

# Wednesday Morning, October 21, 2015

**Actinides and Rare Earths Focus Topic**  
**Room: 230A - Session AC+AS+MI-WeM**

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

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

8:00am **AC+AS+MI-WeM1 The Valence-Fluctuating Ground-State of  $\delta$ -Pu**, *Marc Janoschek*, Los Alamos National Laboratory **INVITED**

Plutonium (Pu) is arguably the most complex elemental metal known because its 5f electrons are tenuously poised at the edge between localized and itinerant configurations. This complex electronic structure leads to emergent behavior—all a direct consequence of its 5f electrons—including six allotropic phases, large volumetric changes associated with these transitions of up to 25%, and mechanical properties ranging from brittle  $\alpha$ -Pu to ductile  $\delta$ -Pu. Pu also exhibits a Pauli-like magnetic susceptibility, electrical resistivity and a Sommerfeld coefficient of the specific heat that are an order of magnitude larger than in any other elemental metal. Finally, while experiments find no sign for static magnetism in Pu, most theories that use the correct volume predict a magnetically ordered state. This discrepancy might be reconciled by recent Dynamical Mean Field Theory (DMFT) calculations that suggest that the electronic ground state of  $\delta$ -Pu is a quantum-mechanical admixture of localized and itinerant valence configurations. The question whether the ground state of  $\delta$ -Pu is indeed a true quantum-mechanical superposition may only be answered via observation of the associated virtual valence (charge) fluctuations among the distinct  $5f^6$ ,  $5f^7$ , and  $5f^8$  configurations. The characteristic energy scale for the associated spin fluctuations is expected to  $T_K \approx 800$  K ( $E_{sf} \approx 70$  meV) that will result in a dynamical spectral response centered at this energy for  $T < T_K$ . We have performed high-energy inelastic neutron spectroscopy at room temperature using a large polycrystalline sample of  $\delta$ - $^{242}\text{Pu}$  with a total mass of  $m \approx 21$  g at the Lujan Center and at the Spallation Neutron Source. Our measurements demonstrate the existence of high energy magnetic fluctuations centered at  $E_{sf} = 84$  meV, in good agreement with the DMFT calculations. In addition, they allow us to extract the magnetic form factor of  $\delta$ -Pu, yielding critical information about its valence state. These unprecedented results place show that the magnetism in Pu is not "missing" but dynamic, but dynamic, and is driven by virtual valence fluctuations. Our measurements provide a straightforward interpretation of the microscopic origin of the large, Pauli-like magnetic susceptibility of  $\delta$ -Pu and associated Sommerfeld coefficient. Furthermore, because the various valence configurations imply distinct sizes of the Pu ion, the valence-fluctuating ground state of Pu also provides a natural explanation for its complex structural properties and in particular the large sensitivity of its volume to small changes in temperature, pressure or doping.

8:40am **AC+AS+MI-WeM3 Exchange Bias in Heterostructures Based on  $\text{UO}_2$** , *Evgeniya Tereshina*, Institute of Physics ASCR, Czech Republic, *Z. Bao*, PANalytical B.V., Netherlands, *L. Havela*, Charles University in Prague, Czech Republic, *R. Springell*, University of Bristol, UK, *S. Danis*, Charles University in Prague, Czech Republic, *A. Mackova*, Nuclear Physics Institute ASCR, Czech Republic, *T. Gouder*, *R. Caciuffo*, Institute for Transuranium Elements (ITU), Germany **INVITED**

Interfacial exchange interaction in bilayers consisting of two dissimilarly ordered magnetic materials (e.g. an antiferromagnet (AF) and a ferro- or ferrimagnet (F)) may give rise to a phenomenon called the magnetic exchange bias (EB) effect [1]. The EB manifests itself as a shift of a magnetic hysteresis loop along the field direction when the bilayer is field-cooled below the Néel temperature ( $T_N$ ) of the AF. This property is of great value for magnetic recording applications. Despite the conceptual simplicity, a generally accepted theory that predicts the EB behavior for an apt pair of materials is still missing. The reason for that might be in poorly defined interface structure in both magnetic and crystallographic aspects.

Critical dependence of EB on magnetic anisotropy brings us the possibility to use actinides with strong spin-orbit interaction as the key ingredient. Here we report exchange bias studies in magnetic bilayers consisting of a stoichiometric  $\text{UO}_2$  film grown epitaxially on different substrates and covered with polycrystalline metallic ( $\text{Ni}_{180}\text{Fe}_{20}$  and Fe) and highly textured oxide ( $\text{Fe}_3\text{O}_4$ ) layers of variable thickness. Large longitudinal exchange bias  $\sim 2.6$  kOe is found in  $\text{UO}_2/\text{Fe}_3\text{O}_4$  bilayers [3] while  $\text{UO}_2$  combined with metallic ferromagnets displays perpendicular exchange coupling with an order of magnitude smaller EB. Interestingly, unusual effects in  $\text{UO}_2/\text{Fe}_3\text{O}_4$  were observed, namely, exchange bias did not vanish at  $T_N$  of  $\text{UO}_2$ . Apart from the fact that single layers of magnetite were showing some EB (not

more than 25 % of the total effect in  $\text{UO}_2/\text{Fe}_3\text{O}_4$ ), the EB in  $\text{UO}_2/\text{Fe}_3\text{O}_4$  bilayers exceeded notably that of the single  $\text{Fe}_3\text{O}_4$ 's to approx. 70 K that was attributed to possible proximity effects of  $\text{Fe}_3\text{O}_4$  on  $T_N$  of  $\text{UO}_2$  and/or to the magnetic anisotropy of  $\text{UO}_2$  preserved locally above  $T_N$ . The effects were observed for the samples of quality controlled by different methods such as X-ray Photoelectron Spectroscopy, conventional X-ray Diffraction, Transmission Electron Microscopy and Rutherford Backscattering Spectroscopy. The work has been supported by the Czech Science Foundation, grant No. 13-25866P.

[1] W. H. Meiklejohn and C. P. Bean, "New magnetic anisotropy", Phys. Rev. B 102, 1413 (1956).

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

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

9:20am **AC+AS+MI-WeM5 Transport and Magnetism of 4f and 5f Systems: What we can Learn from Thermoelectric Power**, *Krzysztof Gofryk*, Idaho National Laboratory **INVITED**

The interplay between different electronic ground states, especially magnetism and superconductivity, has evolved in a climate of discovery in which many of the fundamental rules of condensed matter physics are questioned by materials with unexpected properties. These "emergent properties," such as complex magnetism, heavy-fermion superconductivity, the coexistence of magnetism and superconductivity, and/or Kondo physics emerge from complex materials in which quasiparticles develop different states of organization and correlation. The majorities of these bizarre electronic ground states are encountered in  $f$ -electron systems and are linked to the hybridization between the  $f$ -states and ligand electrons. How these properties evolve with the progressive filling of the  $f$ -shells remains an open question, but it is a key ingredient for their understanding. The 4f and 5f strongly correlated electron systems at the border of magnetism are of active current interest, particularly because the accompanying quantum criticality provides a route towards both strange-metal, non-Fermi-liquid behavior, and unconventional superconductivity. In spite of large theoretical and experimental efforts the nature of the electronic behaviors is still unclear. One way to address the electronic properties of these fascinating materials is to perform extensive transport studies such as Hall, Nernst, or Seebeck effects. In particular, the latter one has gained importance in recent years in thermoelectric materials as potential solutions for applications, such as spot cooling of electronic components, waste heat recovery system and/or remote power generation in space stations and satellites. In addition, the Seebeck coefficient is a sensitive probe of energy relative to the Fermi level, it can therefore be used as a tool to characterize the electronic structure of materials, especially in the vicinity of the narrow gap or pseudo-gap. During the talk I will provide a general introduction to the magnetic and transport characteristics of 4f and 5f electron systems. Then, I will present thermoelectric properties of selected 4f and 5f materials and give an overview on how the thermoelectric power studies can be used to probe electronic properties in this class of materials. I will discuss implications of the results, and their limitations.

11:00am **AC+AS+MI-WeM10 Magnetic Properties of 2-2-1 Rare-earth and Uranium Compounds and their Interaction with Hydrogen**, *Silvie Maskova*, Charles University, Prague, Czech Republic, *R.V. Denys*, Institute for Energy Technology, Kjeller, Norway, *I. Halevy*, Nuclear Research Center Negev, Beer-Sheva, Israel, *K. Miliyanchuk*, *L. Akselrud*, Ivan Franko National University of Lviv, Lviv, Ukraine, *A. Kolomiets*, Lviv Polytechnic National University, Lviv, Ukraine, *V. Yartys*, Institute for Energy Technology, Kjeller, Norway, *M. Giovannini*, University of Genova, Genova, Italy, *L. Havela*, Charles University, Czech Republic

We have been studying some members of large family of  $\text{A}_2\text{T}_2\text{X}$  (A = Rare-Earth (RE) or actinide, T = transition metal, X =  $p$ -metal) compounds crystallizing in the  $\text{Mo}_2\text{FeB}_2$  structure type (space group  $P4/mbm$ ).  $\text{U}_2\text{T}_2\text{X}$  interact with  $\text{H}_2$  only at high pressure ( $\approx 100$  bar) reaching 2 H/f.u. The H absorption produces a lattice expansion, while the tetragonal structure is preserved. The H atoms presumably enter the 8k position inside the  $\text{U}_3\text{T}$  tetrahedra occupied randomly up to 50%. On the other hand, it was found that some  $\text{RE}_2\text{T}_2\text{X}$  compounds can absorb more hydrogen compared to their U-counterparts in much lower H pressures. The amorphization of the structure upon hydrogenation (4 H/f.u.) was found for  $\text{RE}_2\text{Pd}_2\text{In}(\text{Sn})$  with light RE (La, Nd).  $\text{RE}_2\text{Pd}_2\text{In}(\text{Sn})$  with heavy RE behave similar way as  $\text{U}_2\text{T}_2\text{X}$  compounds (2 H/f.u., crystal structure type not changed). For the isostructural indide  $\text{Nd}_2\text{Ni}_2\text{In}$  the hydrogen absorption of 7 H/f.u. leads to the orthorhombic distortion of the crystal structure.

Recently, we have been studying several isostructural  $\text{RE}_2\text{T}_2\text{Mg}$  (T = Ni, Pd). The H absorption in these compounds depends on the type of transition

metal. The compounds with Ni tend to absorb up to 8 H/f.u. The crystal structure is changed to monoclinic (space group  $P21/c$ ). If the transition metal is Pd, the hydrogen absorption is lower, reaching approx. 6 H/f.u. and the crystal structure is modified in different way. The  $Tb_2Pd_2Mg$ -hydride crystallizes in a new ternary structure type ( $Fmmm$ ). In the case of Mg-compounds, the hydrogen absorption is not reversible. Upon desorption of H the initial crystal structure is not restored.

We have found that in U-compounds the ordering temperatures increase upon hydrogenation contrary to the RE-compounds where the ordering temperatures are dramatically reduced. Magnetic properties of U-compounds strongly depend on the inter-U distances. Hydrogen intrusion modifies the lattice by expanding it without changing the crystal-structure type leading to a band narrowing. As a consequence doping of U intermetallics by interstitial hydrogen leads to stronger magnetic properties. On the other hand, the hydrogen absorption has opposite effect on magnetic properties of  $RE_2T_2X$  compounds. For RE compounds, hydrogenation affects mainly the  $4f$ -magnetic moments and their ordering. The exchange coupling is reduced presumably by reducing the concentration of conduction electrons.

11:20am **AC+AS+MI-WeM11 Structural, Electronic, and Magnetic Characteristics of  $Np_2Co_{17}$  and Analogue Compounds Under Pressure.** *Izhak Halevy*, Nuclear Research Center Negev, Israel, *A. Hen*, Institute for Transuranium Elements (ITU), Germany, *I. Orion*, Ben Gurion University, Israel, *E. Colineau*, *R. Eloirdi*, *J.C. Griveau*, ITU, Germany, *F. Wilhelm*, *A. Rogalev*, ESRF, France, *N. Magnani*, *A.B. Shick*, *R. Caciuffo*, ITU, Germany

A previously unknown neptunium-transition-metal binary compound  $Np_2Co_{17}$  has been synthesized and

characterized by means of powder x-ray diffraction,  $^{237}Np$  Mössbauer spectroscopy, superconducting-quantum-interference-device magnetometry, and x-ray magnetic circular dichroism. The compound crystallizes

in a  $Th_2Ni_{17}$ -type hexagonal structure with room-temperature lattice parameters  $a=8.3107\text{\AA}$  and  $c=$

$8.1058\text{\AA}$ . Magnetization curves indicate the occurrence of ferromagnetic order below  $T_C>350$  K. Mössbauer

spectra suggest a  $Np^{3+}$  oxidation state and give an ordered moment of  $\mu_{Np}=1.57\mu_B$  and  $\mu_{Co}=1.63\mu_B$

for the Np atoms located, respectively, at the  $2b$  and  $2d$  crystallographic positions of the  $P6_3/mmc$  space group.

Combining these values with a sum-rule analysis of the XMCD spectra measured at the neptunium  $M4,5$  absorption

edges, one obtains the spin and orbital contributions to the site-averaged Np moment [ $\mu_S=-1.88\mu_B$ ,

$\mu_L=3.48\mu_B$ ]. The ratio between the expectation value of the magnetic-dipole moment and the spin magnetic

moment ( $m_{md}/\mu_S=1.36$ ) is positive as predicted for localized  $5f$  electrons and lies between the values

calculated in intermediate-coupling (IC) and  $jj$  approximations. The expectation value of the angular part of

the spin-orbit-interaction operator is in excellent agreement with the IC estimate. The ordered moment averaged

over the four inequivalent Co sites, as obtained from the saturation value of the magnetization, is  $\mu_{Co}\sim 1.6\mu_B$ .

The experimental results are discussed against the predictions of first-principles electronic-structure calculations

based on the spin-polarized local-spin-density approximation plus the Hubbard interaction. The structural behavior of  $Np_2Co_{17}$  is investigated by means of high pressure diamond-anvil compression measurements and is compared with that of the isostructural compounds  $Lu_2Co_{17}$  and  $Lu_2Ni_{17}$ . The  $Th_2Ni_{17}$ -type hexagonal crystal structure is preserved with no measurable discontinuous volume collapses up to the highest achieved pressure,  $p=43$  GPa. For  $Np_2Co_{17}$ , fits to the Birch-Murnaghan and Vinet equations of state give values of the isothermal bulk modulus and

its pressure derivative of  $B_0=286$  GPa and  $B_0=3$ , revealing that this Np compound is a highly incompressible solid with stiffness comparable to that of superhard covalently bonded materials. The isothermal equation of state for the studied compounds are in excellent agreement with the results of *ab initio* fully-relativistic, full potential local spin-density functional calculations. Theoretical estimates of the bulk modulus are given also for  $Np_2Ni_{17}$ , for which  $B_0$  is predicted to assume values intermediate between those measured for  $Lu_2Ni_{17}$  and  $Np_2Co_{17}$ .

11:40am **AC+AS+MI-WeM12 Alloying  $UH_3$  as a Probe into the  $5f$  Magnetism.** *Ladislav Havela*, *M. Paukov*, *I. Tkach*, *M. Cieslar*, *Z. Matej*, *D. Kriegner*, *D. Drozdenko*, *I. Turek*, *M. Divis*, Charles University, Czech Republic, *N.-T.H. Kim-Ngan*, Pedagogical University, Poland

Several routes of preparation of alloyed U trihydrides,  $UH_3$ , were discovered. Starting from the  $U_6T$  compounds, hydrogenation leads to T atoms embedded in the  $\beta$ - $UH_3$  structure, with transition-metal atoms T occupying one of the U sites. We have been hydrogenating  $\gamma$ -U alloys, using various transition metals helping (together with ultrafast cooling) to retain the bcc U structure down to low temperatures. As such alloys are much more resistant to hydrogen attack, high pressures of  $H_2$  gas had to be applied. The H absorption corresponds to approx. 3H/atoms per 1 U atom. In none of the cases the alloying metals segregate and two different structures were obtained. The hydrides  $(UH_3)_{1-x}Zr_x$  form the  $\alpha$ - $UH_3$  structure, i.e. the bcc structure expands and fills by H. Hence basic electronic properties of  $\alpha$ - $UH_3$  could be established. Starting from  $U_{1-x}Mo_x$ , we obtained  $(UH_3)_{1-x}Mo_x$ , which tends to be  $\beta$ - $UH_3$  like, but has the grain size is 1 nm only, i.e. practically amorphous. This amorphous phase also easily accepts additional dopants, as Zr, Fe, Ti, V...however magnetic properties remain only weakly affected. It is quite remarkable that all such materials are ferromagnets with the Curie temperature in the range 160-205 K, even if the active U sublattice is diluted by more than 30% of other metals. In this respect the hydrides are different than conventional band ferromagnets, sensitive to inter-atomic spacings and alloying. Albeit all are metallic, the U-H interaction, which can have a partly ionic character, plays clearly important role. Electronic structure calculations (performed for the  $\alpha$ - $UH_3$  structure and in ferromagnetic or Disordered Local Moment state, with possible random Zr occupancy) suggest a transfer of U-6d and 7s electrons into H-1s states, reducing the hybridization of 5f and non-f states, supporting thus magnetism even if the U-U spacing is below the Hill limit [1].

[1] I. Tkach et al. Phys.Rev. B 91, 115116 (2015).

# Wednesday Afternoon, October 21, 2015

**Actinides and Rare Earths Focus Topic**  
**Room: 230A - Session AC+AS+MI-WeA**

**Chemistry and Physics of the Actinides and Rare Earths**  
**Moderator:** Ladislav Havela, Charles University, Prague,  
Czech Republic

2:20pm **AC+AS+MI-WeA1 High Resolution X-ray Absorption Spectroscopy as an Advanced Tool for Structural Investigations of Actinides, Tonya Vitova**, Karlsruhe Institute of Technology, Germany  
**INVITED**

Advanced spectroscopy methods, which provide precise speciation, redox state, and electronic structure information, are needed to benchmark and drive improvement of geochemical/thermodynamic modeling and quantum chemical computational methods. The high energy resolution X-ray absorption near edge structure (HR-XANES) spectra contain additional information compared to the conventional XANES spectra, as they are rich in resolved resonant spectral features for specific An oxidation states.<sup>[1]</sup> The An  $M_{4,5}$  edge HR-XANES probes directly the An valence unoccupied 5f states ( $3d \rightarrow 5f$ ) and thus yields insight to the role these frontier orbitals play in hybridization with ligands and bond formation.

The characterization capabilities of the An  $M_{4,5}$  and  $L_3$  edge HR-XANES technique will be highlighted by recent results obtained for both model and complex U, Np and Pu materials. In one example, a single crystal of dicesium uranyl tetrachloride ( $Cs_2UO_2Cl_4$ ) as a model  $UO_2^{2+}$  (uranyl ion) compound was investigated using U  $M_4$  ( $3d_{3/2} \rightarrow 5f$ ) and  $L_3$  ( $2p_{3/2} \rightarrow 5f/6d$ ) edge polarization dependent HR-XANES (PD-HR-XANES) with remarkable energy resolution. Comparison of experimentally determined relative energies of U  $5f\delta$ ,  $5f\phi$ ,  $5f\pi$ , and  $5f\sigma$  orbitals, as well as 5f and 6d orbitals obtained from the spectra, to predictions from quantum chemical Amsterdam density functional theory (ADF) and FEFF codes and show excellent results.<sup>[2]</sup> A number of examples for determination of An redox states in liquids and solid systems will be discussed. Comparison of U/Pu/Np  $M_4/M_5$  HR-XANES spectra of  $UO_2^{2+}$ ,  $NO_2^{2+}$  and  $PuO_2^{2+}$  as well as Pu  $M_5$  HR-XANES and  $L_3$  XANES of various Pu oxidation states in aqueous solution will be presented. In addition, recent results unambiguously demonstrate that U(V) can exist alongside U(IV) and U(VI) in magnetite nanoparticles under anoxic conditions; this underpins the utility of HR-XANES for understanding U retention mechanisms on corrosion products.

[1] At. Vitova, M. A. Denecke, J. Göttlicher, K. Jorissen, J. J. Kas, K. Kvashnina, T. Prüßmann, J. J. Rehr, J. Rothe, Journal of Physics: Conference Series, 430; Bk. O. Kvashnina, S. M. Butorin, P. Martin, P. Glatzel, Phys Rev Lett, 111; Ct. Vitova, K. O. Kvashnina, G. Nocton, G. Sukharina, M. A. Denecke, S. M. Butorin, M. Mazzanti, R. Caciuffo, A. Soldatov, T. Behrends, H. Geckeis, Phys Rev B, 82.

[2] T. Vitova, J. C. Green, R. G. Denning, M. Löble, K. Kvashnina, J. J. Kas, K. Jorissen, J. J. Rehr, T. Malcherek, M. A. Denecke, Inorganic Chemistry, 54, 174-182.

3:00pm **AC+AS+MI-WeA3 Soft X-ray Spectromicroscopy of Actinide Materials, David Shuh**, Lawrence Berkeley National Laboratory **INVITED**  
Soft X-ray synchrotron radiation methodologies are being developed and employed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory to elucidate the electronic structure of actinide materials. Results from these investigations have begun to provide improved fundamental knowledge that can be used as a scientific basis for the enhanced design of special-purpose actinide materials and the overall understanding of actinide materials. The experimental developments at the ALS have centered on the use of the Molecular Environmental Science (MES) scanning transmission X-ray microscope (STXM) at Beamline 11.0.2 for near-edge X-ray absorption spectroscopy (XAS), and on X-ray emission spectroscopy (XES) at several beamlines, focusing primarily on light atom constituents (C, N, O, F) for ligand K-edge XAS, and on metal-ion centers plus light-atom signals for XES. The spectromicroscopy capabilities of the STXM provide the means to investigate and determine the speciation in actinide materials and environmentally-relevant systems with spatial resolution that reaches to the true nanoscale.

An absolutely critical and key enabling component for all of the soft X-ray investigations is the contribution of theory, that when combined with experiment, has firmly provided more detailed knowledge of electronic structure in actinide materials in terms of orbital composition and mixing, and oxidation state. The highlights of recent investigations of metallocenes at the carbon K-edge and uranyl complexes at the nitrogen K-edge will be

highlighted in this respect. The spectromicroscopy attributes of the STXM have enabled the investigation of contaminant speciation in a range of model and real environmental systems. The results of the most recent environmentally-related studies, cesium in clay materials relevant to clean up efforts in Japan, will be presented.

Acknowledgement: Supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences Heavy Element Chemistry Program of the U.S. DOE at LBNL under Contract No. DE-AC02-05CH11231.

4:20pm **AC+AS+MI-WeA7 Resonant Ultrasound Spectroscopy Detects 100 Part-per-billion Effects in Plutonium, Albert Migliori**, Los Alamos National Laboratory  
**INVITED**

The speeds of sound, or, equivalently, the elastic moduli are some of the most fundamental attributes of a solid, connecting to fundamental physics, metallurgy, non-destructive testing, and more. With modern advances in electronics and analysis, changes in elastic moduli are detectable at 100 parts per billion, providing new and important insight into grand challenges in plutonium science. Applied to  $^{239}\text{Pu}$ , the effects of aging are measured in real time as a function of temperature, and the temperature dependence of the elastic moduli of gallium stabilized delta plutonium leads to important questions about the validity of electronic structure theory, and points towards inescapable constraints on any theory of this metal.

This work was supported as part of the Materials Science of Actinides, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0001089.

5:00pm **AC+AS+MI-WeA9 Spectroscopic Studies of the Oxide Layer formed on Plutonium under Ambient Conditions, Alison Pugmire**, Los Alamos National Laboratory, C.H. Booth, Lawrence Berkeley National Laboratory, J. Venhaus, L. Pugmire, Los Alamos National Laboratory

One of the fundamental challenges of modern science lies in understanding the chemistry and physics of the actinides, and in particular, plutonium. It's unpredictable behavior and reactivity has led to a very poor understanding of its metallurgy and corrosion process. This not only poses a basic scientific challenge, but directly affects the safe, long term storage of this material. In an effort to understand the surface chemistry and corrosion of plutonium, knowledge of the surface oxide composition is paramount. The currently accepted description of the oxide layer formed under ambient temperatures and pressures consists of a thick  $\text{PuO}_2$  surface layer over a thin  $\text{Pu}_2\text{O}_3$  layer at the metal interface. However, recent studies by our group indicate this description is inadequate, and the oxide layer formed in the initial stages, in particular, is much more complex. We have recently focused on studying the oxide layer formed on gallium stabilized  $\delta$ -plutonium in ambient conditions (pressure, temperature). We have characterized this layer using multiple spectroscopic techniques, including spectroscopic ellipsometry (SE), x-ray photoelectron spectroscopy (XPS), and x-ray absorption spectroscopy (XAS). This diverse and complimentary suite of experimental techniques will address many long-standing issues regarding the nature of the oxide layer and the corrosion mechanism.

5:20pm **AC+AS+MI-WeA10 Covalent Mixing In Actinide and Lanthanide Compounds: Reliable Assignment of Cation Charges, Paul Bagus**, University of North Texas, C.J. Nelin, Consultant

The importance of covalent and ionic interaction and bonding in heavy metal oxides, for example for the actinide dioxides,  $\text{AnO}_2$ , is controversial with some claiming that the interactions are nearly purely ionic and with others arguing that there is important covalent character. Similar questions also exist for halides and for lanthanide compounds. One way to view this is to consider how close the actual charge state of the cation is to the nominal oxidation state. Our analysis is based on using wavefunctions for embedded clusters which model the bulk oxides. With these wavefunctions, we show that considerable departures of the cation charge from the nominal value are a common occurrence. We also show how the departure from the nominal charge state depends on several factors including: (1) nominal oxidation state, (2) ligand, and (3) position in the row of the periodic table. It is also necessary to determine which metal orbitals are involved in the covalent mixing. For actinides, the natural choice is the open cation 5f shell but the normally empty 6d shell may also contribute to the covalent mixing and, in fact, may even have a larger contribution than the 5f. In order to characterize the extent and importance of the covalent mixing, two factors need to be taken into account: (1) the estimate of the actual charge state of the cations and (2), perhaps even more important, the contribution of the covalent mixing of the cation and anion frontier orbitals to the total energy of the compound. Our approach to address both of these aspects is to limit the variational freedom when we self-consistently optimize the orbitals of

the models used to represent the compounds studied. By restricting the variational space, the importance of the mixing of ligand and metal frontier orbitals can be explicitly measured by determining the difference between a wavefunction where these frontier orbitals are excluded from the variational process and a wavefunction where they are allowed to mix with other orbitals. With this approach, it is possible to make quantitative estimates of energies associated with the covalent mixing as well as the effective charges that can be associated with the cations and ligands. Furthermore, it is possible to visualize the changes in the charge distribution for different degrees of variational freedom with suitable contour plots. We acknowledge support for this work by the Geosciences Research Program, Office of Basic Energy Sciences, U.S. DOE.

5:40pm AC+AS+MI-WeA11 **An XPS and ToF SIMS Investigation of Cerium Oxidation**, *Paul Roussel*, AWE, United Kingdom of Great Britain and Northern Ireland

In this study fcc  $\gamma$ -cerium has been used as a non radioactive surrogate material for fcc  $\delta$ -plutonium. The common cerium oxides are the trivalent sesquioxide and the tetravalent dioxide both of which are iso-structural with the oxides formed on plutonium metal. Similarly, cerium (1) like plutonium (2) displays parabolic oxidation kinetics at low temperatures and linear kinetics elevated temperatures. This makes cerium an ideal surrogate material to study the kinetics and mechanism of plutonium oxidation. The initial oxidation of cerium at 274 K was studied using X-ray Photoelectron Spectroscopy. On exposure to Langmuir quantities of oxygen cerium rapidly oxidizes to the trivalent oxide followed by the slower growth of the tetravalent oxide. The growth modes of both oxides have been determined. It was found the surface formed tetravalent oxide was unstable in ultra high vacuum and reduced to the trivalent oxide by an apparent solid state diffusion reaction with cerium metal. This reduction reaction can be explained by the thermodynamic instability of the tetravalent dioxide with respect to cerium metal. The complexity of this reduction reaction appears to be enhanced by the formation of surface hydroxyl species as a function of time. Time of Flight Secondary Ion Mass Spectrometry was used to support characterization of the surface hydroxyl species.

(1) D. Cubicciotti, J. Am. Chem. Soc., 74 (1952) 1200.

(2) J. L. Stakebake, J. Less Common Met., 123 (1986) 185.

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# Thursday Morning, October 22, 2015

**Actinides and Rare Earths Focus Topic**  
**Room: 230A - Session AC+AS+MI-ThM**

## Nuclear Power and Waste Remediation

**Moderator:** David Shuh, Lawrence Berkeley National Laboratory

8:00am **AC+AS+MI-ThM1 Applications of Synchrotron Methods to f-Element Research in the Nuclear Fuel Cycle, Melissa Denecke**, The University of Manchester, UK **INVITED**

Celebrating 60 years of civil nuclear power generation offers an excellent opportunity to review synchrotron radiation (SR)-based techniques to characterize nuclear materials and elucidate processes relevant to the nuclear fuel cycle. The penetration capability of intense SR X-ray sources allows in situ investigations, including samples within radiological containments or specialized environments. The presentation will concentrate on application of X-ray spectroscopic techniques in studies related to the nuclear fuel cycle (fuel, cladding, recycle, waste disposal).

8:40am **AC+AS+MI-ThM3 Ab Initio Study of Advanced Metallic Nuclear Fuels for Fast Breeder Reactors, Alexander I. Landa**, Lawrence Livermore National Laboratory **INVITED**

The U-TRU-Zr and U-TRU-Mo alloys proved to be very promising fuels for TRU-burning liquid metal fast breeder reactors. The optimal composition of these alloys is determined from the condition that the fuel could remain stable in the bcc phase ( $\gamma$ -U) in the temperature range of stability of  $\alpha$ -U phase. In other words, both Zr and Mo play a role of ' $\gamma$ -stabilizers' helping to keep U in the metastable bcc phase upon cooling. The main advantage of U-Pu-Mo fuels over U-Pu-Zr fuels lies in much lower constituent redistribution due to the existence of a single  $\gamma$ -phase with bcc structure over typical fuel operation temperatures. The nucleation time for the decomposition of the metastable alloys, which controls the constituent redistribution process, is directly connected with the excess enthalpy of solution of these alloys. In the present study we perform KKR-ASA-CPA and EMTO-CPA calculations of the ground state properties of  $\gamma$ -U-Zr and  $\gamma$ -U-Mo alloys and compare their heats of formation with CALPHAD assessments. We discuss how the heat of formation in both alloys correlates with the charge transfer between the alloy components, and how the specific behavior of the density of states in the vicinity of the Fermi level promotes the stabilization of the  $U_2Mo$  compound. Our calculations prove that, due to the existence of a single  $\gamma$ -phase over the typical fuel operation temperatures,  $\gamma$ -U-Mo alloys should indeed have much lower constituent redistribution than  $\gamma$ -U-Zr alloys where a high degree of constituent redistribution takes place. The binodal decomposition curves for  $\gamma$ -based U-Zr and U-Mo solid solutions are derived from Ising-type Monte Carlo simulations incorporating effective cluster interactions obtained from the Screened Generalized Perturbation and Connolly-Williams methods. We also explore the idea of stabilization of the  $\delta$ -UZr<sub>2</sub> compound against the  $\alpha$ -Zr (hcp) structure due to increase of Zr d-band occupancy by the addition of U to Zr. Analogy with stabilization of the  $\omega$  phase in Zr under compression is made. Though the U-Pu-Zr and U-Pu-Mo alloys can be used as nuclear fuels, a fast reactor operation on a closed fuel cycle will, due to the nuclear reactions, contain significant amount of MA (Np, Am, Cm). Calculated heats of formation of bcc Pu-U, Pu-Np, Pu-Am, Pu-Cm, Pu-Zr, Pu-Mo, Np-Zr, Np-Mo, U-Am, Np-Am, Am-Zr and Am-Mo alloys are also presented and compared with CALPHAD assessments. This work was performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and was funded by the Laboratory Directed Research and Development Program at LLNL under project tracking code 12-SI-008.

9:20am **AC+AS+MI-ThM5 Shedding Light on Uranium Corrosion in Nuclear Waste Packages, Charilaos Paraskevoulakos**, University of Bristol, UK

Intermediate level waste (ILW) is encapsulated in grout and stored in stainless steel drums. A proportion of these have become a concern for the UK nuclear community, as significant distortion around the circumference of these drums has been observed. Distortion is ascribed to the generation of voluminous and potentially flammable corrosion products forming on uranium metal, e.g. uranium hydride. Thus potential oxygen influx caused by fracturing of canisters will threaten their suitability for waste disposal, potentially causing release of the encapsulated radioactive material or even ignition of the hydride. The association of the uranium corrosion mechanisms with the mechanical degradation of the encapsulants (stainless steel and grout), is the focus of the current project. Finite Element (FE)

Modelling, accelerated uranium corrosion tests as well as diffraction and tomography using synchrotron X-Rays/gamma rays could be employed to investigate the durability of the ILW packages.

9:40am **AC+AS+MI-ThM6 The Optical Properties of Uranium Carbide Measured by Spectroscopic Ellipsometry, Wigbert Siekhaus, A.J. Nelson, C.K. Saw**, Lawrence Livermore National Laboratory

Uranium carbide inclusions are common in metallic uranium, and uranium carbide itself is being used or being considered as a fuel in both gas-cooled, liquid metal cooled, and supercritical water-cooled reactors. To the best of our knowledge the only study of optical properties deals with high temperature radiance. [1] Here we first characterized a uranium carbide cube (supplied by Oak Ridge National Laboratory) with sides of approximately 3 mm length by X-ray diffraction and X-ray photo-electron spectroscopy and then measured its optical properties with an ellipsometer at angles of incidence between 65 and 75 degrees, and over an energy range from 1.26 to 3.2eV. The signal strength was low over that energy range, and too low to be useful above 3.2eV. The measured  $\Delta$  and  $\Psi$  were converted to the dielectric constants  $\epsilon_1$  and  $\epsilon_2$  shown in the table below using a general oscillator model [2].

E, eV	$\epsilon_1$	$\epsilon_2$	E, eV	$\epsilon_1$	$\epsilon_2$	E, eV	$\epsilon_1$	$\epsilon_2$
1.26	-1.96	5.07	1.95	-0.30	2.73	2.61	2.61	1.32
1.33	-1.69	4.77	2.02	-0.21	2.55	2.68	2.68	1.21
1.40	-1.47	4.45	2.10	-0.12	2.34	2.75	2.75	1.07
1.47	-1.25	4.14	2.18	-0.03	2.18	2.83	2.83	0.94
1.54	-1.06	3.87	2.25	0.04	2.02	2.91	2.91	0.85
1.61	-0.89	3.63	2.32	0.12	1.87	2.98	2.98	0.76
1.69	-0.73	3.44	2.40	0.20	1.73	3.05	3.05	0.67
1.76	-0.60	3.23	2.47	0.28	1.59	3.12	3.12	0.58
1.84	-0.48	2.95	2.54	0.35	1.43	3.20	3.20	0.51

Prepared by LLNL under Contract DE-AC52-07NA27344, LLNL-ABS-670149

[1] D. Manara, F. De Bruycker, K. Boboridis, O. Tougait, R. Eloiardi, M. Malki, High temperature radiance spectroscopy measurements of solid and liquid uranium and plutonium carbides, J Nucl Mater, 426 (2012) 126-138.

[2] R. Synowicki, J.A. Woollam CO. Inc. 645 M Street, Suite 102, Lincoln, NE 68508-2243, USA

11:00am **AC+AS+MI-ThM10 Uranium Wet Oxidation in the Presence of Hydrogen Overpressure, Antonios Banos**, University of Bristol, UK

The radioactive intermediate level (IL) and high level (HL) waste have been accumulated in the UK's legacy ponds and silos for over 60 years. There is a great need for these wastes to be retrieved to follow long term storage. Uranium hydride (UH<sub>3</sub>) has been identified as a reaction product of the corrosion process. Hydride formation occurs due to the increasing concentration of hydrogen gas, generated from the reaction of uranium, Magnox (MagnoxAl80) and other metals. The highly pyrophoric and unstable nature of UH<sub>3</sub> in air poses considerable environmental risks, due to potential radionuclide release. In this work we will try to simulate the corroding conditions by immersing an initially polished uranium sample in water under vacuum and introducing hydrogen gas overpressure to the system. The ternary system will be investigated in different temperatures and pressures with two main questions awaiting to be answered: 1. Is UH<sub>3</sub> identified? For this reason post-examination of the reacted surface will be conducted using Secondary Ion Mass Spectrometry (SIMS), Focus Ion Beam (FIB) milling. 2. If UH<sub>3</sub> is identified, on which part of the reaction is it produced and how this affects the overall reaction? The kinetics will be monitored using a specifically designed set-up comprised from a stainless steel pot and a pressure controller attached on one end and logged to a computer in order for the whole reaction to be recorded and the rate of corrosion through gas generation to be evaluated.

11:40am **AC+AS+MI-ThM12 Resolving the Issues of 5f Covalency and Ionicity in UO<sub>2</sub> and UF<sub>4</sub>, James Tobin**, Lawrence Livermore National Laboratory

Building upon our recent work, a concerted effort to isolate and understand covalency and ionicity in uranium compounds has been pursued. Specifically, the isoelectronic formal charge systems, uranium dioxide and uranium tetrafluoride, have been investigated with a novel mixture of both soft and hard-x-ray spectroscopies. The results to be discussed will include the following: (1) the use of soft X-ray O1s/F1s X-ray absorption spectroscopy (XAS) and U4d X-ray emission spectroscopy (XES) to follow

the 2p/5f bonding via the unoccupied density of states; (2) the utilization of hard X-ray U L3 extended X-ray absorption fine structure (EXAFS) to trivially distinguish the ordering in each; and (3) the use of hard X-ray L3 resonant X-ray emission spectroscopy (RXES) to distinguish 5f occupation/covalency effects in UO<sub>2</sub> and UF<sub>4</sub>. Collaborators include CH Booth, DK Shuh, T. Tyliczszak, G. van der Laan, D. Sokaras, T.-C. Weng, D. Nordlund, S.-W. Yu, W. Siekhaus and P.S. Bagus.

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