

Friday Morning, November 4, 2011

Energy Frontiers Focus Topic

Room: 203 - Session EN+AC-FrM

Materials Challenges for Nuclear Energy

Moderator: L. Petit, Daresbury Laboratory, UK

8:20am **EN+AC-FrM1 Multi-Electron Correlation in UO₂ from Soft X-ray Spectroscopy**, *J.G. Tobin, S.W. Yu*, Lawrence Livermore National Laboratory

Resonant Inverse Photoelectron Spectroscopy (RIPES) and X-ray Emission Spectroscopy (XES) have been used to probe the electronic structure of Uranium Dioxide, UO₂. From these variants of soft x-ray spectroscopy, the nature of the main and satellite features at the U4d_{5/2} edge can be ascertained. This leads to important insights into the multi-electronic correlations underlying the ubiquitous satellite features of UO₂ and implications for future experiments with Pu.

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8:40am **EN+AC-FrM2 New Results from the DOE EFRC on the Materials Science of Actinides**, *P.C. Burns*, University of Notre Dame, **G. Sigmon**, EFRC **INVITED**

The Materials Science of Actinides EFRC has three major themes: (1) Complex actinide materials, with complexity arising from chemistry, structure, and properties; (2) Nanoscale control of actinides; and (3) Behavior of actinide materials in extreme environments of pressure, temperature and radiation fields (including coupled effects). This presentation will cover several recent results that span the range of themes in the EFRC, with emphasis on those that are most significant to the challenges of nuclear energy.

9:20am **EN+AC-FrM4 Proof that UO₂ is an f-f Electron Correlated System**, *S.W. Yu, J.G. Tobin, J.C. Crowhurst*, Lawrence Livermore National Laboratory, *S. Sharma, J.K. Dewhurst*, Max Planck Institute, Halle, Germany, *P. Olalde-Velasco, W.L. Yang*, Lawrence Berkeley National Laboratory, *W.J. Stekhaus*, Lawrence Livermore National Laboratory **INVITED**

We have performed x-ray absorption experiments on uranium dioxide (UO₂) at the O 1s, U 4d, U 4f, and U 5d edges. After comprehensive energy calibrations for O 1s, U 4d, and U 4f spectra, we have used the U 4d and 4f spectra to sort the energetic positions of the 5f and the 6d states in the unoccupied band unambiguously. This demonstrates conclusively that UO₂ is an f-f Mott-Hubbard insulator, where the electronic repulsion between f electrons is responsible for the insulating state. Calculations performed within the U-corrected generalized gradient approximation of the optical response of UO₂ permit direct comparison with the absorption spectra and confirm the experimental results.

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10:00am **EN+AC-FrM6 Atomistic Models for Actinide-Actinide Oxide Interfaces**, *S.M. Valone*, Los Alamos National Laboratory

An important class of materials problems of great interest to nuclear energy production consists of composites of metals and metal oxides, and in particular, actinide metals and actinide oxides. Individually, either type of material, actinide or oxide, can involve strong electron correlation effects. At an interface, the situation becomes even more complex. In traversing a metal-metal oxide interface, a radical compositional change is encountered.

Most atomistic models address only metals, or only ceramics, but rarely both. In addition, the actinide oxides themselves enter multiple oxidation states, depending on the composition. Thus, in traversing an interface, the oxidation state need not change abruptly. As a result, these sorts of interfaces present new challenges that must be met in order to understand this important class of material systems. To address these needs, a new, "fragment" model Hamiltonian is constructed at the atomistic level, as opposed to the one-electron model Hamiltonians that underlie tight-binding and density functional theory methods. The model encompasses both actinides and actinide oxides, and provision is made for transitioning gradually through multiple oxidation states. The extremes of the models, the dioxides and the metals, map closely to existing models for these materials. The model for metals conforms generally to a modified embedded atom method (MEAM), meaning that the embedding function (atomistic site energy model) is analytical. The differences between the fragment Hamiltonian potential and the existing MEAM models appear in the explicit form of the embedding function and in the fact that there are two distinct terms in the embedding energy in the new model. The second term is critical to strongly-correlated-electron materials, as it is an atomistic analog to

terms appearing in Hubbard models. The model also possesses a sense of electron hopping that imparts ways to both regulate the net charge on sites in the material and to change important energy gaps that determine metallic and insulating behavior.

10:20am **EN+AC-FrM7 Structure and Properties of New Actinide Oxalates, Precursors of Fuel Materials**, *C. Tamain, B. Arab-CHapelet*, CEA Marcoule, France, *M. Rivenet, F. Abraham*, UCCS, France, *S. Grandjean*, CEA Marcoule, France

For future generation nuclear fuel cycle, actinide co-conversion processes are one option for the co-management of actinides. Oxalic acid is a well-known reagent to recover actinides thanks to the very low solubility of An(IV) and An(III) oxalate compounds in acidic solution. Therefore, considering mixed-oxide fuel or considering minor actinides incorporation in ceramic fuel materials for transmutation, oxalic co-conversion is convenient to synthesize mixed oxalate compounds, precursors of oxide solid solutions.

Up to now, only U(IV)-Ln(III) oxalate solid solutions have been completely structurally described started from single-crystals. In these oxalate compounds, a mixed-crystallographic site which accommodates both elements in spite of their different charges has been established. The extent of this study on powder compounds allowed to examine the influence of An(IV) and An(III) nature. The switch of actinide's nature causes unexpected structural modifications underlining the complexity of specific transuranium elements physical chemistry and the need to pursue studies on single crystal on these actinides.

As the existing oxalate single crystal syntheses are not adaptable to the actinide-oxalate system, several original crystal growth methods allowing the formation of mixed actinide oxalate crystals were first developed. Applied to the mixed actinide systems, they lead to the formation of the first mixed An(IV)-An(III) oxalate single crystals. The results, including the different structural resolutions, are presented.

10:40am **EN+AC-FrM8 Recent Work on Magnetism, Actinides and Defects at ORNL**, *G.M. Stocks, B.C. Larson*, Oak Ridge National Laboratory **INVITED**

The extent to which the collective effects of defects can be manipulated and controlled yields the combination of structural materials properties – strength, toughness, and resistance to degradation in extreme chemical and radiation environments. In this presentation I shall outline the scope of studies of the fundamental physics of dislocations and radiation-induced displacement cascades being conducted within the Center for Defect Physics (CDP) at Oak Ridge National Laboratory and its partner institutions. Within the CDP, the focus is on the quantitative measurement and direct quantum simulation of defects at the level of unit dislocation and cascade events. For dislocation interactions, the focus is on high-spatial-resolution techniques such as 3D X-ray microscopy and convergent beam electron diffraction, which measure the local strains/stresses near isolated defects *directly* and thereby *quantify* the interactions and dynamics of defects in the bulk. For displacement cascades, the focus is on quantitative measurement of the formation and time evolution of energetic-ion-induced atomic displacement cascades using ultrahigh-resolution time-resolved X-ray diffuse scattering measurements made possible by the ultrahigh brilliance of femtosecond X-ray pulses produced at the Linac Coherent

Light Source (LCLS) and the time-averaged brilliance of the Advanced Photon Source (APS). Theoretically, the focus is on developing high-fidelity models that treat spin and ion dynamics on an equal footing and to address system sizes and time scales commensurate with experiments. I will outline early progress with respect to addressing the feasibility of experimentally observing unit events and on developing *ab initio* electronic structure based theories of combined atomistic and spin dynamics. For the latter, I will show preliminary results for Fe that address the importance of the disruption of the magnetic state of Fe caused by the introduction of defects such as dislocations and displacement cascades that are based on large scale (~10,000 atom) models and order-N electronic structure methods.

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