

# Monday Morning, October 29, 2012

**Actinides and Rare Earths Focus Topic**  
**Room: 6 - Session AC+MI+SS+TF-MoM**

## Electronic Structure and Spectroscopy of Actinides

**Moderator:** A.J. Nelson, Lawrence Livermore National Laboratory

9:00am **AC+MI+SS+TF-MoM3 Strong Correlations and the Electronic Structure of the Actinide Dioxides, R.L. Martin**, Los Alamos National Laboratory **INVITED**

The series of actinide dioxides ( $AnO_2$ ,  $An=Pa, \dots Cm$ ) are difficult challenges for electronic structure theory. The early members of the series are Mott insulators, the band gap corresponding to  $f_7^2$  transitions, while the later members, beginning with  $PuO_2$ , are  $O2p \rightarrow An5f$  charge transfer insulators. I will review recent experimental results (X-ray absorption, photoemission and optical band gaps) which now allow us to distinguish among several many-body approximations to their electronic structure, including the SIC, DFT+U, DMFT+U and hybrid DFT (HSE) approaches.

9:40am **AC+MI+SS+TF-MoM5 Synchrotron Radiation Studies of Actinide Compounds, S.M. Butorin**, Uppsala University, Sweden **INVITED**

Core-to-core resonant inelastic x-ray scattering (RIXS) and valence-to-core RIXS techniques are two complimentary ways for probing the electronic structure in actinide systems. Specific cuts of the core-to-core RIXS maps around  $M\beta$  and  $L$  lines of actinides represent remarkably improved high-resolution x-ray absorption spectra of actinide  $3d$  and  $2p$  edges, respectively, as a result of limited lifetime broadening of core holes present in shallower levels in the final state of the spectroscopic process. That allows for more detailed studies of unoccupied states and better oxidation states assignments. In turn, the valence-to-core RIXS spectra are only limited by the instrumental resolution and provide information about actinide chemical bonding and interactions between valence electrons.

A comparison of experimental data with results of model calculations shows that the resonant spectra of actinide systems recorded at the actinide  $M(3d)$  and  $O(5d)$  thresholds which probe the  $5f$  states can be interpreted using the many-body theory, such as the Anderson impurity model, while the data obtained at the  $L3$  threshold and representing the  $6d$  states of actinides can be described within a single-particle approach, such as LDA+ $U$  (local density approximation with supplemented Coulomb interaction  $U$ ) framework.

In course of discussion of the above statements, we present the RIXS data for a number of actinide systems with emphasis on the results contributing to understanding of the U-O and Pu-O phase diagrams, in particular data for  $UO_{2+x}$ ,  $U_4O_9$ ,  $U_3O_8$  and  $PuO_{2+x}$ . The influence of the Coulomb interaction between  $5f$  electrons on the electronic structure of actinides is also discussed.

10:40am **AC+MI+SS+TF-MoM8 Quasiparticle Dynamics in Uranium Systems from Ultrafast Spectroscopies, T. Durakiewicz**, Los Alamos National Laboratory

Every time we add a new dimension to an experimental method, we open a window to novel, unexpected and fascinating phenomena. Here we show the results of our focused effort of adding time-domain to the powerful experimental techniques of Angle Resolved Photoelectron Spectroscopy (ARPES) and reflectivity. The novel tools are applied to actinides and help us understand the details of the electronic structure of the correlated  $f$ -electron materials.

In the hidden order system  $URu_2Si_2$  we investigate the massive renormalization of the Fermi surface at specific  $k$  values. The application of time-resolved ARPES allowed a direct measurement of the momentum-resolved quasiparticle lifetime which was shown to increase by an order of magnitude at the hidden order transition. Time-resolved ARPES together with the ultrafast reflectivity results provided evidence for forming a multiple gap structure, including the hybridization gap, pseudogap and HO gap [1, 2].

Another actinide system of interest is a Mott insulator  $UO_2$ , where we have investigated the complex dynamics of the Hubbard excitons. We have found that the dynamics can be divided into four distinct processes: instantaneous hop, picosecond lattice deformation, phonon emission and relaxation, and the slow relaxation related to the propagation of Hubbard excitons [3]. We

have also obtained the first direct measurement of Hubbard gap in  $5f$  system [4].

The novel femtosecond pump-probe methods provide unique information about the dynamics of  $5f$  quasiparticles, and open novel possibilities in addressing the long-standing questions about the role of near-Fermi level band renormalization in establishing the physical properties of correlated materials.

### References

- [1] Physical Review B 84, 161101(Rapid Comm.) (2011)
- [2] Physical Review B 84, 161103(Rapid Comm.) (2011)
- [3] Physical Review Letters 106, 207402 (2011)
- [4] manuscript in preparation

11:00am **AC+MI+SS+TF-MoM9 Comparison of Spectroscopic Data with Cluster Calculations of Plutonium, Plutonium Dioxide and Uranium Dioxide, J.G. Tobin, S.W. Yu, B.W. Chung**, Lawrence Livermore National Laboratory, *M.V. Ryzhkov*, Russian Academy of Science-Ekaterinburg, *A. Mirmelstein*, Russian Federation Nuclear Center-Snezhinsk

Using spectroscopic data produced in the experimental investigations of bulk systems, including X-Ray Absorption Spectroscopy (XAS), Photoelectron Spectroscopy (PES) and Bremsstrahlung Isochromat Spectroscopy (BIS) [1-5], the theoretical results within for  $UO_2$  [6],  $PuO_2$  [6] and  $Pu$  [7] clusters have been evaluated. The calculations of the electronic structure of the clusters have been performed within the framework of the Relativistic Discrete-Variational Method (RDV). [6,7] The comparisons between the LLNL experimental data and the Russian calculations are quite favorable. The cluster calculations may represent a new and useful avenue to address unresolved questions within the field of actinide electron structure, particularly that of  $Pu$ . Observation of the changes in the  $Pu$  electronic structure as a function of size suggests interesting implications for bulk  $Pu$  electronic structure.

### Acknowledgements

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 No. DE-AC52-07NA27344. JGT and SWY were supported by the DOE Office of Science, Office of Basic Energy Science, Division of Materials Science and Engineering. Work at the RAS and VNIITF was supported in part by Contract B590089 between LLNL and VNIITF. The Advanced Light Source (ALS) in Berkeley and the Stanford Synchrotron Radiation Laboratory are supported by the DOE Office of Science, Office of Basic Energy Science.

### References

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2. S.-W. Yu, J. G. Tobin, J. C. Crowhurst, S. Sharma, J. K. Dewhurst, P. Olalde-Velasco, W. L. Yang, and W. J. Siekhaus, Phys. Rev. B **83**, 165102 (2011).
3. J.G. Tobin, B.W. Chung, R. K. Schulze, J. Terry, J. D. Farr, D. K. Shuh, K. Heinzelman, E. Rotenberg, G.D. Waddill, and G. Van der Laan, Phys. Rev. B **68**, 155109 (2003).
4. J.G. Tobin, P. Söderlind, A. Landa, K.T. Moore, A.J. Schwartz, B.W. Chung, M.A. Wall, J.M. Wills, R.G. Haire, and A.L. Kutepov, J. Phys. Cond. Matter **20**, 125204 (2008).
5. S.-W. Yu, J. G. Tobin, P. Olalde-Velasco, W. L. Yang, and W. J. Siekhaus, J. Vac. Sci. Tech. A. **30**, 011402 (2012).
6. M.V. Ryzhkov and A.Ya. Kupryazhkin, J. Nucl. Materials **384**, 226 (2009).
7. M.V. Ryzhkov, A. Mirmelstein, S.-W. Yu and J.G. Tobin, "Probing Actinide Electronic Structure through  $Pu$  Cluster Calculations," submitted to Phys. Rev. B, Feb 2012.

# Monday Afternoon, October 29, 2012

**Actinides and Rare Earths Focus Topic**  
**Room: 6 - Session AC+TF+SS+MI-MoA**

**Actinides and Rare Earths: Thin Films and Surface Science**

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

2:00pm **AC+TF+SS+MI-MoA1 Rare Earth 4f Hybridization in Gallium Nitride.** *J.W. McClory, S.R. McHale*, Air Force Institute of Technology, *L. Wang, W.N. Mei*, University of Nebraska-Lincoln, *J.C. Petrosky*, Air Force Institute of Technology, *J. Wu, R. Palai*, University of Puerto Rico – San Juan, *Ya.B. Losovyj*, Louisiana State University, *P.A. Dowben*, University of Nebraska-Lincoln **INVITED**

The location of the Gd, Er and Yb 4f states within the GaN valence band has been explored both experimentally and theoretically. The 4d – 4f photoemission resonances for various rare earth doped GaN thin films (RE = Gd, Er, Yb) provide an accurate depiction of the occupied 4f state placement within the GaN valence band. The resonant photoemission show that the major Er and Gd rare earth 4f weight is at about 5-6 eV below the valence band maximum, similar to the 4f weights in the valence band of many other rare earth doped semiconductors. For Yb, there is very little resonant enhancement of the valence band of Yb doped GaN, consistent with a largely 4f<sup>14-d</sup> occupancy. The placement of the rare earth 4f levels is in qualitative agreement with theoretical expectations.

2:40pm **AC+TF+SS+MI-MoA3 Revisiting the Yb Electronic Structure with Low-Energy Photoemission Spectroscopy.** *F. Offi*, CNISM and Univ. Roma Tre, Italy, *P. Vilmercati, L. Petaccia, S. Gorovikov*, ELETTRA Sincrotrone Trieste, Italy, *A. Ruocco*, CNISM and Univ. Roma Tre, Italy, *M.I. Trioni*, CNR-ISTM, Milano, Italy, *A. Rizzo*, CNISM and Univ. Roma Tre, Italy, *A. Goldoni*, ELETTRA Sincrotrone Trieste, Italy, *G. Stefani*, CNISM and Univ. Roma Tre, Italy, *G. Panaccione*, CNR-IOM, Basovizza-Trieste, Italy, *S. Iacobucci*, CNI-IFN, Rome, Italy

The peculiar electronic structure of rare-earth elements and compounds is mostly defined by the partially filled 4f band. Of particular interest is the investigation of the valence states, which is linked to the degree of hybridization of f electrons with delocalized s-d bands. In the simple case of Yb, the 4f states are fully occupied with a Fermi level of 6s character and a 2+ valency. However, the occupation of the Yb valence band has been the subject of several investigations over the years, intended in particular to separate the contribution of 5d states. Early experimental photoelectron emission (PES) spectra at very low excitation energy ( $h\nu < 10$  eV) have reported a spectral modulation in the region close to the Fermi level that was attributed to the emission from a 5d band. The poor energy resolution did not allow however a detailed investigation of such spectral features. In recent years this low energy photoemission spectroscopy (LEPES) encountered a renewed interest, under the stimulus of the extremely high energy resolution obtainable with laser excited LEPES and given the expectation of a large increase of the bulk sensitivity at these low energies. We monitored the 4f spectral intensity in polycrystalline Yb films in the LEPES regime (between 5.5 and 21 eV photon energy, with experiments at the BaDELPH beamline of the ELETTRA synchrotron radiation facility), observing a moderate increase of the electron attenuation length and, thus, a moderate increase of the information depth when we reach the lowest energies. By lowering the photon energy below about 11 eV a prominent peak at the Fermi level is observed. The analysis of its intensity variation versus photon energy and the comparison of the experimental spectra with *ab initio* density of states (DOS) calculations allow to attribute this structure to a p band crossing the Fermi level, enhanced at selected photon energies due to the influence of the empty DOS, probably amplified by a photoionization cross section effect and by the general increase of the photoelectron yield at low photon energy. In this respect LEPES may thus be considered as a probe of the joint DOS.

3:00pm **AC+TF+SS+MI-MoA4 Erbium Rare Earth Thin Film Hydride Stress Studies as a Function of Processing Techniques.** *J.L. Provo*, J.L. Provo Consulting

An important part of understanding the behavior of rare earth, Group 3A and 4A thin film hydrides is the determination of indirect effects such as stress in the film lattice which can lead to film flaking. In this study, special vacuum sample containers were prepared to observe and record basal-plane film stress levels, and film flaking (optical observations).

The special vacuum sample containers contained erbium deuteride (ErD<sub>2</sub>) and erbium tritide (ErT<sub>2</sub>) films on AT and BT quartz resonator substrates with chromium underlays in pairs prepared by air-exposure, (in-situ)

evaporate-load and reactive evaporation hydriding techniques. The erbium deuteride samples were prepared as controls for aging studies. All samples were processed with PVD Electron Beam deposition techniques, hydriding techniques mentioned above and a 450°C temperature bakeout and exhaust in consideration of the  $\alpha \rightarrow \beta$  crystal phase transformation in crystalline quartz at 573°C.

Samples for the measurement of initial film deposition stress as a function of hydride processing and for the determination of stress produced in ErT<sub>2</sub> films due to the generation of helium-3 with time (i.e., tritium decay) were designed to utilize the double-resonator technique developed by EerNisse(1). Measurements of mass change and induced film stress were determined by frequency measurement changes obtained with a precision frequency counter, data being taken from the output of a one transistor Colpitts type driving oscillator circuit in which the crystal is an integral part.

A summary of initial film deposition stress (tensile) and film aging accumulative stress (compressive) for the erbium films from the different deposition and hydriding techniques is given. Reactively evaporated erbium occluder films were seen to have an initial film deposition tensile stress approximately 5 times less than (in-situ) evaporate-load films and 11 times less than air-exposed loaded films. Accumulative aging compressive stress for erbium occluder films were shown to be more variable but data indicate that reactively evaporated film aging stress is less than that of (in-situ) evaporate-load and air-exposed tritided films.

(1)-J. Appl. Phys. 43, 1330 (1972)

3:40pm **AC+TF+SS+MI-MoA6 Splat Cooling Technique Contributing to Understanding of Uranium Systems.** *L. Havela*, Charles University, Czech Republic, *A. Gonçalves, J.-C. Waerenbogh, L. Pereira*, ITN Sacavém, Portugal, *I. Tkach*, Charles University, Czech Republic, *N.-T. Kim-Ngan*, Pedagogical University Cracow, Poland, *T.B. Scott*, University of Bristol, UK

The splat cooling technique is one of the methods of ultrafast cooling of a melt, particularly suitable for small amounts of material. In particular cases it can help to overcome constraints imposed by thermodynamics. One of them was the issue of magnetic properties of non-stoichiometric Laves phase UFe<sub>2</sub>. This compound has a ferromagnetic ground state (with both U and Fe magnetic moments). An excess of U, achieved by quenching, led to the decrease of T<sub>C</sub> from 162 K for pure compound to 112 K for UFe<sub>1.7</sub> [1]. Quenching was, however, unable to provide Fe-rich material, with expected increase of T<sub>C</sub>. Using splat cooling of a series of materials with various off-stoichiometry from UFe<sub>2</sub> to UFe<sub>6</sub> we found that the cubic Laves phase structure (with sub-micron grains) can absorb excessive Fe up to the stoichiometry UFe<sub>2.3</sub>. Additional excess leads to the segregation of  $\alpha$ -Fe [2]. The increase of T<sub>C</sub> up to 230-240 K was the impact on magnetic properties. The spontaneous magnetization also increases from 1.0  $\mu_B$ /f.u. in UFe<sub>2</sub> to 1.9  $\mu_B$ /f.u. in UFe<sub>2.3</sub>. <sup>57</sup>Fe Mössbauer spectroscopy reveals that the excessive Fe atoms enter the U sublattice and develop higher magnetic moments (approx. 1.0  $\mu_B$ /Fe).

Applying the splat cooling technique on pure and doped U metal had the aim to stabilize the high temperature bcc phase ( $\gamma$ -U) to low temperatures, to be able to establish its basic electronic properties. In particular, changes in magnetic characteristics and electronic specific heat can be expected due to the modest volume expansion comparing to orthorhombic  $\alpha$ -U. We found that splat cooling reduces the necessary concentration of dopants and U with 12 at.% Mo has no traces of  $\alpha$ -U. The Sommerfeld coefficient  $\gamma = 19$  mJ/mol K<sup>2</sup> estimated for pure  $\gamma$ -U is enhanced comparing to 11 mJ/mol K<sup>2</sup> for pure U splat, which is close to values given in literature [3] for the U metal. The splats exhibit a superconducting ground state with T<sub>C</sub> ranging from 1.24 K for pure U to 2.11 K for 15 % Mo. The  $\gamma$ -U superconductivity is characterized by a large critical field exceeding 6 T and a sharp  $\lambda$ -type anomaly in specific heat C<sub>p</sub>(T) with the size corresponding to the BCS theory. The superconductivity of a pure U splat, which contains only traces of  $\gamma$ -U, has much lower critical field (0.33 T) and the weak anomaly in C<sub>p</sub>(T) does not convince about the bulk character of superconductivity.

*This work was supported by Grant Agency of the Czech Republic under the grant No. P204/10/0330.*

[1] A.T. Aldred, J.Magn.Magn.Mater. 10, 42 (1979).

[2] L. Havela et al., Intermetallics 19, 113 (2011).

[3] J.C. Lashley et al., Phys. Rev. B 63, 224510 (2001).

4:00pm **AC+TF+SS+MI-MoA7 Investigation of Rare Earth Doped Lithium Tetraborate Glasses with XAFS and Emission and Excitation Spectroscopy**, *T.D. Kelly, J.W. McClory, D.A. Buchanan, A.T. Brant, J.C. Petrosky*, Air Force Institute of Technology, *Ya.B. Losovyj*, Louisiana State University, *V.T. Adamiv, Ya.V. Burak*, Institute of Physical Optics, *P.A. Dowben*, University of Nebraska-Lincoln

The local structure of rare earth doped lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ ) glasses has been studied by extended x ray absorption fine structure (EXAFS) at the rare earth L shells and by optical emission and excitation spectroscopies. The samples investigated were 1% rare earth doped by weight with Gd and Nd. The EXAFS signal was recorded in fluorescence mode with the energies calibrated for Nd L1 and L3 edges and Gd L3 edge. X rays were applied to the samples to activate emission and excitation centers in the glasses. The spectra were analyzed to determine rare earth occupation sites in the lithium tetraborate crystal structure and the emission and excitation lines due to rare earth doping.

4:40pm **AC+TF+SS+MI-MoA9 Eu-implanted p-type GaN: Charge-Driven Luminescence Hysteresis and Identification of a Possible Charge-State-Alternation Resonance of the Mg Acceptor**, *K.P. O'Donnell, P.R. Edwards, R.W. Martin*, Strathclyde University, Scotland, UK, *K. Lorenz, E. Alves, V. Darakchieva*, ITN Sacavém, Portugal, *M. Bockowski*, Unipress, Poland

Europium-doped p-type GaN shows *spectral switching* and *luminescence hysteresis* when samples are temperature-cycled between room temperature and 20 K (*K.P. O'Donnell et al, Late News paper at ICPS2012, Zurich*). An explanation of this unusual behaviour may be found in the charge-state dependence of the local structure of the Mg acceptor in GaN, recently modelled by J.L. Lyons et al., (*Phys. Rev. Lett.* 108, 156403 (2012)). Eu ions, sensitive to their local environment, may act as 'spectators' of the charge-induced local distortions. The dominant impurity-induced luminescence spectrum at RT (hereafter, Eu0) *switches completely* to another spectrum (Eu1) when samples are cooled below 25 K. Upon subsequent warming of the sample, Eu1 fades with increasing temperature, as expected, but Eu0 *does not reappear* until the temperature exceeds 150 K; its recovery is complete only above 210 K. The noted temperature extremes correspond to hole localisation (carrier freeze-out) and delocalisation, respectively. Here, we extend Lyons' model to consider the possibility of observing the resonance in which the acceptor alternates rapidly between neutral and negative charge states, leading to a spatial oscillation of the associated defect between Eu0 and Eu1 forms, and describe the possible spectral identification of this resonance.

# Tuesday Morning, October 30, 2012

## Actinides and Rare Earths Focus Topic

Room: 6 - Session AC+EN-TuM

## Energetic Materials Issues for Nuclear Power: Fuels, Corrosion and Waste Disposal

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

8:00am **AC+EN-TuM1 Novel Concepts for Enhanced Metallic Nuclear Fuel Performance**, *J.R. Kennedy, R.D. Mariani, D.L. Porter, S.L. Hayes, H.J.M. Chichester*, Idaho National Laboratory, *A.E. Wright, Y.S. Kim, A.M. Yacout, G.L. Hofman*, Argonne National Laboratory, *R.P. Omberg, D.J. Senior*, Pacific Northwest National Laboratory

**INVITED**

The Advanced Fuels Campaign of the Fuel Cycle Research and Development (FCRD) program of the Office of Nuclear Energy (DOE/NE) is charged with the mission to develop and qualify fuel forms that can be used 1) to close the nuclear fuel cycle, 2) to increase fuel performance in reactor, and 3) to be accident tolerant. In the first case, metallic fuels composed of (U,Pu,Np,Am)Zr alloys are being developed with the intention to transmute the transuranic isotopes in fast spectrum reactors. In the second case, increasing fuel performance, fuel forms are being developed that may, for example, allow higher levels of burnup in either fast spectrum or thermal spectrum reactors (lightwater reactors - LWR). In the final case, fuel forms that have an inherently higher level of tolerance to off-normal conditions are being developed in response to the Fukushima Daiichi accident. A number of innovative concepts will be presented with respect to the above including decreased fuel smear densities, annular fuel forms, cladding coatings or liners to prevent fuel-cladding chemical interactions, gas vented fuel pin designs, advanced fabrication methods such as fuel-clad co-extrusion, U-Mo based fuel alloys, and, of particular interest to this session's topical area, targeted fuel alloy additions into the actinide fuel composition that will sequester rare earth fission product migration to the fuel-cladding interface. Rare earth fission products have been implicated in enhancing detrimental fuel-cladding chemical interactions. These fuel development activities are a collaboration of Idaho National Laboratory with Argonne National Laboratory and with Pacific Northwest National Laboratory.

8:40am **AC+EN-TuM3 Low Temperature Oxidation of Plutonium: A Mott-Cabrera Mechanism**, *P. Roussel*, AWE, UK, *A.J. Nelson*, Lawrence Livermore National Laboratory

**INVITED**

X-ray photoelectron spectroscopy was used to study the oxidation of d-stabilized plutonium between 190K and 300K. The gas-solid reaction on this highly reactive surface depends on the surface energy, electronic structure and temperature along with radiological dissociation of the O<sub>2</sub> molecule. The initial oxidation of sputter cleaned Pu metal by O<sub>2</sub> forms Pu<sub>2</sub>O<sub>3</sub> followed by formation of PuO<sub>2</sub> on the Pu<sub>2</sub>O<sub>3</sub> surface. Angle-resolved measurements indicate that the PuO<sub>2</sub> layer thickness is limited to 1.2 nm after continued O<sub>2</sub> dosing at the lower temperatures. These results suggest the Mott-Cabrera mechanism of oxidation at low temperature where the rate limiting step is the diffusion of O<sup>-</sup> anions through the oxide film to the oxide/Pu interface increasing only the thickness of the Pu<sub>2</sub>O<sub>3</sub> layer.

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

9:40am **AC+EN-TuM6 The Sputtering Yields of Depleted Uranium and Uranium Carbide Bombarded and Alloyed by Either 30 keV Gallium or 16 keV Cesium Ions**, *W.J. Siekhaus, N.E. Teslich, P.K. Weber*, Lawrence Livermore National Laboratory

A sample of depleted uranium was abraded with 1200 grid SiC paper and subsequently polished with 3µm and 1µm diamond to a mirror finish. Areas 20µm x 20µm wide that included uranium carbide inclusions were ion-etched with 30 keV Gallium ions with a current of 2.8 nA, for up to 5 minutes. The depths of the "craters" thus generated were measured by electron microscopy and by profilometry and the ratio of the number of uranium atoms removed and the ion fluence was used to determine the sputtering yield for both uranium and uranium carbide.

We show the results in SEM images of sputtered areas and depth measurements on "craters" that include uranium carbide inclusions.

The same procedure was used to determine the sputtering yield of 16keV Cesium ions bombarding uranium. At their respective energies the depth of penetration of Gallium and Cesium (109Å and 50Å, respectively, as calculated by the TRIM[1] code) is much smaller than the crater depths.

The measured depth increases represent therefore the sputtering yields of the Uranium-Gallium and Uranium-Cesium alloys created by ion implantation, since sputtered atoms originate almost exclusively from the first atomic layers of the substrate[2]. Comparison of the measured sputtering yields with those of pure U using Matsunami's equation[3] demonstrates the effect of alloying on sputtering yield.

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

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[3] Matsunami, N. et al., Atomic Data and Nuclear Data Tables, **31**, 1-80, 1984.

10:40am **AC+EN-TuM9 Actinide Subsurface Chemistry in Waste Isolated Pilot Plant, Recent Development**, *M. Borkowski, J.-F. Lucchini, M.K. Richmann, D.T. Reed*, Los Alamos National Laboratory

Waste Isolation Pilot Plant (WIPP) is designed to permanently dispose radioactive waste generated by the US defense program. Waste is placed in a salt bed 2150 feet below the ground level. During the regulatory time repository may be filled with brine and interaction of brine components with actinide is objective of the Actinide Chemistry Repository Science Program. One of the brine components is borate (up to ~160 mM), present in the brine by the dissolution of Borax mineral. Borate chemistry especially in basic media is still unknown and in this study the interesting borate speciation in the basic media is presented. Recently it was reported that neodymium, analog for trivalent actinides, is complexed by tetraborate ion with log K ~4 and that plutonium forms a stronger complex than that of neodymium. Also neptunium (V) forms complexes with borate and spectrophotometric evidence will be presented. Further investigations of borate chemistry and borate complexing properties are also discussed. Complexation power of different polyborate forms may be different. Some are able to form a covalent bond but other forms can only attract cation by a weak electrostatic interaction. Borate provides a wide range of pH buffering capacity from 6 to 12.

11:00am **AC+EN-TuM10 XPS Study of Uranium Oxides with Various Precipitating Agents**, *K.S. Holliday*, Lawrence Livermore National Laboratory, *J. Plaue*, University of Nevada, Las Vegas, *W.J. Siekhaus, A.J. Nelson*, Lawrence Livermore National Laboratory

X-ray photoemission spectroscopy (XPS) and Auger electron spectroscopy (AES) are powerful tools for materials characterization by determining chemical shifts in core level spectra. By combining XPS data with the X-ray excited Auger transitions one is able to have a two dimensional analysis based on both initial state effects and final state relaxation energies. Specifically, combining the chemical shift of the U NOV Auger lines with the chemical shift of the U 4f photoelectron lines defines the Auger parameter (difference in the binding energy of the photoelectron and Auger lines) and results in a reliable method for determining oxidation states independent of calibration. Here, XPS analysis of core-level excitation and X-ray excited Auger transitions were combined to determine the Auger parameter and produce chemical state (or Wagner) plots for various uranium and thorium compounds. In addition this method is combined with valence band spectra to characterize uranium oxides precipitated with different reagents. The calcination of these precipitates is followed at various temperatures in an effort to identify unique characteristics associated with the precipitating reagent.

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Lorenz, K.: AC+TF+SS+MI-MoA9, **3**  
Losovyj, Ya.B.: AC+TF+SS+MI-MoA1, **2**;  
AC+TF+SS+MI-MoA7, **3**  
Lucchini, J.-F.: AC+EN-TuM9, **4**

## — M —

Mariani, R.D.: AC+EN-TuM1, **4**  
Martin, R.L.: AC+MI+SS+TF-MoM3, **1**  
Martin, R.W.: AC+TF+SS+MI-MoA9, **3**  
McClory, J.W.: AC+TF+SS+MI-MoA1, **2**;  
AC+TF+SS+MI-MoA7, **3**  
McHale, S.R.: AC+TF+SS+MI-MoA1, **2**  
Mei, W.N.: AC+TF+SS+MI-MoA1, **2**  
Mirmelstein, A.: AC+MI+SS+TF-MoM9, **1**

## — N —

Nelson, A.J.: AC+EN-TuM10, **4**; AC+EN-TuM3,  
**4**

## — O —

O'Donnell, K.P.: AC+TF+SS+MI-MoA9, **3**  
Offi, F.: AC+TF+SS+MI-MoA3, **2**  
Omberg, R.P.: AC+EN-TuM1, **4**

## — P —

Palai, R.: AC+TF+SS+MI-MoA1, **2**  
Panaccione, G.: AC+TF+SS+MI-MoA3, **2**  
Pereira, L.: AC+TF+SS+MI-MoA6, **2**  
Petaccia, L.: AC+TF+SS+MI-MoA3, **2**  
Petrosky, J.C.: AC+TF+SS+MI-MoA1, **2**;  
AC+TF+SS+MI-MoA7, **3**

Plaue, J.: AC+EN-TuM10, **4**  
Porter, D.L.: AC+EN-TuM1, **4**  
Provo, J.L.: AC+TF+SS+MI-MoA4, **2**

## — R —

Reed, D.T.: AC+EN-TuM9, **4**  
Richmann, M.K.: AC+EN-TuM9, **4**  
Rizzo, A.: AC+TF+SS+MI-MoA3, **2**  
Roussel, P.: AC+EN-TuM3, **4**  
Ruocco, A.: AC+TF+SS+MI-MoA3, **2**  
Ryzhkov, M.V.: AC+MI+SS+TF-MoM9, **1**

## — S —

Scott, T.B.: AC+TF+SS+MI-MoA6, **2**  
Senor, D.J.: AC+EN-TuM1, **4**  
Siekhaus, W.J.: AC+EN-TuM10, **4**; AC+EN-  
TuM6, **4**  
Stefani, G.: AC+TF+SS+MI-MoA3, **2**

## — T —

Teslich, N.E.: AC+EN-TuM6, **4**  
Tkach, I.: AC+TF+SS+MI-MoA6, **2**  
Tobin, J.G.: AC+MI+SS+TF-MoM9, **1**  
Trioni, M.I.: AC+TF+SS+MI-MoA3, **2**

## — V —

Vilmercati, P.: AC+TF+SS+MI-MoA3, **2**

## — W —

Waerenbogh, J.-C.: AC+TF+SS+MI-MoA6, **2**  
Wang, L.: AC+TF+SS+MI-MoA1, **2**  
Weber, P.K.: AC+EN-TuM6, **4**  
Wright, A.E.: AC+EN-TuM1, **4**  
Wu, J.: AC+TF+SS+MI-MoA1, **2**

## — Y —

Yacout, A.M.: AC+EN-TuM1, **4**  
Yu, S.W.: AC+MI+SS+TF-MoM9, **1**