

# Monday Morning, October 18, 2010

## Actinides and Rare Earths Topical Conference

Room: Isleta - Session AC+SS-MoM

### Surface Science of Actinides

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

9:00am **AC+SS-MoM3 High Resolution Auger Electron Spectroscopy of Plutonium Metal and Oxide Surfaces**, *D.P. Moore, A.L. Broach, D.L. Pugmire*, Los Alamos National Laboratory, *H.G. Garcia Flores*, University of Nebraska-Lincoln, *P. Roussel*, Atomic Weapons Establishment

There has been considerable new study of the oxidation of plutonium in recent years. Much of this study has focused on the properties of the thin film oxide layers that form on the plutonium metal surface under exposure to oxygen. For these studies, x-ray photoelectron spectroscopy (XPS) has typically been the technique of choice as it is ideally suited for the study of oxidation states by analyzing XP peak shape and position changes. This allows for the identification of relative changes in the Pu 4f manifold in going from Pu metal, to the Pu sesquioxide ( $\text{Pu}_2\text{O}_3$ ), to the Pu dioxide ( $\text{PuO}_2$ ). But there are advantages of other surface science techniques, specifically Auger electron spectroscopy (AES), over XPS for certain types of studies. Prime among them is that AES has a much higher spatial resolution than XPS allowing for analysis of specific areas and features on a surface down to a few tens of nanometers. And although AES typically suffers from less sensitivity and specificity to chemical state differences in its peak shape and position, modern Auger systems with field emission sources and hemispherical electron analyzers have alleviated much of this shortcoming.

For plutonium, Auger peaks for the metal and dioxide have been used for investigation whereas the Auger peaks for the sesquioxide have not received the same study. Peak positions from derivative spectra have been used for distinguishing between metal and oxide with quantification of the oxides from peak-to-peak heights and estimates of relative sensitivity factors. In order to more fully utilize AES for the study of the oxidation of plutonium surfaces, the relative changes in the Auger peaks in going from Pu metal to all its oxides must be quantified. We have used high resolution AES to identify the Auger peak structure of Pu metal,  $\text{PuO}_2$ , and  $\text{Pu}_2\text{O}_3$ . We have studied the OPP and OVV Auger transitions in the 80 – 110 eV range as well as the NOV transitions at approximately 315 eV via oxygen dosing on Pu metal surfaces. Oxygen doses from less than a Langmuir up to over 500 Langmuirs have been investigated. Relative changes in both the integrated and derivative Auger peak structures for Pu metal,  $\text{PuO}_2$ , and  $\text{Pu}_2\text{O}_3$  have been identified and will be presented. Using this new information we will be able to take advantage of the higher spatial resolution of AES to further study plutonium oxide properties such as layer structure, oxidation kinetics, and auto reduction on polycrystalline plutonium samples.

9:20am **AC+SS-MoM4 The Behavior of Gallium During the Initial Stages of Plutonium/Gallium Alloy Oxidation**, *D.L. Pugmire*, Los Alamos National Laboratory, *H.G. Garcia Flores*, University of Nebraska-Lincoln, *D.P. Moore, A.L. Broach*, Los Alamos National Laboratory, *P. Roussel*, Atomic Weapons Establishment

An area of significant importance to the oxidation of any alloy is the role that the constituent metals play. It has been previously shown that the oxidation rate for the  $\delta$ -phase stabilized, plutonium/gallium alloy can be significantly affected by the gallium content as well as composition of the oxidizing atmosphere ( $\text{O}_2$ ,  $\text{O}_2/\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$ ). Reasons for the observed rate changes upon alloying with gallium are not understood. A previous study of a variety of  $\delta$ -plutonium alloys shows that the significant structure difference between unalloyed  $\alpha$ -plutonium and alloyed  $\delta$ -plutonium cannot be the sole cause of different oxidation rates. This implies that the alloying metal must play some role in the slower oxidation rates observed for gallium-stabilized  $\delta$ -plutonium. In order to elucidate the oxidation mechanism of this commonly employed alloy, it is important to understand the role gallium plays during oxidation. The relatively low concentrations of alloying metals used, typically several atomic percent, can make the activities of gallium during oxidation of  $\delta$ -plutonium difficult to follow. This complication is compounded by the fact that the initial stages of oxidation are inherently a surface phenomenon, thereby significantly limiting the relative amount of affected material. Significant questions remain as to what is a realistic description for the Pu/Ga-oxide, thin-film system during the initial stages of oxidation.

An ultra-high vacuum (UHV) system equipped with surface sensitive techniques, such as x-ray photoelectron spectroscopy (XPS) and Auger

electron spectroscopy (AES), provides a controlled environment ideally suited to study the behavior of gallium during the initial stages of Pu/Ga oxidation. In addition to information about the oxidation states of the plutonium species in the near surface region provided by XPS, both XPS and AES are very useful for studying the relative atomic concentration of elements present at the sample surface (such as oxygen and gallium). While these surface sensitive techniques suffer from relatively high limits of detection, we have been able to qualitatively, and in some cases quantitatively, study the behavior of gallium during the oxidation of the  $\delta$ -plutonium alloy. The gallium content relative to plutonium is observed to decrease within the oxide film during oxidation, with the displaced gallium apparently moving to the oxide/metal interface to form a thin gallium rich region. The results of these studies and their implications on the mechanism of gallium-stabilized,  $\delta$ -plutonium oxidation will be discussed.

9:40am **AC+SS-MoM5 Angle-Resolved Photoemission and the 5f Electronic Structure of Pu Materials**, *J. Joyce, T. Durakiewicz, K.S. Graham, E.D. Bauer, J.N. Mitchell, D.P. Moore, J.A. Kennison, T.M. McCleskey, A.K. Burrell, E. Bauer, Q. Jia*, Los Alamos National Laboratory

#### INVITED

The electronic structure of Pu compounds ranging from Mott insulators to strongly correlated metals is investigated using angle-resolved photoemission (ARPES). The electronic properties of the Pu compounds  $\text{PuCoGa}_5$ ,  $\text{PuSb}_2$ , and  $\text{PuO}_2$  are compared with angle-integrated and temperature-dependent photoemission results for Pu metal. The balance in strongly correlated materials between the central and periodic potentials is directly probed through ARPES. For the strongly correlated metals, details of the sharp quasiparticle peak at the Fermi energy are presented, including crystal momentum dispersion, giving insight into the self-energy and ground state properties of these Pu materials. In  $\text{PuSb}_2$ , the ARPES data at a photon energy of 21.2 eV, indicates a quasiparticle peak that disperses through the Fermi energy. At 40.8 eV photon energy,  $\text{PuSb}_2$  shows f-electron intensity periodic with the lattice. Photoemission results for the Fermi level spectral intensity as well as the more localized 5f states well-removed from the Fermi energy are used to quantify adaptive character for these materials. Both  $\text{PuSb}_2$  and  $\text{PuCoGa}_5$  ARPES data show a dispersive peak which crosses the Fermi energy at a photon energy of 21.2 eV where the conduction states have a larger cross section than the 5f states. The results for 40.8 eV photon energy, with enhanced 5f strength, indicate a peak dispersing through the Fermi energy for  $\text{PuCoGa}_5$  but the  $\text{PuSb}_2$  data indicate an intensity modulated peak near the Fermi energy. The first ARPES results for the Mott insulator  $\text{PuO}_2$  show substantial dispersion consistent with hybrid functional calculations which predict significant covalency for  $\text{PuO}_2$  compared with the earlier ionic actinide dioxides such as  $\text{UO}_2$ . The ARPES, photon energy dependence, and the temperature dependent data for Pu materials will be discussed in terms of 5f adaptive character and the implications for Pu ground state properties.

Work supported by the U.S. Department of Energy, Basic Energy Sciences, the Los Alamos National Laboratory LDRD program, and Campaign II.

10:40am **AC+SS-MoM8 Novel Band Renormalization Mechanism in f-electron Systems**, *T. Durakiewicz, J. Joyce*, Los Alamos National Laboratory, *P.S. Riseborough*, Temple University, *P.M. Oppeneer*, Uppsala University, Sweden, *J.-C. Griveau*, ITU, Germany, *E.D. Bauer*, Los Alamos National Laboratory, *E. Guzikiewicz*, Polish Academy of Sciences, Poland

Several mechanisms may lead to band renormalization in strongly correlated systems. Inter-band scattering was recently shown to produce significant renormalization effects in high temperature superconductors. Here we show, for the first time, that inter-band processes may lead to strong band renormalization in the vicinity of Fermi level in a 5f-electron system,  $\text{USb}_2$ . The Fermi surface of this compound consists of several uniaxial cylindrical sheets. We show that the bare band LDA calculation over-counts the number of sheets, because it lacks the renormalization part. But our high resolution angle resolved photoemission (ARPES) experiments demonstrate that one of the calculated cylinders shrinks below the Fermi level, forming a closed cigar-shaped Fermi surface rather than an open cylindrical one. In normal emission experiments, we measure the dispersion of the bands of interest in the Gamma-Z direction. The measured results disagree with the LDA result, but the bare LDA bands can be renormalized by using a low order self-energy expansion in three-band inter-band scattering model, and very good fit is obtained. We conclude that inter-band scattering in  $\text{USb}_2$  influences the fermiology of this system in terms of changing the shape and number of Fermi sheets.

11:00am **AC+SS-MoM9 The Initial Oxidation of Polycrystalline Thorium**, *M. Bagge-Hansen, R.A. Outlaw, D.M. Manos*, College of William & Mary

11:20am **AC+SS-MoM10 The Non-Equilibrium Nature of Uranium Oxide Surfaces**, *R.K. Schulze, D.P. Johnson, M.A. Hill*, Los Alamos National Laboratory

We examine the surface reactions of bulk single crystal uranium oxide ( $\text{UO}_2$ ) and thin films of uranium oxide on metal using Kelvin probe (surface work function and chemical potential) measurements and x-ray and ultraviolet photoelectron spectroscopy. The processes of surface and sub-surface reactions with small gas phase molecules are examined through *in situ* work function measurements (dynamic) while the surface chemistry and configuration are probed with photoemission and LEED measurements (equilibrium). The hyperstoichiometric uranium oxide ( $\text{UO}_{2+x}$ ) is shown to be composed of, in the surface region, labile interstitial oxygen that can be moved relatively easily in and out of the fluorite structure lattice through control of the headspace oxygen activity. The transport of oxygen in this near surface region of the oxide is examined through changes in the surface work function with exposure to various partial pressures of oxygen. The amount of excess oxygen in the oxide lattice of the surface is shown to affect the reactivity of this surface with small gas phase molecules directly. A measurement and description of the band structure of the uranium oxide surface for different levels of oxygen content ( $\text{UO}_3$ ,  $\text{UO}_{2+x}$ ,  $\text{UO}_2$ ,  $\text{UO}_{2-x}$ ) is presented.

11:40am **AC+SS-MoM11 Characterization of the Surface Changes During the Activation of Erbium/Erbium Oxide for Hydrogen Storage**, *M.T. Brumbach, K.R. Zavadil, C.S. Snow, J.A. Ohlhausen*, Sandia National Laboratories

Erbium is known to effectively load with hydrogen when held at high temperature in a hydrogen atmosphere. To make the storage of hydrogen kinetically feasible, a thermal activation step is required. Activation is a routine practice, but very little is known about the physical, chemical, and/or electronic processes that occur during Activation. This work presents *in situ* characterization of erbium Activation using variable energy photoelectron spectroscopy at various stages of the Activation process. Modification of the passive surface oxide plays a significant role in Activation. The chemical and electronic changes observed from core-level and valence band spectra will be discussed along with corroborating ion scattering spectroscopy measurements.

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# Monday Afternoon, October 18, 2010

## Actinides and Rare Earths Topical Conference

Room: Isleta - Session AC+TF-MoA

### Actinide and Rare Earths Thin Films

**Moderator:** S.W. Yu, Lawrence Livermore National Laboratory

2:00pm **AC+TF-MoA1 EUV and in situ Spectroscopic Ellipsometric Analysis of the Oxidation of Uranium Thin Films, H. Dumais, D.D. Allred, R.S. Turley**, Brigham Young University

Uranium thin films have found a variety of uses: such as EUV mirrors for space application and driver layers on inertial confinement fusion microspheres. Uranium is chemically active and an unprotected surface oxidizes quickly. More is known about the oxidation of bulk than thin films. We have investigated the oxidation of uranium thin films and reactively sputtered uranium oxide films using spectroscopic ellipsometry, electron microscopy and XPS. We find that uranium magnetron sputtered (1-10 mtorr) in Ar/oxygen forms a UO<sub>2</sub> (fcc-structure) over a range of O<sub>2</sub> partial pressures. It is reasonably stable in air for several hours. On the other hand, thin uranium films (20nm) left to oxidize in air forms a higher oxide, probably U<sub>3</sub>O<sub>8</sub>. This observation may help interpret EUV optical data previously made on uranium films.

2:20pm **AC+TF-MoA2 Atomic Layer Deposition of Rare Earth Ion Co-doped Oxides for Optical Applications, J. Hoang, C. Pham, J.P. Chang**, University of California, Los Angeles

Rare earths (REs) exhibit unique shielded f-electrons giving rise to sharp spectral transitions. These transitions are dictated by the RE identity and can be manipulated by engineering the interactions of multiple RE ions. In this work, radical enhanced atomic layer deposition (RE-ALD) is used to design complex metal oxides with multiple dopants, whose concentration variation and spatial distribution control enable the synthesis of a wide range of multifunctional materials with tunable properties including magnetic, spectral, and electronic. Specifically, the control of sensitizer proximity and concentration is used to enhance amplification at 1.54  $\mu\text{m}$  ( $\text{Er}^4_{13/2} \rightarrow ^4_{15/2}$ ) for compact planar optical amplifier applications and promote Er upconversion at 535 nm ( $^2\text{H}_{11/2}, ^4\text{S}_{3/2} \rightarrow ^4_{15/2}$ ) and at 670 nm ( $^4\text{F}_{9/2} \rightarrow ^4_{15/2}$ ). The spatial distributions between  $\text{Er}^{3+}$  and RE (RE =  $\text{Yb}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Ce}^{3+}$ ) are investigated with 1.54  $\mu\text{m}$  emission promotion via direct energy transfer for Yb sensitizers and via cross relaxation for Eu and Ce sensitizers. Polycrystalline thin films are synthesized by sequential radical-enhanced ALD of  $\text{Y}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ , and  $\text{Eu}_2\text{O}_3$  at 350°C using 2,2,6,6-tetramethyl-3,5-heptanedionato analog of the corresponding metal (e.g. RE(TMHD)<sub>x</sub>) and reactive oxygen atoms from a plasma. The composition, microstructure, cation distribution, local chemical bonding and optical properties of the as-synthesized thin films are determined by x-ray and Rutherford backscattering spectroscopies, electron microscopy and photoluminescence measurements. The effect of concentration is examined using a 8:1:x Y:Er:RE cycle sequence with x = 0, 1, 3, 5, 7, while the spatial distribution is investigated using a y:5:y:5 Y:Er:RE ratio with y = 0, 2, 4, 6, 8, 10. High resolution transmission electron microscopy on thin films deposited on nanotubes verify the construction of nanolaminates. Extended x-ray absorption fine structure Yb L<sub>2</sub> edge scans show that the Yb local environment possesses more 2nd nearest neighbor Yb ions as the Yb cycles increases. Photoluminescence (PL) spectra using both 488 nm and 980 nm laser excitations show sharp Er intra 4f peaks with peak intensity centered at 1535 nm at low pump powers (~50 mW for 980 nm excitation). ~8x luminescence enhancement is achieved using a 8:1:3 Y:Er:Yb cycle ratio, while a slight decrease in PL intensity is apparent as the Er and Yb distance increases. Individual PL studies of Eu and Ce codoped Er:Y<sub>2</sub>O<sub>3</sub> samples were found to require higher excitation powers, while tri-doped samples (Yb:Eu and Yb:Ce codoped Er:Y<sub>2</sub>O<sub>3</sub>) are currently under investigation to study further attainable PL enhancement and upconversion efficiency.

2:40pm **AC+TF-MoA3 Electronic Structure and Surface Reactivity of Actinide Systems, Th. Gouder, A. Seibert**, European Commission, JRC, Institute for Transuranium Elements, Germany **INVITED**

Actinide research is motivated by the peculiar properties of the 5f states which are on the verge from itinerancy to localization. These states confer to the actinides rich, yet often unpredictable chemical and physical properties. In this context surface science, focusing on the few topmost atomic layers, plays a particularly important role. In this region decreased bonding leads to 5f-band narrowing and enhances localization effects. On the other hand, the interaction of actinide surface atoms with the environment dominates the reactivity of spent nuclear fuel. Detailed

knowledge of these surface reactions is required for the prediction of the long term storage behavior of spent fuel.

In the talk we will discuss the evolution of the electronic structure of actinide elements confined to thin films. We will describe film preparation by sputter deposition from elemental targets (Th, U, Np, Pu and Am) on strongly and weakly interacting substrates (Mg, Al, Si). Information on the electronic structure is obtained by photoemission spectroscopy. 5f localization occurs both with increasing Z and with decreasing layer thickness. In Pu, which is the last actinide where in the bulk the 5f states are itinerant, the 5f states become localized at one monolayer. For thicker films, photoemission shows precursor effects manifesting as final state multiplets. For Np, the 5f states are always itinerant, even at the submonolayer level, but also here, deviation from the pure band behaviour is observed.

We will then compare actinide surface compounds, focusing on the oxides. The difference between surface and bulk oxides, and the specific contribution of the 5f states will be discussed. In late actinides oxides (down to Pu) the 5f states are well localized and only rare-earth like (An<sub>2</sub>O<sub>3</sub>) sesquioxides and (AnO<sub>2</sub>) dioxides are observed. There is no higher oxide. With decreasing Z, the increasingly bonding 5f states destabilize the An<sub>2</sub>O<sub>3</sub> favoring AnO<sub>2</sub>, and simultaneously enable higher oxidation states beyond AnO<sub>2</sub>. Here again, the presence of the surface with its lowered coordination and increased tendency for 5f localization leads to oxidation states different from the bulk.

Finally, we will give a brief overlook on actinide surface reactions with the environment, where 5f states are involved (catalysis and photochemistry). We will present the surprising surface reduction of PuO<sub>2</sub> thin films by water, which we attribute to a photochemically driven surface reaction involving 5f states. Such processes may fundamentally influence the long term storage properties of spent fuel.

3:40pm **AC+TF-MoA6 Observation of Strong Resonant Behavior in the Inverse Photoelectron Spectroscopy of Ce Oxide, J.G. Tobin, S.W. Yu, B.W. Chung**, Lawrence Livermore National Laboratory, G.D. Waddill, Missouri University of Science and Technology, L. Duda, J. Nordgren, Uppsala University, Sweden

X-ray Emission Spectroscopy (XES) and Resonant Inverse Photoelectron Spectroscopy (RIPES) have been used to investigate the photon emission associated with the Ce3d<sub>5/2</sub> and Ce3d<sub>3/2</sub> thresholds. Strong resonant behavior has been observed in the RIPES of Ce Oxide near the 5/2 and 3/2 edges. Inverse Photoelectron Spectroscopy (IPES) and its high energy variant, Bremstrahlung Isochromat Spectroscopy (BIS), are powerful techniques that permit a direct interrogation of the low-lying unoccupied electronic structure of a variety of materials. Despite being handicapped by counting rates that are approximately four orders of magnitude less than the corresponding electron spectroscopies (Photoelectron Spectroscopy, PES, and X-ray Photoelectron Spectroscopy, XPS) both IPES [1,2,3,4,5] and BIS [6,7,8] have a long history of important contributions. Over time, an additional variant of this technique has appeared, where the kinetic energy (KE) of the incoming electron and photon energy (h $\nu$ ) of the emitted electron are roughly the same magnitude as the binding energy of a core level of the material in question. Under these circumstances and in analogy to Resonant Photoelectron Spectroscopy, a cross section resonance can occur, giving rise to Resonant Inverse Photoelectron Spectroscopy or RIPES. [9-13] Here, we report the observation of RIPES in an f electron system, specifically the at the 3d<sub>5/2</sub> and 3d<sub>3/2</sub> thresholds of Ce Oxide.

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4:00pm **AC+TF-MoA7 Growth and Reactivity of CeO<sub>2</sub>(100) Thin Films**, *D.R. Mullins, T.-L. Chen, F.C. Calaza, S.H. Overbury, M.D. Biegalski, H.M. Christen*, Oak Ridge National Laboratory

Cerium oxide is a principal component in many heterogeneous catalytic processes. One of its key characteristics is the ability to provide or remove oxygen in chemical reactions. The different crystallographic faces of ceria present significantly different surface structures and compositions that may alter the catalytic reactivity. The structure and composition determine the availability of adsorption sites, the spacing between adsorption sites and the ability to remove O from the surface.

To investigate the role of surface orientation on reactivity, CeO<sub>2</sub> films were grown with two different orientations. CeO<sub>2</sub>(100) films were grown ex situ by pulsed laser deposition on Nd-doped SrTiO<sub>3</sub>(100). The structure was characterized by RHEED, XRD and reflectometry. CeO<sub>2</sub>(111) films were grown in situ by thermal deposition of Ce metal onto Ru(0001) in an oxygen atmosphere. The structure of these films has been studied by LEED and STM. Attempts to grow CeO<sub>2</sub>(100) in situ by physical vapor deposition on Pt(100) and Pd(100) failed due to preferential growth of CeO<sub>2</sub>(111) on these supports.

The chemical reactivity was characterized by the adsorption and decomposition of methanol and 2-propanol. Reaction products were monitored by TPD and surface intermediates were determined by soft x-ray photoelectron spectroscopy and infrared spectroscopy. Both of these alcohols readily chemisorbed on either surface in UHV. The decomposition of methanol was less selective on CeO<sub>2</sub>(100) than on CeO<sub>2</sub>(111) with CO and H<sub>2</sub> resulting even from a fully oxidized surface. Water was also produced as on CeO<sub>2</sub>(111), and the CeO<sub>2</sub>(100) surface could be reduced by exposure to methanol at 700 K. Unlike on reduced CeO<sub>x</sub>(111), methanol adsorption on reduced CeO<sub>x</sub>(100) produced only a small increase in reactivity and inhibited formaldehyde formation. 2-propanol produced primarily propene and water with a small amount of acetone.

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4:20pm **AC+TF-MoA8 Photoemission Study of Au-Schottky Barrier Formation on YbGaN Thin Films using Synchrotron Radiation**, *S.R. McHale, J.W. McClory, J.C. Petrosky*, Air Force Institute of Technology, *Y.B. Losovyj*, Louisiana State University

Au-YbGaN Schottky barrier formation was observed using Au evaporation on multiple concentrations of Yb<sub>x</sub>Ga<sub>1-x</sub>N thin films deposited on (111) Si substrates. Low Energy Electron Diffraction was performed to verify the integrity of the Au deposition. Energy dependent, synchrotron generated photoemission spectroscopy ranging from 15 to 26 eV under UHV conditions clearly determined a valence band shift of up to 0.62 eV.

The experiments were conducted at the Louisiana State University (LSU) Center for Advanced Microstructures and Devices (CAMD), using synchrotron radiation dispersed by the 3m toroidal grating monochromator (TGM) beamline, where resolution of the experimental apparatus is approximately 70 meV. Thin films were fabricated using RF plasma-assisted molecular beam epitaxy (PAMBE) at the University of Nebraska (Lincoln) Center for Materials and Nanoscience (NCMN). Yb temperatures during deposition were 500 °C, 700 °C, and 860 °C, resulting in slightly coarse, uniform, and very coarse grained films, respectively. The XRD patterns show a high degree of order in the films.

A least squares fit was used to calculate the valence band maximum (VBM) for each spectrum. Comparing the calculated VBM values for the bare YbGaN sample spectra with those following Au deposition shows that Au clearly affects the YbGaN electronic structure by shifting the valence band

toward the Fermi energy by a maximum value of 0.62 eV at a monolayer of Au coverage. This valence band shift yields a calculated Schottky Barrier,  $\phi_{\text{SB}}$ , of 0.83 eV, determined by the relationship  $E_{\text{g}} - (E_{\text{F}} - E_{\text{VBM}})$ , where the energy gap,  $E_{\text{g}}$ , was approximated at 3.5 eV.

SB calculation via direct spectroscopic data will be supplemented by SB calculation via I-V measurements of the sample surface, using a Keithley 4200 Semiconductor Characterization System and a Signatone Probe Station.

Our research efforts are motivated by radiation detection materials and devices. Radiation detector diodes typically operate in the reverse bias mode, where Schottky contacts are desirable to optimize the signal-to-noise ratio. Therefore, we intend to extend these results to facilitate additional measurements using other Lanthanide-doped III-nitride compounds in a future research endeavor involving potential radiation detection materials. We anticipate that this effort will improve researchers' determination of suitable combinations of materials, and will produce novel, efficient, and more accurate neutron detection devices than currently available.

# Tuesday Morning, October 19, 2010

## Actinides and Rare Earths Topical Conference

Room: Isleta - Session AC+MI-TuM

### Actinide and Rare Earth Magnetic Interfaces & Nanostructures

**Moderator:** T. Durakiewicz, Los Alamos National Laboratory

8:20am **AC+MI-TuM2 An Alternative Model for Electron Correlation in Pu**, S.W. Yu, J.G. Tobin, P. Soderlind, Lawrence Livermore National Laboratory

Using a density functional theory based approach that treats the 5f electrons relativistically, a Pu electronic structure with zero net magnetic moment is obtained, where the 5f orbital and 5f spin moments cancel each other. By combining the spin and orbital specific densities of states with state, spin and polarization specific transition moments, it is possible to reconstruct the experimentally observed photoemission spectra from Pu. Extrapolating to a spin-resolving Fano configuration, it is shown how this would resolve the extant controversy over Pu electronic structure. See J. Phys.: Condens. Matter 20 (2008) 422202 for more detail. Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344. This work was

supported by the DOE Office of Science, Office of Basic Energy Science, Division of Materials Science and Engineering.

8:40am **AC+MI-TuM3 Correlation Effects in Gadolinium Compounds: Comparison of Theory and Experiment**, P.A. Dowben, University of Nebraska - Lincoln **INVITED**

The apparent Gd 4f binding energy in photoemission spectroscopy is strongly affected by both correlation energy contributions, and final state effects in photoemission. The latter are clearly strongly influenced by metallicity and screening [1]. To understand these various contributions to the observed electronic structure of gadolinium compounds, we compare a series of studies on gadolinium compounds and clusters with pure and alloyed gadolinium films [2]. These materials range from the metallofullerenes, in which a metal atom or cluster is encapsulated inside a fullerene, such as in the "buckyball" C<sub>60</sub>, to more conventional rare earth compounds like GdN, Gd<sub>2</sub>O<sub>3</sub>, Gd doped HfO<sub>2</sub> and Gd-Ni alloys. The Gd<sup>3+</sup> ion exhibits bonding and hybridization that is quite different for these various compounds. While the total spin multiplicity of Gd is maximum because of its half-filled 4f state, and the atomic orbitals are strongly hybridized with the C<sub>60</sub> molecules in the example of Gd@C<sub>60</sub> [3] or oxygen in the case of Gd doped HfO<sub>2</sub> [4], while the highest possible symmetry site for gadolinium is generally not favored. These results are to some extent a confirmation of theoretical expectations but there are complications. There is experimental evidence for intra-atomic hybridization with both the unoccupied and occupied Gd 4f states, as well as band dispersion even for the occupied Gd 4f states in some systems [2] and spin dependent screening [5].

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9:20am **AC+MI-TuM5 Electronic Phase Diagram of Rare Earth Mono-Pnictides and Mono-Chalcogenides**, L. Petit, R. Tyer, Daresbury Laboratory, UK, A. Svane, Aarhus University, Denmark, Z. Szotek, W.M. Temmerman, Daresbury Laboratory, UK **INVITED**

The self-interaction corrected local spin density (SIC-LSD) approximation is used to predict the ground state valency configuration of the manifold of rare earth mono-pnictides and mono-chalcogenides. This is a first-principles methodology that adequately describes the dual character of f-electrons, itinerant vs. localized, and the goal is to combine it with high throughput computing, in order to achieve predictive capability in the search for and design of new materials with specific physical properties. For the rare earth mono-pnictides and mono-chalcogenides we predict an electronic phase diagram composed of metallic, semi-conducting and heavy fermion like regions, and exhibiting valency transitions brought about by a complex interplay between ligand chemistry and lanthanide contraction. Our findings, including the ground state lattice parameters, and the "intermediate valent" character of compounds such as SmO and TmSe, are in excellent agreement with the available experimental data.

10:40am **AC+MI-TuM9 Nanotechnology in the Actinides: Uranium Thin Films and Multilayers**, R.S. Springell, University College London, UK **INVITED**

From the modern scientific landscape of nanotechnology research, the manipulation of elements and compounds on a near-atomic scale has contributed to innovations, some of which affect our everyday life. The growth of thin films and multilayers has allowed systematic studies of reduced dimensionality and the electronic interplay between dissimilar materials. Important applications have emerged, notably the GMR effect. However, such studies of systems containing actinide elements are, to our knowledge, absent, but offer exciting possibilities because of potential hybridization involving the 5f electronic states.

The samples are prepared by a dedicated sputtering facility at Oxford University, UK2.

Our investigation into uranium multilayers, which involves both bulk as well as element specific techniques, compares the structural properties<sup>2</sup> and electronic interactions<sup>3,4,5</sup> of uranium interleaved with layers of ferromagnetic Fe, Co, Ni, and Gd. Only in the case of U/Fe is a large magnetic moment induced on the U atoms, close to the interface<sup>5</sup>.

The study of epitaxial uranium films is initially concerned with the nature of the structural constraints incurred by the substrate and buffer<sup>6</sup> and the potential for stabilizing structures otherwise absent in the bulk. a-U (which is the normal ambient orthorhombic phase) grows well on a Nb buffer on sapphire. In the bulk it exhibits a charge-density wave (CDW) at 43 K, so in epitaxial films an interesting question is the minimum thickness for the CDW to appear; we have already observed the CDW down to 10 nm. Using epitaxial hcp-Gd as a buffer, we have produced hcp-U for the first time<sup>7</sup>. The observed c/a = 1.90 is larger than for any other hexagonal element. We report also our first efforts to prepare epitaxial UO<sub>2</sub> films.

11:20am **AC+MI-TuM11 Growth and Characterization of Dy/Y Superlattices**, J. Yu, H. Sato, P.R. LeClair, G.J. Mankey, University of Alabama, J.L. Robertson, R.S. Fishman, Oak Ridge National Laboratory

Inelastic neutron scattering is the world's most powerful tool to study the magnetic excitations of solids. We aim to study spin wave dispersion relations in multilayer structures and how they are affected by the indirect RKKY exchange interaction through nonmagnetic spacers. Dy was chosen as the magnetic film since it has a huge magnetic moment of 10.2 Bohr magnetons and the neutron scattering cross section is directly proportional to the atomic moment. For elastic scattering, a film with thickness of order 100 nm is sufficient, but inelastic neutron scattering has a considerably lower cross-section requiring much more material for measurement. To enable such a study, many samples with tightly-controlled thickness and crystallinity must be fabricated. The neutron experiments can then be performed by stacking 8-10 samples, each with 50-100 superlattice repeats. The number of repeats for each sample is limited by the accumulation of defect structures over the growth front. Using a home-built sputtering system, we have achieved the ability to make suitable samples. The system has computer-controlled magnetron sputtering guns and a sample transfer system which enables continuous sample rotation of a 2" diameter wafer at 900°C during sputtering in an ultra-pure environment. Maintaining a good vacuum is essential since both Y and Dy are highly reactive and form stable

oxides with only a minute amount of oxygen in the sputtering environment. In addition, the dispersion relations of the spin wave modes are highly sensitive to thickness variations, so it is essential to create samples with uniform and repeatable layer thicknesses. We report the growth and characterization of epitaxial Dy/Y multilayer samples and our optimization of the growth temperature to produce samples with well-defined superlattice Bragg peaks in high-angle x-ray diffraction.

Funded by US-DOE through DE-FG02-08ER46499 and research at Oak Ridge National Laboratory's High Flux Isotope Reactor was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

11:40am **AC+MI-TuM12 Study of f Electron Correlations in Uranium- and Cerium-Oxides by BIS and XES**, *S.W. Yu, B.W. Chung*, Lawrence Livermore National Lab, *D.G. Waddill*, Missouri University of Science and Technology, *J.G. Tobin*, Lawrence Livermore National Lab

When a high energy electron beam impinges on a material, some electrons of the incident electron beam are decelerated into the unoccupied states of the material with a spontaneous emission of electromagnetic radiation (bremsstrahlung). This bremsstrahlung process can be considered as the inverse of the photoemission process if the initial and final states are exchanged and the occupied state is replaced by the unoccupied one. BIS (Bremsstrahlung Isochromat Spectroscopy) is a very powerful tool to study the bulk unoccupied electronic structures of materials, minimizing the impact of surface effects.

Recently, we have developed a BIS capability, using an XES-350 system from VG SCIENTA, at the Lawrence Livermore National Laboratory, to investigate the electronic structure of actinides, in which 5f electrons play important roles to determine their physical and chemical properties. Similar to the resonant photoemission, the measured BIS signal can be resonantly enhanced when the electron energy reaches the threshold of the binding energy of a core electron, as a result of the interference between the BIS signal and the x-ray emission signal emitted by a radiative decay of the core hole. In case of cerium-oxide, the BIS signal is enhanced significantly at the 3d → 4f resonance. However, in the case of uranium-oxide, the BIS signal is enhanced only slightly at the 4d → 5f resonance.

The x-ray emission can be described as a spontaneous emission of photons in a transition that are allowed by the dipole selection rules between two electronic states. The implication of the dipole selection rules is that, for example, in the case of K-emission, where 1s holes are created, only states with p-character are allowed to decay and the partial p-type density of state is measured in a x-ray emission spectrum. Therefore, the x-ray emission spectra from a variety of core levels allow us to study the symmetries of the occupied electronic states.

We will present the resonant BIS spectra and x-ray emission spectra (U 4f, 4d, O1s, Ce 3d) of the uranium- and cerium-oxides. Based on these data, we will discuss the detailed electronic structures of f electrons in uranium- and cerium-oxides.

Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under contract DE-AC52-07NA27344. This work was supported by the DOE Office of Science, Office of Basic Energy Science, Division of Materials Science and Engineering.

# Tuesday Afternoon, October 19, 2010

## Actinides and Rare Earths Topical Conference

Room: Isleta - Session AC-TuA

### Science and Technology of Actinides and Rare Earths

Moderator: R.K. Schulze, Los Alamos National Laboratory

2:00pm **AC-TuA1 Enhanced Photoluminescence from Europium-Doped Gadolinium-Based Nanocrystal Scintillators**, *T.-K. Tseng, J. Choi, M.R. Davidson, P.H. Holloway*, University of Florida

Scintillator crystals have traditionally been grown with complex single crystal methods such as Czochralski and Bridgman techniques, which frequently result in high costs and small crystal size. Therefore, development of processes for larger area, polycrystalline ceramic scintillators with high luminescence is of great interest due to their potential for mass production, versatility in shape and size, and low cost. In this study, spherical  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$  and almond-like  $\text{GdVO}_4:\text{Eu}^{3+}$  nanocrystals were synthesized using a water-based solution precipitation method at low reaction temperatures ( $<90^\circ\text{C}$ ) in short times (3 min~1 h). Core/Shell nanostructures with mono-dispersed 220 nm  $\text{SiO}_2$  cores and an ~13 nm  $\text{Gd}_2\text{O}_3$  shell, i.e.  $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ , were prepared. With an additional undoped  $\text{Gd}_2\text{O}_3$  shell to form a  $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}/\text{Gd}_2\text{O}_3$  nanostructure, the quantum yield was 28% higher than that of  $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ . This enhanced photoluminescence (PL) is attributed to a  $\text{Gd}_2\text{O}_3$  surface shell serving (i) as a sensitizer with energy transfer to the  $\text{Eu}^{3+}$  in the  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$  shell, plus (ii) passivation of non-radiative surface quenching sites. Enhanced PL was also demonstrated from polyol-synthesized  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}/\text{Y}_2\text{O}_3$  nanocrystals. Increased PL can also be achieved by incorporating  $\text{Bi}^{3+}$  sensitizer ions into colloidal  $\text{GdVO}_4:\text{Eu}^{3+}$  nanocrystals which were self-assembled into almond-like clusters composed of ~60 nm nanorods. With 2%  $\text{Bi}^{3+}$  co-doped in  $\text{GdVO}_4:\text{Eu}^{3+}$  nanocrystals, PL was enhanced by 45%, 90% and 570% when excited by 280, 323 and 347 nm photons, respectively. This enhancement is attributed to increased absorption from Bi-O bonds, plus extension of the excitation band edge to longer wavelength. For  $\text{Bi}^{3+}$  ion concentrations  $>10\%$ , PL from co-doped nanocrystals decreased due to non-radiative decay from  $\text{Bi}^{3+}$ -induced trapping centers, as well as increased  $\text{Bi}^{3+}$ - $\text{Bi}^{3+}$  energy transfer instead of  $\text{Bi}^{3+}$ - $\text{Eu}^{3+}$  transfer.

2:20pm **AC-TuA2 Memory Effects of  $\text{UF}_6$  Adsorption and Reaction at Metallic Surfaces**, *M.T. Puffett, D.P. Moore, J.D. Farr, R.K. Schulze, K.D. Ianakiev*, Los Alamos National Laboratory

In this study we explore memory effects that arise from the reactivity of  $\text{UF}_6$  with surface hydroxyls (and other entities with a reactive H bond) that may be present at metallic surfaces. These chemical interactions are noted to leave behind low but measurable quantities of uranium oxy fluorides ( $\text{UO}_2\text{F}_2$ ,  $\text{UOF}_4$  and related extended solids). Uranium re-depositions are noted to occur following sequential exposures to varying isotopic content in the  $\text{UF}_6$  gas stream. We explore the role that additional fluorinating agents ( $\text{HF}$ ,  $\text{ClF}_3$ ) play in promoting uranium surface re-fluorination and memory effects in these deposits. The primary surface and radiochemical characterization techniques utilized in this study and include x-ray photoelectron spectroscopy, Auger electron spectroscopy depth profiling, static SIMS and alpha emission spectroscopy. The importance of these memory effects in enabling higher accuracy isotopic determinations and in forensic knowledge

2:40pm **AC-TuA3 Nanocomposites for Thermoelectrics : Erbium Mono-Antimonide Nano Crystals Embedded in Group III -AsSb Host Materials**, *T. Onishi*, University of California, Santa Cruz and NASA Ames Research Center, *T. Favaloro*, University of California, Santa Cruz, *A. Shakouri*, University of California, Santa Cruz and NASA Ames Research Center, *E. Coleman, G.S. Tompa*, Structured Materials Industries Inc., *S. Kraemer, H. Lu, A. Gossard*, University of California, Santa Barbara, *N.P. Kobayashi*, University of California, Santa Cruz and NASA Ames Research Center

The increasing demand for efficiency in energy generation and use has increased interest in thermoelectrics (the direct conversion of heat to electricity), which has the promise to increase energy efficiency – if certain cost-performance metrics are met. However, in the continuing quest of the efficient bulk thermoelectrics material for more than 50 years, the improvement of thermoelectric properties has not been sufficient to widely replace other established power sources.

One of the promising lines of new material development is based on the use of nanostructures to dramatically change the heat transport properties of thermoelectrics while largely leaving the electrical properties intact. In this effort we have focused on developing nanocomposites comprised of thin

films containing semi-metallic nanocrystals. We herein report on the growth of nanocomposites that consist of erbium monoantimonide (semi-metal) in the form of nano crystals or nanocolumns self-assembled with in thin film group III- arsenide/antimonide alloys doped with acceptors. The nano composites are optimized in terms of three factors, electrical conductivity, and thermal conductivity, and Seebeck coefficient to maximize thermoelectric figure of merit.

Using low-pressure metal organic chemical vapor deposition (MOCVD), we have developed the growth processes of the nanocomposites that consist of indium gallium (arsenic) antimonide ( $\text{InGa(As)Sb}$ ) host materials with embedded erbium antimonide (ErSb) nanocrystals. The size of ErSb nano crystals, carrier density and alloy composition of the  $\text{InGa(As)Sb}$  host materials are tuned by controlling of various growth parameters. The following techniques were used to obtain information on the growth of ErSb nanocomposites embedded  $\text{InGa(As)Sb}$  film on n-type  $\text{InSb}$  (100) substrate: Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red-absorption (FTIR), Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), and Transmission Electron Microscopy (TEM).

Acknowledgement:

This research is funded by DARPA and DOE ; supported by Structured Materials Industries Inc. [www.structuredmaterials.com] for the growth; Advanced Studies Laboratories in NASA Ames research Center, and Materials Department, University of California, Santa Barbara for the characterization.

3:00pm **AC-TuA4 TRU Waste Disposal in Waste Isolation Pilot Plant, WIPP**, *M. Borkowski, H. Khaing, J.-F. Lucchini, D.T. Reed, M.K. Richmann, J.S. Swanson, D. Ams*, Los Alamos National Laboratory

The mobility and potential release of actinides into the accessible environment continues to be the key performance assessment concern of nuclear repositories. Actinide, in particular plutonium speciation under the wide range of conditions that can exist in the subsurface is complex and depends strongly on the coupled effects of redox conditions, inorganic/organic complexation, and the extent/nature of aggregation. Understanding the key factors that define the potential for actinide migration is, in this context, an essential and critical part of making and sustaining a licensing case for a nuclear repository. Herein we report on recent progress in a concurrent modeling and experimental study to determine the speciation of plutonium, uranium and americium in high ionic strength Na-Cl-Mg brines. This is being done as part of the ongoing recertification effort in the Waste Isolation Pilot Plant (WIPP).

A key feature of salt-based repositories is the relatively rapid self-sealing nature of the salt. This feature leads to geologic isolation of the waste form, and when reduced metals are present (e.g., iron containers), the system is driven anoxic by corrosion leading to strongly reducing environments. The consequence of this is that the combination of anaerobic microbial activity, reactions of reduced metals, and, when present, reactions of organics leads to the reduction of higher valent Pu(V) and Pu(VI) species to the lower valent Pu(III) and Pu(IV) species. The reduction of Pu(V/VI) species has been studied extensively. Less is known about microbial effects with halophiles although there is no question that bioreduction of higher valent plutonium occurs readily by soil bacteria under anoxic conditions. These lower valent oxidation states have lower solubilities and correspondingly lead to lower solubility and mobility of the plutonium.

The oxidation-state specific solubility of actinides were established in brine as function of  $\text{pC}_{\text{H}^+}$ , brine composition and the presence and absence of organic chelating agents and carbonate. An oxidation-state invariant analog approach using  $\text{Nd}^{3+}$  and  $\text{Th}^{4+}$  was used for  $\text{An}^{3+}$  and  $\text{An}^{4+}$  respectively. These results show that carbonate and hydrolysis predominate at  $\text{pC}_{\text{H}^+}$  above 8. Organic complexation is more important for  $\text{An}^{3+}$ . Carbonates are the key factor for U(VI) solubility. Modeling efforts are focused on the use of Pitzer parameters to correct for high-ionic strength effects and show that there is still some uncertainty about the predominant carbonate and hydrolytic species, particularly when longer-term timeframes are considered.

4:00pm **AC-TuA7 Elastic Moduli of Pure Alpha, Beta, Gamma Plutonium—Three Different Metals**, *A. Migliori*, Los Alamos National Laboratory

From 10 K to 580K plutonium changes phase from monoclinic alpha to body centered monoclinic beta to orthorhombic gamma structures. Each crystal structure is rare or unique for an elemental metal. Measurements presented here provide the first high-accuracy values for a single high-purity specimen of the elastic moduli of unalloyed polycrystal plutonium as a function of temperature throughout the entire range of existence of the alpha, beta, and gamma phases. The bulk and shear moduli, essential

thermodynamic material properties, reflect important and huge changes with temperature, such that these phases present as three different metals. Unlike phase transformations in many other elements where the bonding, nearest-neighbor distances, and physical properties are closely related among phases, in the three lowest-temperature phases of plutonium, the relationships are missing, and support the extreme sensitivity of plutonium properties to phase, temperature, and almost-certainly, electronic structure. We describe here the characteristics and implications of these newly-observed properties.

4:20pm **AC-TuA8 Self Diffusion Coefficients of Trivalent Element Ions in Moderately Dilute Aqueous Solutions: Comparative Study between Lanthanum and f-elements.** *H. Latrous*, Faculté des sciences de Tunis, Tunisia, *R. Besbes*, IPEST, Tunisie, Tunisia, *N. Ouerfelli*, Faculté des Sciences de Tunis, Tunisia, *A. manef*, IPEST, Tunisie, Tunisia

Our work continues our studies on the trivalent ions 4f and 5f elements. In this paper, we have summarized data relatives to measurements of self-diffusion coefficients, conductance, mobility and activity coefficients for trivalent f-elements ions. Self-diffusion coefficients,  $D_i$  of the trivalent f-elements aquo ions series have been determined in aqueous electrolyte support at 25°C using the open-end capillary method (O.E.C.M.), from concentration 0 to 1.5M. We verify its variation with concentration and ionic strength of medium.

Variation of  $D_i/D_i^\circ$  versus  $\sqrt{C}$  (C: molar concentration) for  $\text{La}^{3+}$  in acid medium pH=2.5, verify Nernst-Hartley expression. Activity coefficients  $\gamma_{\pm}$  for  $\text{LaCl}_3$  at pH = 2.5 deduct from diffusion measurements are compared with recent data measured by *f.e.m* and are discussed in term of association phenomena (ion-pairing).

4:40pm **AC-TuA9 Synthesis and Characterization of Scintillating  $\text{Gd}_2\text{SiO}_5:\text{Ce}$  Nanoparticles using Hot-Solution Growth.** *J. Choi*, *T.-K. Tseng*, *M.R. Davidson*, *P.H. Holloway*, University of Florida

Scintillation detectors are commonly used for measuring radiation from nuclear materials. To date the scintillating material has been a single crystal, commonly doped with a rare earth ion that controls the wavelength and intensity of radioluminescence. Scintillating nanoparticles have the potential to replace the expensive, energy-intensive, limited volume single crystal detectors. In this study, scintillating  $\text{Gd}_2\text{SiO}_5:\text{Ce}^{3+}$  (GSO) nanoparticles with 5~10 nm diameters were prepared by a two-pot hot-solution growth (HSG at 200~300 °C) method. The Ce dopant concentration was varied between 0.2%~5% and concentration quenching was examined by photoluminescence (PL). Low (0.5% Ce) doped GSO nanoparticles exhibited good PL from both as-synthesized and calcined (1100°C for 2 h in air) nanoparticles. Concentration quenching for nanoparticles occurred at higher Ce concentrations than for bulk samples; this will be discussed. The PL emission was from the 5d to two 4f levels ( $^2T_2$  to  $^2F_{7/2}$  and  $^2F_{5/2}$  transitions) of  $\text{Ce}^{3+}$  at 420~450 nm. Photoluminescent excitation (PLE) spectra showed that the emission resulted from the direct excitation of the 4f~5d transition of  $\text{Ce}^{3+}$  excited between 270~375 nm. X-ray diffraction (XRD) and transmission electron microscopy (TEM) data showed that the GSO nanoparticles were amorphous as grown, but well crystallized after calcining. Quantum yield and radioluminescence data will be presented and discussed.



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