronic structures to be dramatically different to that of the bulk [5,6]. Here, we will show how these surfaces support strongly spin-split electronic states, and discuss the intriguing interplay of spin-orbit coupling and electronic interactions that they host.

*Key collaborators on this work include Veronika Sunko (St Andrews and Max-Planck Institute for Chemical Physics of Solids, Dresden), Federico Mazzola (StA), and Helge Rosner, Pallavi Kushwaha, Seunghyun Khim, and Andy Mackenzie (MPI-CPFS).*

- [1] Hicks *et al.*, Phys. Rev. Lett. 109 (2012) 116401
- [2] Kushwaha *et al.*, Science Adv. 1 (2015) e1500692
- [3] Moll *et al.*, Science 351 (2016) 6277
- [4] Kikugawa *et al.*, Nature Commun. 7 (2016) 10903
- [5] Kim *et al.*, Phys. Rev. B 80 (2009) 035116
- [6] Noh *et al.*, Phys. Rev. Lett. 102 (2009) 256404

**5:00pm MI+2D+AC+NS-TuA9 Understanding the Interfacial Interaction and Isotope Effects in Organic Spin Valve Structures, Alexandra Steffen, N. Herath, J. Keum, H. Zhang, K. Hong, J. Jakowski, J. Huang, J. Browning, C.M. Rouleau, I.N. Ivanov, V. Lauter, Oak Ridge National Laboratory**

Spin-dependent phenomena, such as the extended spin relaxation time and spin diffusion length due to the very weak spin-orbit coupling found in organic spin valves (OSV), are of interest from the view of both fundamental research and development of low power spintronic devices.

While deuteration is widely used for contrast variation measurements under the assumption that the deuterated structure shows identical characteristics in comparison to the protonated version, recently, strong isotopic effect on optoelectronic properties was reported and a remarkable reduction in the open circuit voltage was found [1].

In OSV systems, the interfacial properties are crucial for the understanding of the origin of the macroscopic properties. Still, to identify the exact behavior of the interfaces remains challenging, especially for buried soft matter/hard matter interfaces. Here, we utilize via Polarized Neutron Reflectometry to study depth-resolved the magnetic and chemical structure.

Our system under investigation are prototype spintronic devices with LSMO/polymer/Co trilayer structure, where polyfluorene (PFO) is selected as an optimal 'hole' conducting polymer through the model pre-screening based on the electron affinity and electron's effective mass values obtained from theoretical calculations. Using the exceptional syntheses and deuteration capabilities we have recently completed syntheses of four PFO isotopes, *i.e.*, protonated (P), main-chain deuterated (MD), side-chain deuterated (SD) and fully deuterated (FD) PFOs. By creating such modified polymers, the subatomic, intermolecular and interfacial interactions are modified and characteristics like the  $\pi$ - $\pi$  interaction become tunable. For neutron scattering experiments, the nuclear cross-section varies with the isotopic substitution, thus via changing the contrast with chain-specific deuteration, different parts of a sample are investigated individually.

While our main goal is the understanding the effect of deuterium substitution on the spin-dependent electron transport, in this presentation, we will focus on the details of the structural and magnetization profiles on both LSMO/polymer and polymer/Co interfaces and their impact on the coupling between magnetic layers. We will present the results obtained via Polarized Neutron Reflectometry and discuss the interpretation of the depth-resolved magnetometry study.

- [1] Ming Shao *et al.*, The isotopic effects of deuteration on optoelectronic properties of conducting polymers. *Nature Communications*, 5:3180, January 2014.

5:20pm **MI+2D+AC+NS-TuA10 Dispersion and Spin Structure of Conduction Bands of Single-layer TMDC's on Au(111)**, *Philipp Eickholt\**, M. Holtmann, Westfälische Wilhelms-Universität Münster, Germany, C.E. Sanders, M. Dendzik, M. Bianchi, P. Hofmann, Aarhus University, Denmark, M. Donath, Westfälische Wilhelms-Universität Münster, Germany

In the field of 2D materials, single-layer transition metal dichalcogenides, especially MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub> and WSe<sub>2</sub>, play an important role. Due to their exceptional optical and electronic properties, they are promising materials for optoelectronic applications [1]. The key to understand the material properties is a profound knowledge of the electronic structure. While the occupied electronic structure was investigated in a number of studies, the crucial information about the dispersion and spin structure of the conduction bands is still missing.

Spin- and angle-resolved inverse photoemission (SRIPE) [2] is the ideal technique to study dispersion and spin structure of the unoccupied electronic bands. In this talk, we present a SRIPE study of the conduction bands of single-layer WS<sub>2</sub> [3] and MoS<sub>2</sub> [4] grown on Au(111).

The focus of the presentation will be on the lowest conduction band near the K valley, which is decisive for the optoelectronic properties of the materials. The results will be discussed in consideration of a recent pump-probe (TR-ARPES) experiment [5], which determined the band gap of the “pumped” system.

[1] D. Xiao *et al.*, Phys. Rev. Lett. **108**, 196802 (2012)

[2] S.D. Stolwijk *et al.*, Rev. Sci. Instrum. **85**, 013306 (2014)

[3] M. Dendzik *et al.*, Phys. Rev. B **92**, 245442 (2015)

[4] A. Bruix *et al.* Phys. Rev. B **93**, 165422 (2016)

[5] A. Grubišić Cabo *et al.*, Nano Lett. **15**, 5883 (2015)

5:40pm **MI+2D+AC+NS-TuA11 Unraveling the Spin Structure of Unoccupied States in Bi<sub>2</sub>Se<sub>3</sub>**, *Markus Donath*, C. Datzner, A. Zumbütle, Westfälische Wilhelms-Universität Münster, Germany, J. Braun, LMU München, Germany, T. Förster, A.B. Schmidt, Westfälische Wilhelms-Universität Münster, Germany, J. Mi, B. Iversen, P. Hofmann, Aarhus University, Denmark, J. Minár, University of Pilzen, Czech Republic, H. Ebert, LMU München, Germany, P. Krüger, M. Rohlfing, Westfälische Wilhelms-Universität Münster, Germany

In topological insulators, spin-orbit coupling leads to the emergence of metallic topological surface states crossing the fundamental band gap. The optical control of spin currents in topological surface states opens new perspectives in (opto-) spintronics. To understand these processes, a profound knowledge about the dispersion and the spin polarization of both the occupied and the unoccupied electronic states is required. We present a joint experimental and theoretical study on the unoccupied electronic states of the topological insulator Bi<sub>2</sub>Se<sub>3</sub> [1]. We discuss spin- and angle-resolved inverse-photoemission results in comparison with calculations for both the intrinsic band structure and, within the one-step model of (inverse) photoemission, the expected spectral intensities. This allows us to unravel the intrinsic spin texture of the unoccupied bands at the surface of Bi<sub>2</sub>Se<sub>3</sub>.

[1] Datzner *et al.*, Phys. Rev. B **95**, 115401 (2017)

# Tuesday Evening Poster Sessions

## Actinides and Rare Earths Focus Topic

Room: Central Hall - Session AC-TuP

### Actinide and Rare Earth Poster Session

#### **AC-TuP2 Sputter-Deposited Layers for Solid Phase Microextraction, Tuhin Roychowdhury, D. Patel, M.R. Linford, Brigham Young University**

Solid phase microextraction (SPME) is an effective analyte sampling method. It works by placing a coated fiber above a sample (headspace mode) or immersing it in a liquid sample such that molecules (analytes) of interest can be selectively captured and concentrated. The extracted species are then released into a chromatograph for separation, identification, and quantification. It is a 'green' method as no additional solvent is required in this process. Recently, we have developed a new class of SPME fibers that offer extraordinary capacity, sensitivity, and speed. They are prepared by sputtering a material under conditions that lead to a robust nanoporous coating on the fiber. In particular, silicon sputtering generates a porous surface that can be additionally oxidized, leading to a high density of silanol groups than can be subsequently silanized or used in other depositions. The surfaces and materials generated for SPME in this project have been characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), spectroscopic ellipsometry (SE), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and wetting. They confirm the synthesis of highly porous, hydrophobic materials. The performance of our 2 micron sputtered coatings has been compared to that of thicker (7 micron) commercial coating. Our fiber consistently outperforms the commercial fiber, showing significantly higher capacity, for example, for high molecular weight polycyclic aromatic hydrocarbons (PAHs). PAHs are a significant environmental pollutant. (They are produced from industrial wastes, incomplete combustion of fossil fuels, and natural emissions, and are detrimental to human health and the environment due to their carcinogenicity.) Hence, there is a need to identify these toxic pollutants. Real world samples, e.g., hops have also been analyzed. Different sputter coating thicknesses have been prepared and evaluated.

#### **AC-TuP3 Mechanical Behavior Improvement of Coated Epoxy Resins Exposed To Environmental Effects, Dorina Mihut, A. Afshar, S. Hill, Mercer University, G. Negrea, Technical University Cluj Napoca, Romania, R. Alyamani, A. Aldhubaie, Mercer University**

##### **Abstract:**

Epoxy resins based materials are widely used as a matrix component for marine, aviation, transportation and civil infrastructures as they are light weight and are offering high strength and stiffness-to-weight ratio as well as good corrosion resistance. However, during their usage these materials are exposed to exterior environmental effects which can significantly degrade their mechanical properties and preclude their prolonged use. The present research investigates the influence of metallic and ceramic coatings in order to enhance the mechanical behavior of the epoxy resin based substrate materials to a combination of exterior factors: ultraviolet (UV) radiation, moisture and erosion. The metallic and ceramic coatings were deposited using high vacuum DC magnetron sputtering equipment. The pristine and coated polymer based samples were further exposed to continuous and cyclic UV radiation and moisture (ASTM G 154 standard). The samples' morphology was characterized using optical microscopy and X-ray diffraction analysis was used for determining the chemical composition of the coatings. The mechanical properties of all samples were tested using the standardized three points bending test and their erosion behavior was also tested using an erosion tester.

# Wednesday Morning, November 1, 2017

## Novel Trends in Synchrotron and FEL-Based Analysis

### Focus Topic

Room: 9 - Session SA+2D+AC+MI-WeM

### Recent Advances of Diffracting/Scattering and Spectroscopic Methods for Correlated and 2D Materials

**Moderators:** Hans-Peter Steinrück, University Erlangen-Nuernberg, Germany, Kristina Edström, Uppsala University, Sweden

8:00am **SA+2D+AC+MI-WeM1 Studies of Surfaces and Catalysis in real time with X-ray Free Electron Laser**, *Anders Nilsson*, Stockholm University, Sweden **INVITED**

In heterogeneous catalysis, reactants adsorbed on surfaces are converted to products, which eventually desorb via various intermediates. The transition state separates reactants and intermediates from products and the free energy required to reach it determines the kinetics of an elementary chemical reaction. Many surface reaction intermediates are, however, transient species with a short residence time and the population of species in the transition state region is near-zero making their observation a challenge during steady state conditions. Ultrafast pump-probe techniques have, however, opened up opportunities by promoting a sufficient population of molecules in transient states to allow detection on short time scales. Here recent results on probing chemical reactions on surfaces using X-ray free-electron lasers LCLS (Linac Coherent Light Source) at SLAC National Accelerator Laboratory) will be presented. Four examples will be shown CO desorption, Oxygen activation, CO oxidation and CO hydrogenation on Ru(0001). We demonstrate that both transient intermediates and the transition state region can be detected in surface chemical reactions.

8:40am **SA+2D+AC+MI-WeM3 New Generation RIXS of 3d-TM Oxides**, *Giacomo Ghiringhelli*, Politecnico Milano, Italy **INVITED**

Resonant inelastic soft x-ray scattering huge potential is quickly becoming reality. RIXS is element and site selective, like x-ray absorption spectroscopy. It is momentum resolved, like x-ray diffraction. And it probes several kinds of excitations at a time, from charge transfer and electron-hole pair generation, to orbital (*dd* or *ff*) excitations, to spin waves and lattice modes, unlike any other energy loss spectroscopy. Moreover, the elastic component of the spectra carries information on commensurate and incommensurate orders, such as charge density waves (CDW) and orbital order. The ERIXS endstation at the ID32 beam line of the ESRF is the founder of a new generation of RIXS instruments capable of exploiting all the strongpoints of this technique, thanks to the very high resolving power (30,000 at 1 keV), the diffractometer-like manipulator and the full control of photon polarization provided by the combination of the APPLE II source and the polarimeter on the analyzer.

I will review some of the results obtained in the first year of operations of ID32, with a special focus on cuprate superconductors studied at the Cu  $L_3$  edge. High resolution RIXS has been used to determine the relation between crystal structure and the extent of hopping integrals in parent compounds, revealing why apical oxygens are detrimental to superconductivity [1]. Ultra-high resolution RIXS has provided a direct measurement of the momentum-dependent electron phonon coupling in undoped and superconducting samples, and has revealed new collective modes related to charge density waves (CDW) in underdoped Bi2212. Polarization analysis has definitively demonstrated the spin-flip character of the mid-IR spectral region in superconducting compounds. And the quasi-elastic part of RIXS spectra has brought new evidence of the universality of charge ordering phenomena in cuprates, including striped cuprates [2] and single layer Bi2201. Finally the feasibility of high resolution RIXS in standing wave geometry has been successfully demonstrated, adding depth control on this bulk sensitive technique.

[1] Y. Y. Peng, G. Dellea, M. Minola, M. Conni, A. Amorese, D. Di Castro, G. M. De Luca, K. Kummer, M. Salluzzo, X. Sun, X. J. Zhou, G. Balestrino, M. Le Tacon, B. Keimer, L. Braicovich, N. B. Brookes and G. Ghiringhelli, [https://arxiv.org/abs/1609.05405]

[2] H. Miao, J. Lorenzana, G. Seibold, Y. Y. Peng, A. Amorese, F. Yakhov-Harris, K. Kummer, N. B. Brookes, R. M. Konik, V. Thampy, G. D. Gu, G. Ghiringhelli, L. Braicovich, M. P. M. Dean, [https://arxiv.org/abs/1701.00022]

9:20am **SA+2D+AC+MI-WeM5 Resonant Inelastic X-ray Scattering on Low-Dimensional Correlated Transition Metal Oxides and Oxide Heterostructures**, *Thorsten Schmitt*, Paul Scherrer Institut, Switzerland **INVITED**

Resonant inelastic X-ray scattering (RIXS) is a powerful bulk-sensitive photon-in / photon-out spectroscopic probe of the electronic structure of condensed matter with atomic and orbital sensitivity. It is a unique tool for studying excitations from the electronic ground state in correlated transition-metal oxides, being directly sensitive to lattice-, charge-, orbital- and spin-degrees of freedom. In this talk, we report RIXS investigations of the  $\text{LaTiO}_3$  layers in  $(\text{LaTiO}_3)_n/(\text{LaAlO}_3)_5$  superlattices undergoing a transition from  $\text{Ti}^{3+}$  to  $\text{Ti}^{4+}$  oxidation state upon reducing  $n$  and thickness as well as temperature-driven metal-insulator transitions in thin films of  $\text{CaVO}_3$ .

$(\text{LaTiO}_3)_n/(\text{LaAlO}_3)_5$  superlattices (SL) composed of a band-insulator ( $\text{LaAlO}_3$ ) and a Mott-insulator ( $\text{LaTiO}_3$ ) present an enhanced insulating character when  $n$  is reduced. We prepared a set of SLs ( $n=10, 5$  and 2 unit cells) and investigated these with X-ray absorption spectroscopy (XAS) and RIXS. XAS shows a clear change in the Ti valence going progressively from the nominal  $\text{Ti}^{3+}$  ( $3d^1$ ,  $n=10$  u.c.) for bulk  $\text{LaTiO}_3$  to an almost pure  $\text{Ti}^{4+}$  ( $3d^0$ ,  $n=2$  u.c.). RIXS reveals two spectral developments when reducing the  $\text{LaTiO}_3$  thickness  $n$ : 1) reduction of intra- $t_{2g}$  / intra- $e_g$  splitting and increase of  $t_{2g}$  to  $e_g$  separation and 2) increase of the charge transfer excitation spectral weight. The changes in the energy of the orbital levels observed as a function of  $n$  reveal a clear change of the local  $\text{TiO}_6$  distortion. We suggest that an inverse Jahn-Teller effect, inducing the octahedra to assume higher symmetry, is responsible for the observed orbital energy shifts. This peculiar effect is partially caused by strain, triggering a  $3d^1 \rightarrow 3d^0$  electron transition at the interfacial Ti sites.

Bulk  $\text{CaVO}_3$  is a correlated paramagnetic metal. Thin films of  $\text{CaVO}_3$  undergo a metal-insulator transition (MIT) when the thickness is reduced below ca. 20 u.c.. Our XAS and RIXS measurements at the V  $L$ -edge across this dimensionality driven MIT in  $\text{CaVO}_3$  reveal a large transfer of spectral weight from fluorescent to Raman modes upon entering the insulating state. We observe a large reduction in the charge excitation bandwidth and V-O covalence across the thickness and temperature-driven MIT. Further analysis of the charge modes suggests a bandwidth-controlled MIT, assisted by the presence of strong correlations.

11:00am **SA+2D+AC+MI-WeM10 Doping of Graphene Exploited with Spectromicroscopy**, *Carla Bittencourt*, University of Mons, Belgium **INVITED**

Limitations in characterisation and theoretical modelling tools have been a major obstacle for the engineering of novel functional materials with properties enhanced by their nanoscale morphology, because detailed understanding of the structure-property-operando relationships are required. In this perspective technology has entered in a period of convergence between theory and characterisation tools, traditional spectroscopic techniques are being combined with microscopy to characterise individual nano-objects. In this context advances in the design and fabrication of x-ray focusing systems allow modifying conventional X-ray spectroscopies using synchrotron light to be used to study individual nanostructures and selected regions of a nanoscale sample. These spectroscopies are amongst the most powerful tools in material science providing elemental, electronic, structural and chemical information. Recent trends include in-operando analysis of individual nanostructures.

In my talk I will report recent results obtained using spectromicroscopy techniques to study the doping of suspended graphene flakes. The nitrogen doping of suspended graphene was performed via ion implantation. We will show that inclusion of up to 20 at.% nitrogen can be reached, while maintaining a  $sp^2$ -network. The evolution of nitrogen species: pyridinic, graphitic, and pyrrolic, at different doping stages and annealing temperatures is observed by scanning X-ray photoelectron microscopy (SPM). Variations in the ratio between  $sp^2$  nitrogen species is observed for increasing treatment time; thermally heating the doped carbon nanostructure results in quenching of the  $sp^3$  component, suggesting the graphitic nitrogen as the most thermal stable species. The effect of the interaction of molecular oxygen with nitrogen doped graphene will be discussed.

11:40am **SA+2D+AC+MI-WeM12 Multi-modal and Multi-dimensional Synchrotron Investigation of Functional Materials**, *Karen Chen-Wiegart*, Stony Brook University/Brookhaven National Laboratory **INVITED**

Multi-modal and multi-dimensional characterization at synchrotrons can provide unprecedented information for complex, heterogeneous materials system. A multi-modal approach combines multiple synchrotron techniques to gain complementary information. Furthermore, with imaging techniques

specifically, multi-dimensional imaging includes techniques such as tomography, spectroscopic microscopy, or in *situ/operando* imaging. These capabilities are particularly powerful when used to study complex structures with morphological and chemical heterogeneity. This talk will address the applications in energy storage and conversion materials, including Li-ion batteries, Li-S batteries, and solid-oxide fuel cells. Other examples, including nano-/meso-porous metals, cultural heritage and surface treatment on metals will also be briefly discussed.

## Novel Trends in Synchrotron and FEL-Based Analysis

### Focus Topic

Room: 9 - Session SA+AC+MI-ThM

## Frontiers in Probing Properties and Dynamics of Nanostructures and Correlation Spectroscopy

**Moderators:** Jan Vogel, Institut Néel, CNRS/UGA, Grenoble, France, Christian Gutt, University of Siegen, Germany

### 8:00am SA+AC+MI-ThM1 X-rays Revealing Exotic Properties of Magnetoelectric Multiferroics and Related Materials, *Elke Arenholz*, Lawrence Berkeley National Laboratory **INVITED**

Engineering novel materials with structural, electronic and/or magnetic characteristics beyond what is found in bulk systems is possible today through the technique of thin film epitaxy, effectively a method of 'spray painting' atoms on single crystalline substrates to create precisely customized thin films or layered structures with atomic arrangements defined by the underlying substrate. The abrupt change of composition at as well as charge and spin transfer across interfaces can also lead to intriguing and important new phenomena testing our understanding of basic physics and creating new functionalities.

We use soft x-ray spectroscopy and scattering to probe and understand the electronic, magnetic and structural characteristics of novel engineered materials such as magnetoelectric multiferroics, i.e. materials that exhibit simultaneous order in their electric and magnetic ground states. These materials hold promise for use in next-generation memory devices in which electric fields control magnetism but are exceedingly rare in bulk form. Engineering magnetoelectric multiferroics by interleaving two or more atomically thin layers is an intriguing new approach. A very recent example is establishing room temperature coexisting ferromagnetic and ferroelectric order in  $\text{LuFeO}_3/\text{LuFe}_2\text{O}_4$  superlattices. [1] We used soft x-ray spectroscopy and microscopy to characterize the magnetic order and ferroelectric polarization of the system.

Similarly intriguing is engineering the orbital symmetry of emergent quantum states near the Fermi edge at interfaces determining the mobility of interfacial conduction electrons in novel heterostructures. Using soft x-ray linear dichroism (XLD), we investigated the orbital states of interfacial electrons in  $\text{Al}_2\text{O}_3/\text{SrTiO}_3$  and developed an interesting route to engineer emergent quantum states with deterministic orbital symmetry [2].

[1] J. A. Mundy *et al.*, Nature **537**, 523 (2016).

[2] Y. Cao *et al.*, npj Quantum Materials **1**, 16009 (2016).

### 8:40am SA+AC+MI-ThM3 X-ray Reflectivity Investigations of Ultrafast Dynamics in Magnetic Multilayer Structures, *Christian Gutt*, T. Sant, D. Ksenzov, U. Pietsch, University of Siegen, Germany, J. Luening, Sorbonne University, F. Capotondi, E. Pedersoli, M. Manfreda, M. Kiskinova, Elettra-Sincrotrone Trieste, Italy, M. Klaui, H. Zabel, University of Mainz **INVITED**

*Exciting a ferromagnetic material with an ultrashort IR laser pulse is known to induce a reduction of magnetic order and ultrafast spin diffusion processes. Both processes produce disorder on 100s fs scales and their role in a deterministic creation and switching of magnetic order is still poorly understood. Here, we demonstrate that a nanoscale magnetization-reversal exists in the vicinity of domain walls in the near-surface region of a ferromagnetic Co/Pd thin film upon IR excitation. This magnetization-reversal is driven by the different transport properties of majority and minority carriers through a magnetically disordered domain network. We followed the ultrafast temporal evolution by means of an ultrafast resonant magnetic scattering experiment in surface scattering geometry, which enables to exploit the domain network within the top 3 nm to 5 nm layers of the FM film. We observed magnetization-reversal close to the domain wall boundaries that becomes more pronounced moving closer to the film surface. Its lateral extension has allowed us to measure the ultrafast spin-diffusion coefficients and ultrafast spin velocities for majority and minority carriers upon IR excitation.*

### 9:20am SA+AC+MI-ThM5 Spray Deposition of Water-processed Active Layers of Hybrid Solar Cells Investigated with In situ X-ray Scattering Methods, *Volker Körstgens*, F. Buschek, M. Wörle, Technische Universität München, Germany, W. Ohm, DESY, Germany, H. Iglev, Technische Universität München, Germany, S.V. Roth, DESY, Germany, R. Kienberger, P. Müller-Buschbaum, Technische Universität München, Germany

In the development of non-conventional solar cells not only the achievements of highest power conversion efficiencies and maximum lifetime of devices is of interest. Also the sustainability of the production process of the devices comes into focus. In order to achieve an all-embracing green technology, the materials applied and the required energy for device fabrication are of importance. Materials in terms of functional components or as additives in the processing should be non-toxic and environmentally friendly. In an optimum approach no organic solvents should be used for the coating of any of the layers of the corresponding devices. High temperature processing steps should be reduced or avoided to increase the energy payback times of the solar cells. Following this idea, we developed hybrid solar cells with an active layer based on low temperature processed titania and a water-soluble polymer [1]. In our approach titania nanoparticles are produced with laser ablation in liquid in order to initiate a functionalization of titania with the polymer for the active layer. Combining these titania nanoparticles and water-soluble poly[3-(potassium-6-hexanoate)thiophene-2,5-diyl] (P3P6T) hybrid solar cells are realized. In order to improve conversion efficiencies of these devices a vertical compositional gradient of the two components of the active layer was introduced. For the fabrication of hybrid photovoltaic devices we applied spray-coating as the deposition method for the active layer which could easily scale-up to industrial cost-effective fabrication. For the deposition of the active layer with laser-ablated particles spray deposition provides a good control of the film thickness. The morphology of the active layer is of major importance for the performance of hybrid solar cells. We are especially interested in how the morphology changes with ongoing deposition process. Therefore we followed the development of the morphology of the active layer in situ with high spatial and temporal resolution. The mesoscale was probed with in situ GISAXS, whereas the crystallinity of the polymer and the inorganic component was investigated with in situ GIWAXS. The changes of the morphology and the influence on photovoltaic performance with the introduction of a compositional gradient are discussed. As the synchrotron-based investigation allowed for a high temporal resolution of 0.1 s, insights into the very first stages of the deposition process were obtained. From the overall situ study improvements for the spray deposition procedure are derived that allow for a better control of the morphology of the devices.

[1] Körstgens *et al.*, Nanoscale **7**, 2900 (2015)

### 9:40am SA+AC+MI-ThM6 New Instrumentation for Spin-integrated and Spin-resolved Momentum Microscopy – METIS and KREIOS, *Thomas Schulmeyer*, M. Wietstruk, A. Thissen, SPECS Surface Nano Analysis GmbH, Germany, G. Schoenhense, Johannes Gutenberg-Universität, Germany, A. Oelsner, Surface Concept GmbH, Germany, C. Tüsche, Max Planck Institute for Microstructure Physics, Germany

Two new momentum microscopes are presented by SPECS: our newly developed time-of-flight momentum microscope METIS and the energy dispersive and filtered momentum microscope KREIOS. Both are using an optimized lens design which provides simultaneously highest energy, angular and lateral resolution. The lens provides a full  $2\pi$  solid acceptance angle with highest angular resolution. In contrast to standard ARPES measurements with conventional hemispherical analyzers, electronic structure data from and beyond the 1st Brillouin zone is recorded without any sample movement. In addition the lens of such an instrument can work in a lateral imaging mode for microscopy as well. This enables navigation on the sample and reduces the size of the area under investigation in ARPES down to a few micrometers in diameter. This combination of large acceptance angle, high angular resolution and small acceptance area, makes this instrument the ideal tool for electronic structure studies on small samples or sample areas. The design is compact with a straight optical axis. Operation modes are  $(k_x, k_y, E_k)$  data acquisition by operation in energy filtered k-space imaging, (ToF)-PPEM mode, energy-filtered real space imaging and micro-spectroscopy mode.

The 3D  $(k_x, k_y, E_k)$  data recording is done with a 2-dimensional delayline detector, with a time resolution of 150 ps and count rates up to 8 Mcps. It uses channelplates with 40  $\mu\text{m}$  spatial resolution. While the x,y position of an incoming electron is converted into  $k_x, k_y$  wave vector, the kinetic energy  $E_k$  is determined from the flight time  $t$  in METIS or obtained directly by the energy filter in KREIOS. Spin-resolved imaging is achieved by electron reflection at a W(100) spin-filter crystal prior to the 2-dimensional delayline detector. Electrons are reflected in the [010] azimuth at  $45^\circ$  reflection angle. Varying the scattering energy one can choose positive, negative, or vanishing reflection asymmetry.

Besides a description on how the instruments work data from both instruments on different single crystalline materials will be presented.

11:00am **SA+AC+MI-ThM10 X-ray Photon Correlation Spectroscopy Studies of Soft Matter and Biomaterials, Laurence B. Lurio**, Northern Illinois University **INVITED**

The use of x-ray photon correlation spectroscopy to study dynamics in soft materials and bio-materials will be reviewed. Examples will be presented from the dynamics of colloidal suspensions, polymers and concentrated proteins.

11:40am **SA+AC+MI-ThM12 Forefront Applications of XPCS, Anders Madsen**, European XFEL GmbH, Germany **INVITED**

Recent advances in dynamics studies of condensed matter by X-ray photon correlation methods will be discussed. Classical X-ray Photon Correlation Spectroscopy (XPCS) requires a (partially) coherent beam and a reliable detector and has benefitted a lot from recent synchrotron source upgrades and the advent of novel 2D pixel detectors. Weakly scattering systems and fast dynamics can now be characterized much better than only a few years back. The next generation of X-ray sources - X-ray Free-Electron Lasers (XFEL) - will deliver many orders of magnitude more coherent intensity than the present generation of synchrotrons but at the same time the pulsed nature of XFELs requires new XPCS-like techniques to be developed. In the presentation I discuss a few new methods that take advantage of the XFEL pulse pattern and allow dealing with the pertinent problem of beam induced damage to the samples. Examples of Scientific applications in soft- and hard-condensed matter will be given as well as an outlook to the forthcoming European XFEL facility where time-resolved coherent X-ray experiments will be carried out at the MID station.

## Tribology Focus Topic

**Room: 10 - Session TR+AC+TF+VT-ThM**

## Lubricant, Coatings, and Biotribology

**Moderator: J. David Schall, Oakland University**

8:00am **TR+AC+TF+VT-ThM1 Superlubricity of Hard Compliant Carbon Coatings with Green Lubricants: Role of Surface Chemistry and Structural Changes, Maria-Isabel De Barros Bouchet**, Ecole Centrale de Lyon - LTDS, France **INVITED**

Reduction of energy loss by mechanical friction has been strongly required in recent years for improving fuel efficiency especially for automotive engine. Even at a modest rate, it is of primary importance to reduce parasitic energy losses and provide environmental sustainability. An approach to achieve this target is the development of new lubrication technologies, combining new lubricant formulations and cutting-edge coatings transferable to industrial applications. Since superhard carbon material like tetrahedral amorphous carbon (ta-C) and Nano-Crystalline Diamond (NCD) coatings combine both crucial properties, high hardness with an ultra-smooth surface roughness, they have attracted a growing interest in the last decade. While the friction coefficient is generally extremely high under ultra high vacuum conditions, in the earlier years we have discovered the ability of these coatings to be lubricated by selected biodegradable green molecules like fatty acids, glycerol mono-oleate GMO and polyols, as well as their mixture with synthetic base oil such as Poly-Alpha Olefines (PAO). Some of these compounds are able to lubricate ta-C and NCD coatings with a friction coefficient below 0.01 (so-called superlubricity) in thin-film EHL/mixed regime and below 0.03 in severe boundary regime without significant wear. As this case of superlow friction is extremely promising for many applications fields, the related mechanism has been investigated and a special attention has been paid to the surface chemistry and structural changes of the carbon coatings. By coupling advanced extreme surface analyses (PES and XANES), we show that the mechanism of friction reduction is related to the tribo-formation of quasi-2D planar graphene-like structures at the top of the colliding asperities (thickness about 1 nm). Eventually, the graphene can be slightly oxidized by the OH-groups coming from the tribo-decomposition of the lubricant molecules trapped between asperities. Moreover, the rubbed sub-surface is enriched with sp<sup>2</sup>-hybridized carbon, such as in a soft a-C material, during the friction. These strong structural changes certainly ease the tribochemical-formation of the carbon rings present in the graphene-like structure as pointed out by atomistic computer simulations.

1. M. Kano, J. M. Martin, K. Yoshida, M.I. De Barros Bouchet, Friction J., 2 (2) (2014) 156.

2. M.I. De Barros Bouchet, J.M. Martin, J. Avila, M. Kano, K. Yoshida, T. Tsuruda, S. Bai, Y. Higuchi, N.i Ozawa, M. Kubo and M. C. Asensio, Scientific Reports, 2017 (DOI: 10.1038/srep46394).

8:40am **TR+AC+TF+VT-ThM3 Role of Deuterium and Hydrogen in the Physical Understanding of Nano-friction in a-C:H/D Thin Films, F.G. Echeverrigaray, S.R. Sales de Mello, A.F. Michels**, UCS, Brazil, F. Alvarez, UNICAMP, Brazil, **Carlos Figueroa**, UCS, Brazil

The friction phenomenon is a complex manifestation of the nature. In spite of phenomenological laws can describe the friction force at different scales, the fundamental physical understandings of such a phenomenon do not have consensus. Phenomena such as phononic, electronic, magnetic, and also electrostatic effects and models were developed in order to explain the meta- and nano-friction behavior of materials. In this work, we report the friction behavior of a diamond spherical dome sliding on different amorphous carbon thin films containing different amounts of hydrogen and/or deuterium inspecting at the meta-nanoscale indentation. Two important situation are reported. Firstly, for samples where hydrogen was replaced by deuterium in the thin film bulk, the friction coefficient decreases for increasing deuterium included in the carbon underneath structure. Secondly, for samples where hydrogen content is increased on the surface, the friction coefficient decreases with the increasing of the ratio H/C at the surface. In this paper, we discuss two different physical mechanisms describing these peculiar experimental results: dissipation effects associated with phonon coupling and van der Waals forces contributions coexisting and determining the friction behaviour of a-C:H/D for the cited studied situations.

9:00am **TR+AC+TF+VT-ThM4 Imaging X-Ray Absorption Spectroscopic Investigation of the Mechanisms Behind the Environmental Dependence of the Tribological Properties of Amorphous Carbon Surfaces, Filippo Mangolini**, University of Leeds, UK, M. Koshigan, Ecole Polytechnique Montréal, Canada, M.H. Van Benthem, J.A. Ohlhausen, Sandia National Laboratories, J.B. McClimon, J. Hilbert, University of Pennsylvania, J. Fontaine, Ecole Centrale de Lyon, France, R.W. Carpick, University of Pennsylvania

Among the variants of diamond-like carbon films developed for the ever-increasing performance and durability requirements of tribo-mechanical applications, silicon oxide-containing hydrogenated amorphous carbon (a-C:H:Si:O) is of interest as it exhibits good tribological performance across a broader range of environments compared to hydrogenated amorphous carbon, and higher thermo-oxidative stability. However, the scientific basis for this improved behavior is not established. In this work, we develop a fundamental understanding of the structural transformations occurring in a-C:H:Si:O when sliding against steel in different environments (from high vacuum to controlled hydrogen and oxygen pressures). The results of tribological experiments revealed that upon increasing the oxygen pressure in the experimental chamber from 10 mbar to 1000 mbar, the coefficient of friction increased from 0.02±0.01 to 0.06±0.01, whereas upon increasing the hydrogen pressure from 50 mbar to 2000 mbar, the coefficient of friction decreased from 0.08±0.01 to 0.02±0.01. The subsequent near edge X-ray absorption fine structure (NEXAFS) spectroscopic measurements and X-ray photoelectron spectroscopy (XPS) analyses provided insights into the structural transformations and chemical reactions occurring in a-C:H:Si:O upon sliding. Independently of the gas, a stress-induced conversion from sp<sup>3</sup>- to sp<sup>2</sup>-bonded (disordered) C-C bonds occurs. When sliding in hydrogen, the newly-generated, strained sp<sup>2</sup> carbon layer reacts with hydrogen molecules to form a hydrogenated amorphous carbon interfacial material. Upon increasing the hydrogen pressure, the fraction of C-H bonds increases in the near-surface region of the wear tracks formed on a-C:H:Si:O. This is proposed to progressively lower the shear strength of the material at the sliding interface, thus resulting in a decrease of friction with hydrogen pressure. When sliding in oxygen, the dissociative reaction of oxygen molecules with strained sp<sup>2</sup> C-C bonds leads to the formation of C=O groups. Additionally, increasing the oxygen pressure during tribological testing leads to an increase in oxygen concentration in the near-surface region of a-C:H:Si:O together with an increase in the fraction of Si atoms in high oxidation states. These surface chemical changes and structural transformations are proposed to increase friction with oxygen pressure by progressively increasing the shear strength of the material generated at the sliding interface.

9:20am **TR+AC+TF+VT-ThM5 Structure Evolution in Tribological Interfaces Studied by Multilayer Model Alloys, Martin Dienwiebel, E. Cihan**, Karlsruhe Institute for Technology (KIT), Germany **INVITED**

During sliding of surfaces the near surfaces undergo significant changes in terms of topography, composition and microstructure and a so-called "third body" or "tribomaterial" forms which differs strongly from the bulk materials in terms of topography, composition and microstructure. Initially we use multilayer model alloys of an Au/Ni layer system to study effects of grain size on steady-steady friction by varying the layer spacing and the number of layers. Experiments are performed in a UHV microtribometer, the analysis of microstructure before and after tribological stressing is done by FIB and STEM and the chemistry is investigated by XPS. During sliding of surfaces the near surfaces undergo significant changes in terms of topography, composition and microstructure and a so-called "third body" or



“tribomaterial” forms which differs strongly from the bulk materials in terms of topography, composition and microstructure. Initially we use multilayer model alloys of an Au/Ni layer system to study effects of grain size on steady-state friction by varying the layer spacing and the number of layers. Experiments are performed in a UHV microtribometer, the analysis of microstructure before and after tribological stressing is done by FIB and STEM and the chemistry is investigated by XPS.

11:00am **TR+AC+TF+VT-ThM10 Carbon, Carbon Everywhere, from Catalysts to Hip Implants, Laurence Marks, Northwestern University** **INVITED**

Friction is a pervasive problem, by some estimates consuming about 5% of the GDP of the economies of the developed world, and a recent analysis has indicated that about one third of the fuel energy in automobiles goes to overcoming frictional losses. While the importance of minimizing friction can be traced back at least as far as the tomb of Tehuti-Hetep, circa 1880 B.C., where a man can be seen pouring a lubricant to assist moving a statue, there are still many unknowns in the field of tribology which encompasses friction as well as other critical processes such as wear and lubrication. For many of the phenomena in tribology there are still numerous unknowns. When it comes to biological systems most work to date has assumed that different mechanisms are taking place than occur for inorganic systems. While there are differences, there are also significant similarities particularly in implants when inorganic and biological meet. We have recently shown that for metal implants in-vivo the same type of graphitic materials that appear in many areas ranging from heterogeneous catalysis to oil lubrication are present. Beyond just lubrication, corrosion of these materials is not special to biological systems, but has strong similarities to established factors such as grain boundary precipitation and a significant role for molybdenum as reducing the occurrence of breakdown of the protective oxide film via complex processes involving solute trapping. These and related recent results will be described.

11:40am **TR+AC+TF+VT-ThM12 Tribology of Cellular Interfaces, Angela Pitenis, J.M. Urueña, S.M. Hart, T.T. Hormel, C.S. O'Bryan, S.L. Marshall, K.D. Schulze, P.P. Levings, T.E. Angelini, W.G. Sawyer, University of Florida** **INVITED**

Human health, mobility, and quality of life critically hinge on the body's ability to provide adequate lubrication between most contacting and sliding biological interfaces. Soft, aqueous, and mucinated biopolymer networks lining all moist epithelia enable the body to provide lubricity over a wide range of contact pressures and sliding speeds. The exquisite slipperiness and softness of biological sliding interfaces present significant experimental challenges for fundamental studies on their tribological performance. Physiological contact pressure conditions must be matched in in vivo, ex vivo, and in vitro studies that aim to acquire physiologically-relevant friction measurements. While biotribological investigations using living cells, cell layers, and tissues necessitate low contact pressure measurements, such studies frequently rely on the application of low forces to achieve accommodating contact pressures (kPa range), and traditional methods can decrease the contact area below a physiologically-relevant threshold. The softness of a cell layer ( $E \sim 10$  kPa) provides an order-of-magnitude estimate for the amount of mechanical pressure that may be applied to cells during tribological testing; contact pressures about 5 kPa and shear stresses in excess of 200 Pa are sufficient to wreak significant damage to a cell layer. Recently, direct contact tribological experiments on a living cell layer without incurring any measurable cell death in the sliding path has become possible through the application of a soft, thin, spherically-capped membrane hydrogel probe. With this experimental configuration, in vitro tribological experiments were performed against a monolayer of mucin-producing human corneal epithelial cells (hTCEpi) for 10,000 reciprocating cycles at physiologically-relevant contact pressures and challenging sliding speeds. The gel-cell sliding interface under applied normal loads of  $\sim 200$   $\mu$ N resulted in measured friction coefficients of  $\mu \sim 0.06$  and achieved shear stresses on the order of 60 Pa, which is below the critical shear stress for inducing cell death; excellent cell survival rates ( $\sim 99.8\%$ ) were measured after extended duration tribological experimentation.

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 Keum, J.: MI+2D+AC+NS-TuA9, **10**  
 Kienberger, R.: SA+AC+MI-ThM5, **15**  
 King, A.H.: SU+AC+MI+MS-TuM1, **7**  
 King, P.D.C.: MI+2D+AC+NS-TuA7, **10**  
 Kioussis, N.: MI+2D+AC+NS-TuA3, **10**  
 Kirby, B.J.: MI+2D+AC+SA+SS-TuM13, **7**  
 Kiskinova, M.: SA+AC+MI-ThM3, **15**  
 Klauui, M.: SA+AC+MI-ThM3, **15**  
 Klicpera, M.: AC+MI+SA+SU-MoM3, **1**  
 Kobayashi, T.: AC+AS+SA-TuM10, **5**  
 Kolmakov, A.: SU+AC+MI+MS-TuM5, **7**  
 Körstgens, V.: SA+AC+MI-ThM5, **15**  
 Koshigan, M.: TR+AC+TF+VT-ThM4, **16**  
 Krüger, P.: MI+2D+AC+NS-TuA11, **11**  
 Ksenzov, D.: SA+AC+MI-ThM3, **15**  
 Kumari, S.: MI+2D+AC+SA+SS-TuM12, **7**  
 Kuroda, K.: MI+2D+AC+NS-TuA1, **9**

## — L —

Lander, G.H.: AC+MI+SA+SU-MoM8, **2**  
 Lauter, V.: MI+2D+AC+NS-TuA9, **10**  
 Legut, D.: AC+AS+SA+SU-MoA2, **3**;  
 AC+MI+SA+SU-TuA9, **9**  
 Leite, M.S.: SU+AC+MI+MS-TuM5, **7**  
 Levings, P.P.: TR+AC+TF+VT-ThM12, **17**  
 Levitov, L.S.: MI+2D+AC+SA+SS-TuM2, **6**  
 Li, X.: MI+2D+AC+NS-TuA3, **10**  
 Linford, M.R.: AC-TuP2, **12**  
 Long, J.R.: AC+AS+SA-TuM10, **5**  
 Luening, J.: SA+AC+MI-ThM3, **15**  
 Lurio, L.B.: SA+AC+MI-ThM10, **16**

## — M —

Madsen, A.: SA+AC+MI-ThM12, **16**  
 Magnani, N.: AC+MI+SA+SU-MoM8, **2**  
 Maldonado, P.: AC+MI+SA+SU-MoM8, **2**  
 Manfreda, M.: SA+AC+MI-ThM3, **15**  
 Mangolini, F.: TR+AC+TF+VT-ThM4, **16**  
 Marks, L.: TR+AC+TF+VT-ThM10, **17**  
 Marshall, S.L.: TR+AC+TF+VT-ThM12, **17**  
 Maskova, S.: AC+MI+SA+SU-MoM4, **1**  
 Mason, J.A.: AC+AS+SA-TuM10, **5**  
 Matej, Z.: AC+AS+SA+SU-MoA10, **3**  
 Matsumura, Y.: SU+AC+MI+MS-TuM12, **8**  
 McClimon, J.B.: TR+AC+TF+VT-ThM4, **16**  
 Mi, J.: MI+2D+AC+NS-TuA11, **11**  
 Michels, A.F.: TR+AC+TF+VT-ThM3, **16**  
 Middleburgh, S.: AC+MI+SA+SU-MoM4, **1**  
 Mihut, D.: AC-TuP3, **12**  
 Miliyanchuk, K.: AC+MI+SA+SU-MoM4, **1**  
 Minár, J.: MI+2D+AC+NS-TuA11, **11**  
 Minasian, S.G.: AC+AS+SA-TuM10, **5**  
 Mottaghi, N.: MI+2D+AC+SA+SS-TuM12, **7**  
 Müller-Buschbaum, P.: SA+AC+MI-ThM5, **15**

## — N —

Nakanishi, H.: MI+2D+AC+SA+SS-TuM5, **6**  
 Negrea, G.: AC-TuP3, **12**  
 Nelson, A.J.: AC+AS+SA-TuM4, **5**  
 Nilsson, A.N.: SA+2D+AC+MI-WeM1, **13**  
 Nordlund, D.: AC+AS+SA+SU-MoA1, **3**

## — O —

O'Bryan, C.S.: TR+AC+TF+VT-ThM12, **17**  
 Oelsner, A.: SA+AC+MI-ThM6, **15**  
 Ohlhausen, J.A.: TR+AC+TF+VT-ThM4, **16**  
 Ohm, W.: SA+AC+MI-ThM5, **15**  
 Oleshko, V.: SU+AC+MI+MS-TuM5, **7**  
 Oppeneer, P.M.: AC+MI+SA+SU-MoM8, **2**  
 Ouladdiaf, B.: AC+MI+SA+SU-MoM3, **1**  
 Öztürk, E.: AC+AS+SA-TuM11, **6**

## — P —

Paolasini, L.: AC+MI+SA+SU-MoM8, **2**  
 Patel, D.: AC-TuP2, **12**  
 Paukov, M.: AC+AS+SA+SU-MoA10, **3**;  
 AC+AS+SA+SU-MoA2, **3**  
 Pearson, J.E.: MI+2D+AC+NS-TuA4, **10**  
 Pedersoli, E.: SA+AC+MI-ThM3, **15**  
 Piekarz, P.: AC+MI+SA+SU-TuA9, **9**  
 Pietsch, U.: SA+AC+MI-ThM3, **15**  
 Pitenis, A.A.: TR+AC+TF+VT-ThM12, **17**  
 Plakhova, T.V.: AC+AS+SA-TuM10, **5**  
 Powell, B.A.: AC+AS+SA-TuM5, **5**  
 Prodi, A.: AC+MI+SA+SU-MoM8, **2**

## — R —

Réal, F.: AC+MI+SA+SU-TuA3, **9**  
 Rementer, C.R.: MI+2D+AC+SA+SS-TuM13, **7**  
 Rodriguez-Nieva, J.R.: MI+2D+AC+SA+SS-TuM2, **6**  
 Rogalev, A.: MI+2D+AC+SA+SS-TuM6, **7**  
 Rohlfing, M.: MI+2D+AC+NS-TuA11, **11**

Rosa, P.: AC+MI+SA+SU-MoM10, **2**  
 Roth, S.V.: SA+AC+MI-ThM5, **15**  
 Rouleau, C.M.: MI+2D+AC+NS-TuA9, **10**  
 Roychowdhury, T.: AC-TuP2, **12**  
**— S —**  
 Sales de Mello, S.R.: TR+AC+TF+VT-ThM3, **16**  
 Sanders, C.E.: MI+2D+AC+NS-TuA10, **11**  
 Sant, T.: SA+AC+MI-ThM3, **15**  
 Sawyer, W.G.: TR+AC+TF+VT-ThM12, **17**  
 Schmidt, A.B.: MI+2D+AC+NS-TuA11, **11**  
 Schmitt, T.: SA+2D+AC+MI-WeM5, **13**  
 Schoenhense, G.: SA+AC+MI-ThM6, **15**  
 Schulmeyer, T.: SA+AC+MI-ThM6, **15**  
 Schulze, K.D.: TR+AC+TF+VT-ThM12, **17**  
 Seibert, A.: AC+AS+SA+SU-MoA2, **3**  
 Severo Pereira Gomes, A.: AC+MI+SA+SU-TuA3, **9**  
 Shiwaku, H.: AC+AS+SA-TuM10, **5**  
 Shuh, D.K.: AC+AS+SA+SU-MoA1, **3**;  
 AC+AS+SA-TuM10, **5**  
 Soderholm, L.: AC+AS+SA+SU-MoA3, **3**  
 Sokaras, D.: AC+AS+SA+SU-MoA1, **3**  
 Steffen, A.C.: MI+2D+AC+NS-TuA9, **10**  
 Stroschio, J.A.: MI+2D+AC+SA+SS-TuM2, **6**  
**— T —**  
 Talin, A.A.: SU+AC+MI+MS-TuM5, **7**  
 Taniguchi, T.: MI+2D+AC+SA+SS-TuM2, **6**

Thissen, A.: SA+AC+MI-ThM6, **15**  
 Tian, G.: AC+AS+SA-TuM10, **5**  
 Tobin, J.G.: AC+AS+SA+SU-MoA1, **3**  
 Tolbert, S.H.: MI+2D+AC+NS-TuA3, **10**  
 Trappen, R.: MI+2D+AC+SA+SS-TuM12, **7**  
 Turek, I.: AC+AS+SA+SU-MoA2, **3**  
 Tusche, C.: SA+AC+MI-ThM6, **15**  
 Tyliczszak, T.: AC+AS+SA+SU-MoA1, **3**  
 Tyliczszak, T.: AC+AS+SA-TuM10, **5**  
**— U —**  
 Uchida, H.-H.: SU+AC+MI+MS-TuM12, **8**  
 Urueña, J.M.: TR+AC+TF+VT-ThM12, **17**  
 Uyaner, M.: AC+AS+SA-TuM11, **6**  
**— V —**  
 Vallet, V.: AC+MI+SA+SU-TuA3, **9**  
 Van Benthem, M.H.: TR+AC+TF+VT-ThM4, **16**  
 van der Laan, G.: AC+AS+SA+SU-MoA1, **3**  
 Van Humbeck, J.F.: AC+AS+SA-TuM10, **5**  
 Virot, F.: AC+MI+SA+SU-TuA3, **9**  
**— W —**  
 Walkup, D.: MI+2D+AC+SA+SS-TuM2, **6**  
 Wang, K.L.: MI+2D+AC+NS-TuA3, **10**  
 Wang, S.: AC+AS+SA-TuM10, **5**  
 Watanbe, K.G.: MI+2D+AC+SA+SS-TuM2, **6**  
 Wdowik, U.D.: AC+MI+SA+SU-TuA9, **9**  
 Weiss, A.M.: AC+AS+SA-TuM3, **5**

Wen, H.: MI+2D+AC+NS-TuA4, **10**  
 Weng, T.C.: AC+AS+SA+SU-MoA1, **3**  
 Wietstruk, M.: SA+AC+MI-ThM6, **15**  
 Wilhelm, F.: MI+2D+AC+SA+SS-TuM6, **7**  
 Wong, K.: MI+2D+AC+NS-TuA3, **10**  
 Wörle, M.: SA+AC+MI-ThM5, **15**  
 Wu, D.: MI+2D+AC+NS-TuA3, **10**  
**— Y —**  
 Yaita, T.: AC+AS+SA-TuM10, **5**  
 Yang, H.: MI+2D+AC+SA+SS-TuM3, **6**  
 Yang, P.: AC+MI+SA+SU-MoM5, **1**  
 Yousefi Sarraf, S.: MI+2D+AC+SA+SS-TuM12, **7**  
 Yu, G.: MI+2D+AC+NS-TuA3, **10**  
 Yu, S.W.: AC+AS+SA+SU-MoA1, **3**  
 Yulaev, A.: SU+AC+MI+MS-TuM5, **7**  
**— Z —**  
 Zabel, H.: SA+AC+MI-ThM3, **15**  
 Zhang, H.: MI+2D+AC+NS-TuA9, **10**  
 Zhang, Q.: MI+2D+AC+NS-TuA4, **10**  
 Zhang, W.: MI+2D+AC+NS-TuA4, **10**  
 Zhang, Z.: MI+2D+AC+NS-TuA3, **10**  
 Zhitenev, N.B.: MI+2D+AC+SA+SS-TuM2, **6**  
 Zholdayakova, S.: SU+AC+MI+MS-TuM12, **8**  
 Zumbülte, A.: MI+2D+AC+NS-TuA11, **11**