

Wednesday Afternoon, November 2, 2011

Actinides and Rare Earths Focus Topic

Room: 209 - Session AC+MI-WeA

Magnetic and Electron Correlation Effects in Actinides and Rare Earths

Moderator: J.G. Tobin, Lawrence Livermore National Laboratory

2:00pm AC+MI-WeA1 Electronic Structure Theory of Complex Ordered Actinide Materials, *P.M. Oppeneer*, Uppsala University, Sweden **INVITED**

Actinide materials display many complex and correlated behaviors that originate from the special properties of the open f-shell atom embedded in a specific material's environment. First-principles investigations provide a route to assess these anomalous phenomena in a materials specific way, providing direct, fundamental insight.

Here we consider recently obtained *ab initio* modeling results for actinide materials that are in the focus of current interest: actinide oxides, such as NpO₂, PuO₂, and higher-oxides, U₃O₈, and Np₂O₅, the hidden order (HO) material URu₂Si₂, and correlated plutonium compounds.

NpO₂ is one of the very few materials in which complex multipolar order has been identified. Using the density-functional theory (DFT)-based LDA+*U* method we provide a first-principles theory of multipolar order and superexchange in NpO₂. DFT+*U* calculations offer a precise microscopic description of the 3*q*-antiferro ordered phase. We find that the usually neglected higher-order multipoles (electric hexadecapoles and magnetic triakontadipoles) are at least equally significant as the electric quadrupoles and magnetic octupoles [1].

We further investigate light actinide oxides in higher oxidation states, such as U₃O₈, PuO_{2+x}, and Np₂O₅, for which non-collinear magnetic ordering is predicted. The possible further oxidation of PuO₂ to PuO_{2+x} is studied using DFT+*U* calculations in combination with x-ray absorption measurements [2].

The Pu monochalcogenides are intriguing materials, in which a correlated temperature gap develops, reminiscent of the behavior seen in Kondo insulators. Using dynamical mean field theory (DMFT) in comparison to LDA+*U* calculations, we show that dynamical self-energy fluctuations are important for the formation of an unusual gap. Static approximations to the self-energy as the LDA+*U* fail to provide a gap.

For URu₂Si₂ we report extensive electronic structure investigations [3], using full-potential LSDA, LSDA+*U*, and DMFT approaches to assess the origin of the hidden order. Our investigation show that the itinerant f-electron picture provides an excellent description of the materials properties of this fascinating compound. The Fermi surface which is crucial for the HO transition and the occurrence of unconventional superconductivity is accurately given. Our study points to the formation of long-lived spin fluctuations that are the driving quasiparticles for the HO.

1. M.-T. Suzuki, N. Magnani, and P.M. Oppeneer, Phys. Rev. B **82**, 241103(R) (2010).
2. A. Modin, Y. Yun, M.-T. Suzuki et al., Phys. Rev. B **83**, 075113 (2011).
3. P.M. Oppeneer, J. Ruzs, S. Elgazzar, M.-T. Suzuki, T. Durakiewicz, and J.A. Mydosh, Phys. Rev. B **82**, 205103 (2010).

2:40pm AC+MI-WeA3 Anomalous Quasiparticle Dynamics in the Hidden Order state of URu₂Si₂, *T. Durakiewicz, G.L. Dakovski, Y. Li, S.M. Gilbertson, G. Rodriguez, A.V. Balatsky, J.X. Zhu, K. Gofryk, E.D. Bauer, P.H. Tobash, A. Taylor, J.L. Sarrao*, Los Alamos National Lab, *P.M. Oppeneer*, Uppsala Univ., Sweden, *P.S. Riseborough*, Temple Univ., *J.A. Mydosh*, Leiden Univ., the Netherlands **INVITED**

An exotic phase of unknown nature emerges from a heavy fermion state in URu₂Si₂ at T₀ = 17.5 K. The nature of this hidden order (HO) state is being vigorously debated, while the massive removal of entropy due to the HO transition evades explanation. Here we use time- and angle-resolved photoemission spectroscopy (tr-ARPES) to elucidate the itinerant nature of HO. We show how the Fermi surface is renormalized by shifting states away from the Fermi level at specific hot spots. By measuring the ultrafast dynamics we identify the location and lifetime of the quasiparticle states forming at the hotspots. We find that the quasiparticle lifetime increases from 42 fs to few hundred fs across the HO transition, and the hidden order parameter is related to the anisotropic gapping of the Fermi surface.

4:00pm AC+MI-WeA7 Advanced X-ray Spectroscopies on 4f and 5f Systems, *J. Bradley, M. Lipp*, Lawrence Livermore National Laboratory, *A. Sorini*, SLAC National Accelerator Laboratory

Photon-in photon-out x-ray spectroscopies allow for a bulk-sensitive, high-pressure compatible look at rare earth and actinide electronic structure. The techniques couple to well-defined and meaningful quantum mechanical observables, including orbital occupation number and magnetic moment. These observables are key differentiators between theoretical treatments of strongly correlated systems, and they also provide meaningful and correct intuitive understanding. Here we will present a selection of measurements, both at ambient and high pressure, that exemplify the kind of insight these techniques can provide. In particular, we will address the question of rare earth volume collapse, where considerable controversy has existed between competing (Mott vs. Kondo) theoretical treatments.

4:20pm AC+MI-WeA8 Hard X-Ray Photoelectron Spectroscopy and Electronic Structure of Single Crystal UPd₃, UGe₂, and USB₂, *M.F. Beaux, T. Durakiewicz, J.J. Joyce, E.D. Bauer, J.L. Sarrao*, Los Alamos National Laboratory, *L. Moreschini, M. Grioni*, Ecole Polytechnique Federale, Switzerland, *F. Offi*, Universita Roma Tre, Italy, *M.T. Butterfield*, KLA-Tencor, *G. Monaco*, European Synchrotron Radiation Facility, France, *G. Panaccione*, Laboratorio Nazionale TASC-INFN-CNR, Italy, *E. Guziewicz*, Polish Academy of Sciences

Hard X-ray Photoelectron Spectroscopy (HAXPES) with 7.6 keV photons has been performed on single crystals of UPd₃, UGe₂, and USB₂ at the European Synchrotron Radiation Facility (ESRF). The greatly reduced surface sensitivity of HAXPES enabled observation of the bulk core levels in spite of surface oxidation. An 800 meV splitting within the Sb 3d core level was observed. The splitting of the Sb core levels is attributed to manifestations of two distinct Sb binding sites within the USB₂ single crystal as supported by consideration of interatomic distances and enthalpy-of-formation. Photoelectron mean-free-path vs oxide layer thickness considerations were used to model the effectiveness of HAXPES for probing bulk features of in-air cleaved samples.

4:40pm AC+MI-WeA9 Actinide Dioxides under Pressure, *L. Petit*, Daresbury Laboratory, UK

The self-interaction corrected local spin density approximation is used to investigate the oxidation of actinide dioxides under pressure. The methodology enables us to determine the ground state valency configuration of the actinide 5f electrons and to study the localization/delocalization transition that occurs under pressure. We argue that this delocalization facilitates the oxidation of the actinide dioxides and present results for the estimated transition pressures.

5:00pm AC+MI-WeA10 Hybridization and Electronic Structure in Pu Compounds, *J.J. Joyce, T. Durakiewicz, K.S. Graham, M.F. Beaux, E.D. Bauer, J.N. Mitchell, T.M. McCleskey, E. Bauer, Q.X. Jia, R.L. Martin, J.X. Zhu, J.M. Wills*, Los Alamos National Laboratory, *L. Roy*, Savannah River National Laboratory, *G.E. Scuseria*, Rice University

The electronic structure of Pu materials is directly tied to the details of the 5f electron bonding and hybridization. In compounds where direct 5f-5f bonding is negligible due to crystal structure and wavefunction overlap, hybridization is the key component for 5f electron influence on electronic properties. We examine two strongly correlated materials, PuCoGa₅ and PuO₂ that span the range of interesting materials from Mott insulator to heavy fermion superconductor. The synergy between synthesis, spectroscopy and modeling has provided a unique opportunity to explore details of the energy and crystal momentum dependence of Pu compound electronic structure through angle-resolved photoemission on single crystal samples and advanced modeling based on theories beyond density functional theory.

The strength of the 5f electron hybridization may be quantified through dispersion in 5f electron peaks from the angle-resolved photoemission. In the case of PuO₂, we see over two eV of dispersion in the hybridized (O 2p - Pu 5f) valence band. For PuCoGa₅, the quasiparticle peak at the Fermi energy shows 50 meV or more of dispersion in reciprocal space over a range covering slightly less than half the zone center to zone boundary. We are unable to follow the peak dispersion beyond this point as it crosses above the Fermi energy. These energy dispersions place significant constraints on models, which might be used to describe the electronic structure of these strongly correlated materials. For PuCoGa₅, models, which place the 5f electrons in a localized configuration without significant hybridization, would not agree with the experimental results. In the case of PuO₂, the dispersion measured in photoemission agrees well with the

hybrid functional calculations for PuO₂ and further support the increase in hybridization moving from ionic UO₂ to covalent PuO₂.

5:20pm **AC+MI-WeA11 Structure and Magnetic Properties of Actinide-Based Thin Films**, *L. Havela*, Charles University, Czech Republic, *N.-T. Kim-Ngan*, Pedagogical University Cracow, Poland, *A. Adamska*, Charles University, Czech Republic, *A.G. Balogh*, TU Darmstadt, Germany, *T. Gouder*, European Commission, JRC Institute for Transuranium Elements, Germany

INVITED

Actinide-based sputter deposited films were so far used in the context of surface-science studies (such as [1]) and for exploration of electronic structure by photoelectron spectroscopy (e.g. [2,3]). In addition, sputter deposition was used in attempts to synthesize amorphous uranium alloys for ex-situ studies of magnetic properties. Such early (late 1980's) attempts in U.S. [4] or Japan [5] were undertaken in simple setups and lack proper diagnostics of the deposited material. Considering strong electropositivity of U, oxidation has to be suspected for films prepared in HV conditions. More recently, U metal in multilayers with possibility of epitaxial growth were sputter deposited with the aim to induce uranium magnetic moments [6]. We have used sputter deposition to investigate structure and magnetic properties of various U-based compounds as a function of deposition conditions (deposition rate, substrate type and temperature). Employing diagnostics by XPS, Glancing Angle XRD, and RBS, it was established that UN films have a long-term stability, which allows comfortably to make ex-situ studies over months. The reason can be seen in pronounced compressive residual strains, imposed during the deposition, which prevent progressing the surface oxidation into the bulk of several hundred nm thick films. Departing more from a fully crystalline state, the antiferromagnetism of UN is masked by a weak ferromagnetism, as usual for nanograined AF structures, and finally both moments and their order disappears [7]. Similar suppression of magnetism was found for ferromagnetic US [8].

Recently we undertook sputter-deposition experiments on Fe-rich U-Fe alloys derived from the Laves phase UFe₂, which combines the 3*d* and 5*f* magnetism in a compound with a relatively high Curie temperature ($T_C = 162$ K). An Fe-excess is expected to increase the T_C value markedly. Nanocrystalline material obtained up to the stoichiometry UFe_{2.3} by splat cooling, with the excessive Fe atoms entering the U sublattice has T_C enhanced up to 230-240 K. More Fe leads to the segregation of α -Fe. We succeeded to synthesize amorphous films by U and Fe co-sputtering, with stoichiometry up to UFe₃. T_C is enhanced up to 450 K in this case.

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- [2] T. Gouder et al., Phys.Rev.Letters 84 (2000) 3378.
- [3] L. Havela et al., Phys.Rev.B 65 (2002) 235118.
- [4] P.P. Freitas et al., J.Appl.Phys. 63 (1988) 3746.
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- [6] R. Springell et al., Phys. Rev. B 77 (2008) 064423.
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Thursday Morning, November 3, 2011

Actinides and Rare Earths Focus Topic

Room: 207 - Session AC+SS-ThM

The Surface Science of Actinides and Rare Earths

Moderator: R. Schulze, Los Alamos National Laboratory

8:00am AC+SS-ThM1 **The XPS of Heavy Metal Oxides: New Insights Into Chemistry**, P.S. Bagus, University of North Texas, E.S. Iltis, Pacific Northwest National Laboratory, C.J. Nelin, Consultant **INVITED**

The XPS of Rare Earth and Actinide oxides are commonly used to obtain information about the oxidation state of the metal by taking various features of the spectra as fingerprints of the metal oxidation state. However, it is possible to obtain detailed information about the nature of the chemical interactions from these features by using the predictions of rigorous theoretical analyses. One of our important concerns is to make direct assessments of the covalent character of the metal-ligand interaction; i.e., the mixing of O(2p) with partly occupied, or unoccupied, metal levels to form bonding and anti-bonding orbitals. We relate this covalent character to the XPS features. In particular, we investigate the connection between the covalent character of the interaction and the satellite intensity. We also investigate the characterization of the satellites and discuss their assignment as shake satellites, an assignment that is naturally connected with the extent of the covalent mixing of the metal and oxygen levels. Furthermore, we examine how vibrational excitations can lead to broadening of the XPS features and suggest that the observed broadening of XPS peaks may contain, hitherto not utilized, information about the chemical interactions in an oxide. Our focus will be on the XPS of two Rare Earth oxides, CeO₂ and LaAlO₃, and two actinide oxides, UO₂ and UO₃; these systems have different electronic character that permit the mechanisms discussed above to be explored and compared. Our theoretical analyses are based on relativistic molecular orbital wavefunctions, WF's, for both initial states, before ionization, and final states, after ionization. The WF's are for materials models that contain explicit cations and anions embedded in a point charge field. With the variationally optimized orbitals for these WF, covalent mixing is naturally taken into account. The cluster WF's include one-body and many-body effects and do not use parameters that are adjusted to make calculated relative energies and intensities fit to experiment.

8:40am AC+SS-ThM3 **New Insights into the Oxidation/Corrosion of Plutonium**, D.L. Pugmire, H.G. Garcia Flores, D.P. Moore, A.L. Broach, Los Alamos National Laboratory, P. Roussel, Atomic Weapons Establishment, UK **INVITED**

An understanding of the oxidation and corrosion processes of plutonium metal at room temperature is important to the safe, effective use and storage of this reactive metal. The oxidation rate for the δ -phase stabilized, plutonium/gallium alloy (a commonly employed alloy) can be significantly affected by a number of parameters including the gallium content and the composition of the oxidizing atmosphere (O₂, O₂/H₂O, H₂O). The nature of plutonium oxidation has typically been thought of as the growth of a dioxide (PuO₂) overlayer on the metal to a thickness at which the film begins to spallate (μ 's). Based on thermodynamic arguments, it has been pointed out that a relatively thin layer of the sesquioxide (Pu₂O₃) should exist at the dioxide/metal interface for thick oxide films.

Historically, the oxidation/corrosion of plutonium has been studied by oxygen uptake of samples at elevated temperatures inferred from mass gain measurements. Accuracy of these experimental setups likely limited measurements to oxide films thicker than ~0.05 to 0.1 μ (50 - 100 nm). This is at the upper-limit of the thicknesses typically observed for plutonium oxide films. Little work has been published for studies of plutonium oxide thin-films (< 50 nm) on metal substrates. Additionally, very little is known about the role that gallium plays during the oxidation of the alloy other than it can significantly slow the rate.

We report here our studies of the initial stages of plutonium oxidation with O₂ in the thin-film regime with x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The results indicate that not only does a Pu₂O₃ layer exist in thin plutonium oxide films, but that the sesquioxide exists as a substoichiometric species on a metal substrate, and is probably best described as Pu₂O_{3-y}. It also appears that the oxide thin-film is comprised mainly of the sesquioxide species, with PuO₂ accounting only for a relatively thin portion of the overall oxide film thickness. While the surface sensitive techniques employed here suffer from relatively high limits of detection, we have also been able to qualitatively, and in some cases quantitatively, study the behavior of gallium during the oxidation of the δ -plutonium alloy. The gallium content relative to plutonium is observed to decrease within the oxide film during oxidation, with the

displaced gallium moving to the oxide/metal interface to form a thin gallium rich region. These new results will be compared and contrasted with existing literature. Additionally, how these results have altered our understanding of the Pu/O thin-film system and the oxidation/corrosion of plutonium will be discussed.

9:20am AC+SS-ThM5 **The Oxidation of Uranium Dioxide at High Pressures in Pure Oxygen**, J.C. Crowhurst, Z. Dai, J.M. Zaig, K.B. Knight, A.J. Nelson, W.J. Siekhaus, I.D. Hutcheon, Lawrence Livermore National Laboratory

The oxidation of uranium dioxide has received much experimental and theoretical attention over the last several decades in large part because of its relevance to the operation and storage of uranium-based nuclear fuel. The oxidation process is inherently complicated, involving the formation of multiple different phases via distinct mechanisms even at relatively low temperatures. In the range of a few hundred degrees centigrade oxidation is generally assumed to be a two step process[1]: UO₂ → U₃O₇/U₄O₉ → U₃O₈. At low pressures the intermediate phases adopt crystal structures that are modifications of the UO₂ fluorite structure and are slightly denser. By contrast, U₃O₈ forms a considerably less dense orthorhombic structure (by some 23%). The large volume expansion resulting from the oxidation of UO₂ to U₃O₈ is a potentially serious concern in the event of oxidation of a fuel element, with consequent splitting of protective sheaths and the spalling of powder.

While attention has been focused on the oxidation of UO₂ at elevated temperatures, the associated experiments have all been performed at low partial pressures of oxygen. It is unclear how pressure affects the oxidation process – particularly in the context of the formation of U₃O₈, with its large volume change with respect to UO₂. We have examined the oxidation of a nominal single crystal of UO₂ in pure oxygen at elevated pressures up to approximately 0.9 GPa (9000 atm) and temperatures of up to 450 °C. In-situ Raman scattering measurements were made as a function of temperature in order to monitor the oxidation. Recovered material was examined using electron based techniques including SEM, TEM, and electron diffraction and also using x-ray photoelectron spectroscopy.

Material synthesized under high pressure has a Raman spectrum that is different from both the UO₂ starting material and the common form of U₃O₈. Also, compared with common U₃O₈, we find that it has fewer crystalline defects and mostly adopts a hexagonal rather than orthorhombic form. Figure 1 of the supplemental document compares Raman spectra of UO₂ in oxygen with synthesized material. Fig. 2 compares electron diffraction obtained from recovered material with U₃O₈ synthesized at ambient pressure.

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9:40am AC+SS-ThM6 **Radiation Effects on Hydrogen Reactivity in Narrow Uranium-Uranium and Uranium-LiD (or Air) Gaps using MCNPX Code**, M.A. Schildbach, W.J. Siekhaus, Lawrence Livermore National Laboratory

Preferential uranium hydriding occurs frequently in narrow gaps. There are different hypotheses about its causes, one of which could be radiation-induced chemistry in gaps. Both ²³⁸U and ²³⁵U generate ionizing α , β , and γ radiation capable of vibrationally or translationally exciting, ionizing, or dissociating H₂, all of which increase the reactivity of H₂ with uranium. Dissociation of H₂ is necessary to initiate hydriding, and it has been shown that the sticking coefficient of H atom is about 1200 times higher than H₂'s[1]. Here we use the MCNPX radiation transport code to calculate the energy dependent electron flux generated from the ^{234m}Pa β decay and from photoelectrons generated by brems-strahlung. We apply the code to gaps occurring in two ²³⁸U cylindrical pieces welded together and filled on the inside with LiD with a 100 μ m gap between ²³⁸U and LiD, and having a 100 μ m gap in ²³⁸U itself, typical for step-joint-welded uranium shells.

The MCNPX Monte Carlo Code - as configured now - tracks the life cycle of electrons throughout the material and calculates the electron flux as a function of energy, putting results into "energy bins" 1 keV wide. We find that at 2 keV (\pm 5 keV, the last energy bin) the calculated electron flux in the U-U gap is approximately 19 times larger than in the U-LiD gap, and fifty two times larger than in the U-air gap on the outside of the cylindrical

shells. Cross-sections for electron-hydrogen collisions peak, however, below 1 keV energy. We establish the upper limit of the effect of electron-hydrogen collisions by extrapolating the MCNPX electron flux results from the last bin to energies as low as 1 eV by fitting a function to the flux between 2 and 20 keV. To calculate the fraction of H₂ vibrationally or translationally excited, ionized, or dissociated per cm²/s, we integrate the product of the energy dependent cross sections (listed in reference [2]) and the energy dependent electron flux over the relevant energy range. The fraction of H₂ molecules calculated to be dissociated is small, but significant during long-time exposure. Future work will extend the MCNPX code below 1keV (as is done for biological radiation damage), to avoid energy extrapolation.

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

References

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10:40am **AC+SS-ThM9 Study of the Gd₅Ge₄ (010) Surface.** *C. Yuen, G. Miller, P.A. Thiel*, Ames Laboratory - US DOE

Certain intermetallics of Gd, Ge, and Si exhibit giant magnetocaloric effects, yet very little is known about their surfaces. We have investigated one such system, Gd₅Ge₄, with the goal of elucidating its clean and oxidized surface structure, using STM and XPS. The clean Gd₅Ge₄ (010) surface exhibits a step-terrace morphology after repetitive sputtering and annealing at 900 K. Step heights are equal to half the bulk unit cell length in the <010> direction, consistent with the existence of an equivalent plane in the middle of the unit cell. Surface compositions of Gd and Ge are close to the bulk composition. However, at higher temperatures—between 900 K and 1200 K—the surface becomes Gd poor by 10 at.%. In STM, at these temperatures, the fine structure on the terraces changes, and a different type of terrace with a different step height emerges. We propose that the preferred surface termination is rich in Gd (which has lower surface energy than Ge), and that this termination is exposed after annealing at 900 K. At higher temperature, we propose that Gd (which has higher vapor pressure than Ge) evaporates preferentially, leading to the changes described above and exposing a Ge-rich surface termination. Finally, we find that Gd oxidizes preferentially.

11:00am **AC+SS-ThM10 Using Spatially Controlled Thin-Films Coatings Around Rare-Earth doped Nanophosphors for High Efficiency Energy Applications.** *J.A. Dorman, A. Joshi, G. Kuzmanich, J.H. Choi, J.P. Chang*, University of California Los Angeles

The development of rare-earth (RE) doped phosphors allows for the conversion of photons to energies that are more usable for the desired application. Additionally, these RE phosphors have long lifetimes, on the order of ms, which offer potential in many energy conversion and energy transfer devices. Currently, RE phosphors are used in fiber optics amplifiers, broad absorption solar cells and various other lighting applications. Energy transfer mechanisms of the excited RE states, such as defect quenching and sensitizer/emitter interactions, must be understood in order to achieve high efficiency energy conversion and propagation.

In order to increase the efficiency of solar cells, high efficiency phosphors need to synthesize in order to convert photons at the edge of the absorption band into higher energy photons while avoiding undesired quenching effects. In effort to produce these high efficiency phosphors, spatially controlled RE doped thin films are deposited around nanoparticles (NP) to produce a core-shell nanophosphor. Reduction in luminescent quenching can be achieved by increasing the distance between the surface quenching site and active ions through the deposition of a precisely controlled thin film around the NP. Secondly, the luminescent fingerprint can be further controlled through doping of the shell structure by increasing the absorption spectrum or the introduction of emission peaks. Deposition of a thin film around an Y₂O₃:Er³⁺ core NP is achieved via atomic layer deposition or sol-gel synthesis to compare the effect of a spatially controlled vs. a random dopant distribution. Primarily, this work focuses on the emission of visible photons through upconversion, making them ideal components in broad absorption solar cells. By spatially controlling the position and concentration of the RE ions within the nanostructure, increased luminescence is observed due to energy transfer between the dopant ions within a critical interatomic distance. Passivation of surface sites with increasing film thickness was shown to increase luminescent lifetimes up to 53%, with a critical shell thickness of 8 nm, while lowering the theoretical lifetimes extracted from Judd-Ofelt parameters. The effect of the spatially

controlled Yb ions was probed through the extraction of the upconversion photon requirement, showing a statistical decrease in photons from 2.16 to 1.43, or ~30 %. Finally, the effective energy transfer distance and energy transfer coefficients were studied as a spacer layer is added to the system, showing energy transfer up to ~3 nm, confirming the Förster-Dexter theory.

11:20am **AC+SS-ThM11 Growth and Characterization of Scandia Stabilized Zirconia and Samaria Doped Ceria Multi-Layer Thin Films.** *S. Thevuthasan*, Pacific Northwest National Laboratory, *M.I. Nandasiri*, Western Michigan University, *T. Varga, V. Shuthanandan, S.P. Sanghavi, S.V.N.T. Kuchibhatla*, Pacific Northwest National Laboratory, *A. Kayani*, Western Michigan University

Recent studies showed a colossal enhancement in the ionic conductivity of multi-layer oxygen-ion conducting thin films compared to most commonly used solid oxide fuel cell (SOFC) electrolytes. It has been observed that, the oxygen ionic conductivity of nano-scale hetero-structures increases with the increase in number of layers. However, some of these findings were questioned due to the inability to distinguish electronic and ionic conductivity. Thus, here we investigated the scandia stabilized zirconia and samaria doped ceria (SDC/ScSZ) multi-layer system to understand the oxygen-ion conductance in multi-layer hetero-structures.

In this study, the growth of SDC and ScSZ multi-layer thin films was carried out using the optimized growth conditions, dopant concentrations and film properties established for single-layer SDC and ScSZ epitaxial thin films. The epitaxial SDC and ScSZ multi-layer thin films were grown on Al₂O₃(0001) substrates by oxygen plasma-assisted molecular beam epitaxy (OPA-MBE) at 650°C. The number of layers in the multi-layer hetero-structures was varied from 2 to 20 by keeping the total film thickness constant at 140 nm. Following the growth, thin films were characterized by various in-situ and ex-situ characterization techniques including reflection high energy electron diffraction (RHEED), x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), and x-ray photoelectron spectroscopy (XPS). The initial streaky RHEED pattern indicates the epitaxial growth of SDC/ScSZ multi-layer thin films. Furthermore, RHEED patterns indicate the transition of the initial smooth surface to a rough surface with the increase in number of layers. The individual layer thickness was found to be approximately 7 nm for the twenty-layer film as confirmed by x-ray reflectivity data. RBS was also used to find the composition and thickness of the films. HRXRD patterns of ScSZ/SDC thin films exhibit only CeO₂(111) and ZrO₂(111) reflections, indicating the growth of epitaxial SDC(111) and ScSZ(111) multi-layers. XPS depth profile confirmed the uniform dopant concentration in both SDC and ScSZ layers, which was found to be 7 and 6 atom % for Sc and Sm, respectively. In the near future, the ionic conductivity of SDC and ScSZ multi-layer thin films will be measured by four probe conductivity method.

Thursday Afternoon, November 3, 2011

Actinides and Rare Earths Focus Topic

Room: 207 - Session AC+TF-ThA

The Structure, Properties and Chemistry of Thin Films of Actinides and Rare Earths

Moderator: L. Havela, Charles University, Czech Republic

2:00pm **AC+TF-ThA1 Plutonium Sorption and Reactivity at the Solid/Water Interface.** *M. Schmidt, P.A. Fenter, S.S. Lee, R.E. Wilson, L. Soderholm*, Argonne National Laboratory **INVITED**

Reliable long-term predictions about the safety of a potential nuclear waste repository must be based on a sound, molecular-level comprehension of the geochemical behavior of the radionuclides. We apply *in situ* crystal truncation rod (CTR) measurements and resonant-anomalous X-ray reflectivity (RAXR) in combination with alpha-spectrometry to elucidate the sorption behavior of tetravalent actinides on muscovite under varying solution conditions.

Key retention mechanisms, particularly in clay formations, are surface mediated processes. In order to be able to understand these processes analytical techniques that allow selectively probing the mineral/water interface and elucidating processes at the interface under *in situ* conditions are required. X-ray reflectivity techniques (CTR, RAXR) have proven to be valuable tools for geochemical studies concerning the sorption behavior of metal ions [1]. More recently they have also been applied to study the sorption behavior of actinides [2].

From CTR measurements the complete adsorption structure, consisting of adsorbed water and the ions adsorbed as inner sphere, outer sphere or extended outer sphere complex can be derived. RAXR extends this approach by providing elemental specificity to the CTR measurements, thus characterizing the contribution of a particular element to the structure.

Using a purpose-built sample cell for radiological experiments, X-ray reflectivity data was collected *in situ* from muscovite ($\text{KA}_2[(\text{OH},\text{F})_2\text{AlSi}_3\text{O}_{10}]$) in contact with the actinide-bearing solutions varying in composition (ionic strength, actinide concentration and speciation, background electrolyte). The data is complemented by precise quantitative analysis by means of alpha-counting experiments. The results clearly show the strong influence of the actinides' aqueous chemistry on their sorption behavior. It will be shown that a full description of the sorption behavior requires parameters such as the hydration enthalpy, complexation constants, hydrolysis constants, and polymer formation constants. At low actinide concentrations the formation of hydrated surface complexes is observed in good agreement with the large hydration enthalpies of the highly charged ions. At large excess of background electrolyte sorption occurs under preservation of the complexation by the anion. When a threshold metal ion concentration is exceeded sorption of polymers is observed which grow up to 150Å in size, while covering only small fractions of the surface.

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2. Fenter, P.; Lee, S. S.; Park, C.; Soderholm, L.; Wilson, R. E.; Schwindt, O., GCA, 2010, 74, 6984-6995.

2:40pm **AC+TF-ThA3 Crystal Chemistry of Thorium Oxy Compounds Containing Tetrahedral Oxyanions.** *A.J. Albrecht, P.C. Burns*, University of Notre Dame

Here we examine the crystal chemistry and structural topologies of Th compounds containing various cations that are coordinated by oxygen atoms in tetrahedral arrangements. We define the structural unit to be the part of the structure that consists of those polyhedra that contain higher valence cations, with an emphasis on their connectivity. In most cases, structures also contain interstitial units that balance the charge of the structural unit. In the compounds under study, which include both new structures and those from the literature, we find structural units ranging from clusters and chains, through sheets, to extended frameworks. The structural units in thorium compounds are of particular interest because they provide insights into the possible structures of compounds consisting of tetravalent transuranium cations, especially Np and Pu.

3:00pm **AC+TF-ThA4 Solution Route to High Quality Epitaxial Actinide Films Form Oxides to Carbides.** *T.M. McCleskey, E. Bauer, A.K. Burrell, B.L. Scott, Q.X. Jia, T. Durakiewicz, J.J. Joyce, S.A. Kozimor, S.D. Conradson, R.L. Martin*, Los Alamos National Laboratory
We report on the solution based synthesis of epitaxial thin films of neptunium oxide and plutonium oxide. Actinides represent a tremendous

challenge to first principle calculations of orbital energies due to the complicating features that arise from f orbital interactions. Theoretical development from first principle calculations relies on predictions of continuous materials with no boundaries. To test these theories requires experimental results using high quality single crystals. For many materials this can be a straight forward process. For actinide oxides the experimental work is complicated by the radioactivity that makes CVD processes challenging from a safety perspective and by the recalcitrant nature of the oxides. The challenge of modeling actinide oxides is best represented in Mott insulators such as UO_2 . Theoretical calculations that worked with transition metals predict UO_2 to be a metal as opposed to an insulator with a 2.3 eV band gap. Recent reports predict the same metallic behavior for NpO_2 . Many theoretical reports have highlighted the need for experimental work on single crystals. In the absence of single crystals they rely on work done on powders as in the case of PuO_2 . We report here on epitaxial films of PuO_2 that are thin enough to measure the optical band gap directly. XRD has been used to determine the alignment of the PuO_2 relative to the substrate and EXAFS confirm the stoichiometry.

3:40pm **AC+TF-ThA6 U(VI) Uranyl Cation-Cation Interactions in Framework Germanates.** *J.M. Morrison, P.C. Burns*, University of Notre Dame

The crystal structure determinations of four highly complex U(VI) germanate framework compounds reveal three distinct U(VI) sites—two that are coordinated by five equatorial oxygen atoms each to form pentagonal bipyramids and one that is coordinated by six oxygen atoms to form a distorted octahedron without the uranyl ion [1]. This is uncommon as most inorganic U(VI) compounds contain the uranyl ion, $(\text{UO}_2)^{2+}$. Also present are cation-cation interactions which occur when an oxygen atom of the uranyl ion also acts as an equatorial oxygen atom in a neighboring U(VI) polyhedron. CCI's are present in fewer than 2% of U(VI) compounds. Finally, a disordered system with the possibility of a one-dimensional GeO_5 chain has led us to suggest three structural models with regard to Ge coordination. The interesting structural and chemical complexities of these CCI-bearing compounds will be presented along with a discussion of the densities of CCI-bearing U(VI) compounds.

[1] Morrison, J.M.; Moore-Shay, L. J.; Burns, P.C. *Inorg. Chem.* **2011**, 50, 2272-2277.

4:20pm **AC+TF-ThA8 The Crystal Chemistry of Uranyl Selenates and their Relations with Uranyl Sulfates.** *E.M. Wylie, P.C. Burns*, University of Notre Dame

Uranyl sulfate minerals have been studied for several decades owing to their importance in understanding ore genesis, as well as the interaction of uranium mine and mill workings with the environment. In contrast, no uranyl selenate minerals have been described, although several uranyl selenites are known. We are exploring the crystal chemistry of synthetic uranyl selenates produced under mild hydrothermal techniques. We have obtained crystals of several compounds and characterized them with single-crystal X-ray diffraction. They contain a sheet of edge-sharing uranyl pentagonal bipyramids and selenate tetrahedra that is topologically identical to those found in the zippeite group of uranyl sulfate minerals. These synthetic materials provide further insights into layered uranyl phases, including the relationships between the configurations of the structural sheets and their corresponding interlayer complexes. These structures will be placed in the context of known synthetic and natural uranyl sulfate and selenate compounds.

4:40pm **AC+TF-ThA9 Radiation-Induced Degradation of Photoluminescence in YAG:Ce.** *S.G. Gollub, D.G. Walker, S.L. Weeden-Wright*, Vanderbilt University

Thermographic phosphors are ceramic based materials whose photoluminescence is temperature dependent. We fabricated the phosphor YAG:Ce to determine its sensitivity and selectivity to various radiation environments. In particular we investigated the effects of non-ionizing radiation on the photoluminescent spectra. No change to the spectrum was observed after exposure to 1 MRad of x-ray radiation. Because x-rays are typically ionizing, we did not expect to see any significant degradation. When the material was bombarded with protons, which are known to cause displacement damage in many materials, a degradation was observed. Results of damage cross section and stopping power were commensurate with predicted values using SRIM. Results are shown as a function of proton energy and dose.

5:00pm AC+TF-ThA10 **The Behavior of Uranyl Peroxide Pyrophosphate Nanoscale Cage Clusters in Aqueous Solution, K.L. Pellegrini, P.C. Burns, J. Szymanowski, J. Ling, J. Qiu**, University of Notre Dame

Twenty-six nanoscale cage clusters built from uranyl polyhedra have been reported to self-assemble in aqueous solutions over a range of pH conditions [1]. All contain peroxide groups that bridge between uranyl polyhedra, and some contain additional linkages such as pyrophosphate and oxalate. The focus of the current study is the U₂₄P₁₂ cluster that consists of 24 uranyl hexagonal bipyramids and 12 pyrophosphate groups. We have optimized the synthesis of this cluster to obtain pure yields. Subsequently, we have examined the behavior of the cluster in solution using electrospray ionization mass spectroscopy and small angle X-ray scattering. These studies are emphasizing the persistence of this cluster under a variety of conditions, as well as their aggregation in solution. Such materials are of considerable interest because of potential applications in an advanced nuclear energy system, including in fuel recycling. Results to date show that the U₂₄P₁₂ cluster persists in aqueous solution for several days under a range of conditions, and can be induced to aggregate via addition of various counterions.

1. Burns, P.C. *Mineralogical Magazine*. **2011**, 75, 1-25 Open Access on petercburns.com

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