

Wednesday Afternoon, October 21, 2015

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

Chemistry and Physics of the Actinides and Rare Earths

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

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

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

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

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

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

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

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

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

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

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

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

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

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

One of the fundamental challenges of modern science lies in understanding the chemistry and physics of the actinides, and in particular, plutonium. It's unpredictable behavior and reactivity has led to a very poor understanding of its metallurgy and corrosion process. This not only poses a basic scientific challenge, but directly affects the safe, long term storage of this material. In an effort to understand the surface chemistry and corrosion of plutonium, knowledge of the surface oxide composition is paramount. The currently accepted description of the oxide layer formed under ambient temperatures and pressures consists of a thick PuO_2 surface layer over a thin Pu_2O_3 layer at the metal interface. However, recent studies by our group indicate this description is inadequate, and the oxide layer formed in the initial stages, in particular, is much more complex. We have recently focused on studying the oxide layer formed on gallium stabilized δ -plutonium in ambient conditions (pressure, temperature). We have characterized this layer using multiple spectroscopic techniques, including spectroscopic ellipsometry (SE), x-ray photoelectron spectroscopy (XPS), and x-ray absorption spectroscopy (XAS). This diverse and complimentary suite of experimental techniques will address many long-standing issues regarding the nature of the oxide layer and the corrosion mechanism.

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

The importance of covalent and ionic interaction and bonding in heavy metal oxides, for example for the actinide dioxides, AnO_2 , is controversial with some claiming that the interactions are nearly purely ionic and with others arguing that there is important covalent character. Similar questions also exist for halides and for lanthanide compounds. One way to view this is to consider how close the actual charge state of the cation is to the nominal oxidation state. Our analysis is based on using wavefunctions for embedded clusters which model the bulk oxides. With these wavefunctions, we show that considerable departures of the cation charge from the nominal value are a common occurrence. We also show how the departure from the nominal charge state depends on several factors including: (1) nominal oxidation state, (2) ligand, and (3) position in the row of the periodic table. It is also necessary to determine which metal orbitals are involved in the covalent mixing. For actinides, the natural choice is the open cation 5f shell but the normally empty 6d shell may also contribute to the covalent mixing and, in fact, may even have a larger contribution than the 5f. In order to characterize the extent and importance of the covalent mixing, two factors need to be taken into account: (1) the estimate of the actual charge state of the cations and (2), perhaps even more important, the contribution of the covalent mixing of the cation and anion frontier orbitals to the total energy of the compound. Our approach to address both of these aspects is to limit the variational freedom when we self-consistently optimize the orbitals of

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

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

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

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

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

© *British Crown Copyright 2015/AWE*

Authors Index

Bold page numbers indicate the presenter

— B —

Bagus, P.S.: AC+AS+MI-WeA10, **1**
Booth, C.H.: AC+AS+MI-WeA9, **1**

— M —

Migliori, A.: AC+AS+MI-WeA7, **1**

— N —

Nelin, C.J.: AC+AS+MI-WeA10, **1**

— P —

Pugmire, L.: AC+AS+MI-WeA9, **1**

— R —

Roussel, P.: AC+AS+MI-WeA11, **2**

— S —

Shuh, D.K.: AC+AS+MI-WeA3, **1**

— V —

Venhaus, J.: AC+AS+MI-WeA9, **1**
Vitova, T.: AC+AS+MI-WeA1, **1**