

Actinides and Rare Earths Focus Topic
Room: 22 - Session AC+AS+SA+SU-MoA

Chemistry and Physics of the Actinides and Rare Earths
Moderator: David Shuh, Lawrence Berkeley National Laboratory

1:40pm **AC+AS+SA+SU-MoA1 Oxidation and Crystal Field Effects in Uranium**, *James G. Tobin*, University of Wisconsin-Oshkosh, *S.W. Yu*, Lawrence Livermore National Laboratory, *C.H. Booth*, Lawrence Berkeley National Laboratory, *T. Tylliszczak*, Lawrence Berkeley Lab, University of California, Berkeley, *D.K. Shuh*, Lawrence Berkeley National Laboratory, *G. van der Laan*, Diamond Light Source, UK, *D. Sokaras*, *D. Nordlund*, *T.C. Weng*, Stanford Synchrotron Radiation Lightsource, *P.S. Bagus*, University of North Texas

An extensive investigation of oxidation in uranium has been pursued. [1] This includes the utilization of soft x-ray absorption spectroscopy, hard x-ray absorption near-edge structure, resonant (hard) x-ray emission spectroscopy, cluster calculations, and a branching ratio analysis founded on atomic theory. The samples utilized were uranium dioxide (UO₂), uranium trioxide (UO₃), and uranium tetrafluoride (UF₄). A discussion of the role of nonspherical perturbations, i.e., crystal or ligand field effects, will be presented. The conclusions are as follows. (1) The hypothesis of the potential importance of CF effects in the XAS branching ratio (BR) analysis of 5f states was incorrect. (2) Both UO₂ and UF₄ are n_{5f} = 2 materials. The combination of the 4d XAS BR and RXES analyses is particularly powerful. (3) CF broadening in the L₃ RXES spectroscopy does not preclude a successful analysis. (4) The prior experimental result that n_{5f} (UO₂) = 3 and the proposed causation by covalent bonding was incorrect. UO₂ is an n_{5f} = 2 material and analysis within a simple, ionically localized picture provides the correct result. (5) UO₃ appears to be an n_{5f} = 1 material. (6) While the 4d XAS BR analysis is blind to CF effects, crystal field and covalence remain important. (7) For localized actinide systems, the 4d XAS BR analysis founded upon the utilization of the intermediate coupling scheme remains a powerful tool. (8) For delocalized actinide systems, the BR analysis is problematic.

[1] J. G. Tobin, S.-W. Yu, C. H. Booth, T. Tylliszczak, D. K. Shuh, G. van der Laan, D. Sokaras, D. Nordlund, T.-C. Weng, and P. S. Bagus, *Phys. Rev. B* **92**, 035111 (2015)

2:00pm **AC+AS+SA+SU-MoA2 Electron Spectroscopy Studies of U and U-Mo Hydrides**, *Ladislav Havela*, *M. Paukov*, *M. Dopita*, *L. Horak*, *M. Divis*, *I. Turek*, Charles University, Prague, Czech Republic, *T. Gouder*, *A. Seibert*, *F. Huber*, European Commission, Joint Research Centre, Karlsruhe, Germany, *D. Legut*, VSB - Technical University of Ostrava

U hydride was the first material indicating that 5f states can yield ferromagnetism analogous to 3d metals. However, the electronic structure of UH₃ is not yet well understood, and it is not clear to which extent it can be described by conventional band structure calculations. We have been studying structure and electronic properties of UH₃ and (UH₃)_{1-x}Mo_x films synthesized by reactive sputtering. Primary diagnostics was performed by in-situ XPS. The U-4f core level spectra exhibit a development as a function of partial pressure of H₂ in Ar ($p_{Ar} = 8 \cdot 10^{-3}$ mbar). Their intensity gradually decreases, they shift by 0.2 eV towards higher binding energies (BE) and an extended (9 eV wide) satellite structure develops on the high BE side of both 4f peaks. This tendency saturates at 5% H₂ concentration, and we assume that this pressure is sufficient to form UH₃. XRD and X-ray reflectivity proved indeed the β -UH₃ structure of deposited films, which were polycrystalline, but highly textured. Ferromagnetism of the UH₃ films has the correct Curie temperature $T_C \approx 165$ K. Magnetic coercivity of the films is enormous, the width of hysteresis loop exceeds 10 T at low temperatures. Details of the valence band observed in UPS reveal a transformation of the triangular emission of the U metal into a sharp feature at the Fermi level accompanied by a broad shoulder around 0.5 eV for the hydride. A distinct development was noticed also for the U-6p states, which become narrower and shift by 1.2 eV to higher BE in the hydride, which can be interpreted as an impact charge transfer from U towards H. Besides photoelectron spectroscopy, the variations of electronic states were monitored also by BIS spectra collected for the 1486.6 eV photon energy. The spectroscopy results are confronted with different types of in-initio calculations.

As U-Mo alloys tend to form nanocrystalline β -UH₃ based hydrides, we were curious about reactive sputter deposition of the U-Mo alloys. We found that the tendency to form hydrides is best suppressed by Mo for room temperature sputtering (γ -U alloy without H is the product), but cooling the substrate to 77 K helps to maintain the hydride phase even for even higher Mo concentrations.

This work was supported by the Czech Science Foundation under the grant No. 15-01100S.

2:20pm **AC+AS+SA+SU-MoA3 Comparative Structural Studies of Tetravalent f ions in Solids and in Aqueous Solutions**, *Lynda Soderholm*, Argonne National Laboratory

INVITED
Predicting a metal ion's aqueous chemistry – including its stability, reactivity, and solubility – requires molecular-level knowledge of the various factors influencing speciation and complex formation. This chemistry is particularly complicated for f-ions, where the electrostatic, non-directional bonding provides flexibility to their coordination environments, which can vary widely depending on the ligating species. This presentation will focus on our efforts to establish trends in f-ion solution behavior and to provide a direct link between metal correlations in solution and the thermodynamic stability constants that are used to derive relative free energies of available metal-ligand complexes. Although several examples will be provided, the discussion will center on a comparison between the behaviors of tetravalent Th, Pu, and Ce and how differences in the complexes formed in solution impact the composition and structure of precipitates that form. High-energy X-ray scattering (HEXS) experimental results will be used to demonstrate how changing conditions can influence solution chemistry, with a specific emphasis on the role of the anion. X-ray surface-based techniques will be used to provide a link between solution speciation and the complexes that form on mineral surfaces. The structures of molecular species isolated as single-crystals from these solutions will be directly compared with the solution and surface-adsorbed species. This work is supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Biosciences and Geosciences, Heavy Element Chemistry, under contract No. DE-AC02-06CH11357.

4:00pm **AC+AS+SA+SU-MoA8 Interfacial Dynamics in Radiation Environments and Materials: An Energy Frontier Research Center**, *Sue Clark*, Pacific Northwest National Laboratory

INVITED
The US Department of Energy's Office of Environmental Management (EM) is faced with remediating millions of liters of highly radioactive wastes that resulted from the production of nuclear weapons during the Cold War. These legacy wastes are stored in large, underground tanks at former nuclear weapons production sites in the US. Not only are these wastes radioactive, but they are also highly alkaline and concentrated in electrolytes. Using currently available technologies and approaches, EM estimates that processing these wastes into waste forms for disposal in a geologic repository will take at least 5 decades and over \$300 billion dollars. Basic research on the chemical and physical behavior of these materials in such extreme conditions is needed to provide a foundation of innovation to accelerate processing and reduce aggregate costs.

IDREAM is an Energy Frontier Research Center (EFRC) conducting fundamental research to support innovations in processing high-level radioactive wastes (HLW). Activities in IDREAM are designed to support the transformation of HLW processing by elucidating the basic chemistry and physics required to control and manipulate interfacial phenomena in extreme HLW environments (e.g., non-equilibrium, heterogeneous, and chemically complex). This foundational knowledge is required to achieve IDREAM's vision to master molecular-to-mesoscale chemical and physical phenomena at interfaces in complex environments characterized by extremes in alkalinity and low-water activity, and driven far from equilibrium by ionizing (g,b) radiation. Further, understanding these processes will enable prediction of waste aging over the many decades required to complete this difficult cleanup task.

Currently, IDREAM activities focus on the aluminate anion in alkaline solutions, and its nucleation into boehmite (aluminum (oxy)hydroxide, Al(OH)₃) and gibbsite (aluminum hydroxide, Al(OH)₃), as they are key principal components of bulk waste materials to which a variety of other metal ions and radionuclides partition. In this presentation, initial results on interfacial reactivity between aluminate, boehmite, and gibbsite will be discussed. The impact of g and b radiation on boehmite and gibbsite will also be presented.

4:40pm **AC+AS+SA+SU-MoA10 Real Structure of Nanocrystalline Uranium based Hydrides Studied By the X-ray Scattering Methods**, *Milan Dopita*, *L. Havela*, *L. Horak*, *M. Paukov*, Charles University, Prague, Czech Republic, *Z. Matej*, MAX-IV, Lund, Sweden

Interaction of hydrogen with uranium is not only an important issue for its nuclear and military applications but also contributes to understanding of the 5f magnetism. Uranium hydrides provide a unique tool to observe an impact of expansion of the U lattice, allowing formation of U moments and their ferromagnetic ordering. However, the electronic structure of uranium

hydrides is not fully understood yet. Especially, the role of the real structure, i.e. the influence of the lattice defects, particle size in the nanocrystalline bulk materials and the preferred orientation of crystallites – the texture, the strains and stresses in the case of films is not well described, but can significantly influence electronic and magnetic properties of materials.

In our contribution we report the real structure of bulk and powder Mo- and Zr-alloyed uranium hydrides, prepared by rapid (splat) cooling and high pressure synthesis, and Mo alloyed uranium hydride films synthesized by reactive sputtering, using X-ray scattering methods. The sample series with different alloying element concentration as well as at different hydrogen pressure were prepared. Since the classical powder diffraction methods, as the profile analysis and/or Rietveld method, reach the limits of their applicability for the nanocrystalline uranium hydrides alloys in terms of the real structure description, the use of more advanced methods is necessary. Here we describe the total scattering method – pair distribution function analysis, and Debye equation calculation for simulations of the intensity scattered from nanocrystalline clusters.

The key results of our study were the determination of the phase composition and its evolution, as well as detailed atomic positions, which can influence the U-U spacings in individual phases, tuning the $5f$ magnetism. The methods are able to describe the particle size and defect distributions, the stress, strains, and textures in the films. In addition, the depth profiles and evolution of above mentioned parameters can be determined. Such X-ray analysis provides useful characterization of the sputter-deposited films, which are also used for fundamental electron spectroscopy studies of UH_3 -based films, exhibiting much lower surface contamination by oxygen than comparable bulk material.

This work was supported by the project “Nanomaterials centre for advanced applications”, Project No. CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

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