

Tuesday Morning, October 29, 2013

Actinides and Rare Earths Focus Topic
Room: 102 C - Session AC+AS+SS-TuM

The Surface Science of Actinides and Rare Earths

Moderator: D. Shuh, Lawrence Berkeley National Laboratory

8:00am **AC+AS+SS-TuM1 From Berkeley to Bristol: Defect Structures in Actinide Oxides, G.C. Allen, University of Bristol, UK**
INVITED

The first generation of British gas-cooled reactors used natural uranium metal as fuel but UO₂ is far and away the most important fuel in use today. It is in fact the first in a complex family of oxides, initially based on the fluorite UO₂ unit cell (U₄O₉ and U₃O₇) but giving way to layered-type oxides as the O/U ratio increases (U₃O₈ and UO₃). Oxidation in UO₂ is known to occur via accumulation of point oxygen interstitials and defect aggregates such as Willis, cuboctahedral and split-interstitial clusters. Spectroscopic evidence is used to demonstrate that the link between defect clusters and the U₄O₉ and U₃O₇ structures can be rationalised in terms of multiple Willis, cuboctahedral and split-interstitial clusters. DFT models have been used to examine the stability of different defect clusters in UO₂ supercells. The formation energy of each cluster is calculated along with the variation of their concentrations with increasing the temperature. All interstitial clusters are found to be charge compensated by U⁵⁺ ions, suggesting this is the highest uranium oxidation state reached amongst the fluorite based structure.

8:40am **AC+AS+SS-TuM3 Covalent Interactions in Metal Oxides, P.S. Bagus, University of North Texas, E.S. Ilton, Pacific Northwest National Laboratory, C.J. Nelin, Consultant**

The covalent character of ionic metal compounds, in particular oxides, may lead to substantial departures from nominal oxidation states. [1, 2] Since this covalent character changes the effective charge of the cation, it contributes to the chemical and physical properties of these compounds. We present a new and novel method of determining the degree of the covalent mixing by projection of cation and ligand orbitals [2, 3] on the total wavefunctions for clusters used to model the electronic structure of these compounds. An important advantage of this method is that it provides estimates of the uncertainties of the assignments of effective charges to the cations and anions. Such estimates of the uncertainty directly reflect the overlap of cation and anion orbitals and, hence, their potential for chemical bonding; estimates of the uncertainty of charge assignments are not generally available. There is evidence that the properties of the spectra from X-Ray photoemission spectroscopy, XPS, [2] and X-Ray Adsorption spectroscopy, XAS, [4] reflect the extent of the covalent mixing of the cation and anion orbitals. We will consider how the covalent character changes between the initial and final state configurations in these spectroscopies, which arise from the screening of the core-hole, affect the interpretation of the core-level spectroscopies.

1. P. S. Bagus and E. S. Ilton, Phys. Rev. B **73**, 155110 (2006).
2. P. S. Bagus, E. S. Ilton, and C. J. Nelin, Surf. Sci. Rep. (in press).
3. C. J. Nelin, P. S. Bagus, and M. R. Philpott, J. Chem. Phys. **87**, 2170 (1987).
4. S. G. Minasian, J. M. Keith, E. R. Batista, K. S. Boland, D. L. Clark, S. D. Conradson, S. A. Kozimor, R. L. Martin, D. E. Schwarz, D. K. Shuh, G. L. Wagner, M. P. Wilkerson, L. E. Wolfsberg, and P. Yang, J. Am. Chem. Soc. **134**, 5586 (2012).

9:00am **AC+AS+SS-TuM4 Historical Perspective on Studies of the Surface Reactivity of Actinides at the AWE, UK, D.A. Geeson, AWE, UK**
INVITED

Actinides play an important role in the business of the AWE.

The corrosion behaviour of uranium- and plutonium-based systems is of particular interest with a view to considering material stability during long-term storage as well as aspects of surface segregation and fundamental electronic structure.

The historical use of modern surface science techniques to investigate many aspects of the actinide gas-solid interface is reviewed with emphasis on the development of in-house capabilities and their adaptation for use in a nuclear environment studying highly hazardous materials. Key conclusions from several aspects of corrosion phenomena are presented together with strategies for continuing studies. Examples are drawn from; the corrosion of uranium in dry and moist atmospheres, the mechanism of initiation of

hydriding on uranium surfaces, the oxidation of plutonium alloys, americium segregation in plutonium and inverse photoemission studies of actinide surfaces.

AWE's engagement with the wider UK and international community, as part of a broad strategy to collaboratively support our work in areas of more novel aspects of actinide surface phenomena, is described.

The discussion concludes with consideration of the future direction of studies at AWE supported by the provision of enhanced capabilities to explore surface and bulk phenomena.

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11:00am **AC+AS+SS-TuM10 Exploring Plutonium Electronic Structure Using a Unique Photoemission Capability, J.J. Joyce, Los Alamos National Laboratory**
INVITED

The understanding of complex materials has made remarkable advances in recent years. Much of this understanding has been realized through new spectroscopy capabilities at synchrotron facilities. While the vast majority of materials can take advantage of public synchrotrons, transuranic materials are excluded when multiple containment barriers are incompatible with the chosen spectroscopy. Photoemission requires no physical barrier between photons, sample surface and the electron analyzer, thus photoemission on Pu materials is generally not allowed at public synchrotrons.

The Laser Plasma Light Source has been developed at Los Alamos for transuranic photoemission. Using several different variants of photoemission we have explored a range of Pu materials which has led to a significant improvement in our understanding of transuranic electronic structure. Examples of these successes will be given along with details of the unique facility. Using the capabilities of our transuranic photoemission system we exploit opportunities in angle-resolved photoemission (ARPES) providing insight into the details of both the energy and crystal momentum for a material. Additional information is obtained using tunable photons used to isolate the 5f electron contribution to the valence electronic structure. Between ARPES and tunable photoemission, we construct a fairly detailed picture of the bonding and hybridization for transuranic materials. By adding temperature-dependent photoemission to the experimental tools, we cross over phase transition boundaries as well as quantify electron-phonon coupling. We also have the capability for 1.5 and 3 keV core-level spectroscopy using a monochromatized x-ray source.

By combining the above photoemission tools with a variety of surface preparation capabilities including cleaving, laser ablation, and thermal desorption, we have a flexible photoemission facility that provides unique insight into the electronic structure of transuranic materials. We will show photoemission results for PuCoGa₅, PuCoIn₅, PuO₂, PuTe and Pu metal that span the range of materials from Mott insulators to heavy fermion superconductors. The latest developments in Pu electronic structure combine a multivalent configuration for Pu with ongoing efforts to quantify the localized/delocalized 5f electron boundary. We will discuss details of Pu electronic structure in light of both valence configurations and localization.

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