

Actinides and Rare Earths Focus Topic Room A215 - Session AC+AS+LS-TuM

Chemistry and Physics of the Actinides and Rare Earths

Moderators: Melissa Denecke, IAEA, Austria, James G. Tobin, University of Wisconsin-Oshkosh

8:00am **AC+AS+LS-TuM1 Study of the Early Actinide Oxides and Fluorides – Systematics of the Electronic Structure, Thomas Gouder, R. Eloiardi, R. Caciuffo**, European Commission - Joint Research Centre, Germany **INVITED** Oxidation properties of uranium have a great influence on the stability of nuclear waste. U^{VI} has

a 1000 times higher solubility in water than U^{IV} , and so the dissolution of UO_2 based spent fuel nuclear waste strongly depends on the oxidation state of the surface. Oxygen incorporation into the surface of UO_2 first results in the formation of $U(V)$, found in UO_{2+x} and mixed valent oxides, and then formation of U^{VI} . But despite early reports on the existence of a pure $U(V)$ phase (U_2O_5) there are no spectroscopic data on pure $U(V)$. This may be due to its position between the highly stable UO_2 and UO_3 . Also, apparent mixed surface phases containing U^{IV} , U^V and U^{VI} may result from the strong redox gradient between the oxidizing environment and the reduced bulk, present in most corrosion experiments. Replacing bulk samples by thin films allows avoiding this problem, by confining the reaction to a thin region where final conditions are reached everywhere simultaneously, keeping the system homogeneous. This opened the path for a systematic study of the evolution of the electronic structure of uranium upon oxidation and follow the outer shell configuration from $5f^2$ (U^{IV}), to $5f^1$ (U^V) to $5f^0$ (U^{VI}).

We will present electron spectroscopy (XPS, UPS and BIS) and Electron Energy Loss (ELS) study of U_2O_5 compare results to the neighbouring oxides (UO_2 and UO_3). U_2O_5 has been produced by exposing UO_2 successively to atomic oxygen, leading to UO_3 , and to atomic hydrogen. Films have been deposited on polycrystalline gold foils (inert substrate). During gas exposure the samples were heated to 400°C to ensure fast diffusion and equilibrium conditions.

Determination of the U oxidation states was based on the characteristic U-4f core level satellites, separated from the main lines by 6, 8 and 10 eV for U^{IV} , U^V and U^{VI} , respectively. We managed producing films which showed exclusively a single 8 eV satellite, indicating the presence of pure U^V . The formation of U^V was confirmed by the intensity evolution of the $U5f$ valence emissions. Also the linewidth of the XPS $5f$ line decreases from UO_2 , with the $5f^1$ final state multiplet, to U_2O_5 , with a $5f^0$ final state singlet. The U-5d line also displays a multiplet structure due to interaction with the open $5f$ shell (U^{IV} and U^V). Evolution of the $O2p/O1s$ intensity ratio indicates increasing covalence of the U-O bond in higher oxides.

U oxide spectra will be compared to spectra of ThO_2 . Multiplet splitting and its dependence on the open shell was followed by comparing $5f^2$ (UO_2) and $5f^0$ (ThO_2) systems. Finally XPS/BIS of the valence region will be presented for various oxides (UO_2 , U_2O_5 , UO_3 and ThO_2) and fluorides (UF_4 and ThF_4).

9:20am **AC+AS+LS-TuM5 Multiscale Characterization of Lanthanide and Actinide Nanoparticles Embedded in Porous Materials, Stefan Minasian, S. Alayoglu, S. Aloni**, Lawrence Berkeley National Laboratory; *J. Arnold*, University of California at Berkeley; *E. Batista*, Los Alamos National Laboratory; *A. Braun, C.H. Booth, A. Herve*, Lawrence Berkeley National Laboratory; *Y. Liu*, University of California at Berkeley; *L. Moreau*, Lawrence Berkeley National Laboratory; *T. Lohrey, J. Long, M. Straub, S. Robin, D. Russo*, University of California at Berkeley; *D.K. Shuh*, Lawrence Berkeley National Laboratory; *J. Su, P. Yang, X. Zhang*, Los Alamos National Laboratory **INVITED**

Decades of synthetic work has shown that desirable physical properties can be obtained by tailoring the size and composition of main-group and transition metal nanoparticles. The origin of these phenomena can be traced to a variety of factors that are intrinsic to nanoparticles, including but not limited to (1) quantization of the electronic states and (2) increasing contributions from nanoparticle surfaces. Despite this progress, very few methods provide the level of synthetic control needed to prepare lanthanide and actinide nanoparticles with well-defined sizes and compositions. Furthermore, many conventional methods of characterization are unable to determine the relative roles of volume and surface chemistry on physical behavior involving the 4f- and 5f-electrons.

We established syntheses for lanthanide and actinide nanoparticles by adapting a conceptual approach employed previously by Fischer and Suh to form d-block transition metal and main-group element nanoparticles in metal organic frameworks (MOFs). Implantation of lanthanide and actinide precursor molecules in covalent organic frameworks (COFs) was achieved by sublimation, followed by decomposition to form nanoparticles via exposure to reactive gases and/or elevated temperatures. A multi-pronged imaging and spectroscopic strategy was developed to fully characterize the complex multi-component materials. The characterization techniques are complementary in that they provide atomic to micron-scale probes, element and bulk-level selectivity, and measurements that are individual and statistically significant (Figure 1). Transmission electron microscopy (TEM) showed that the COF-5 templates limited UO_2 nanoparticle growth to between 1-3 nm, which is similar to the COF-5 pore size (2.7 nm). In addition, small-angle X-ray scattering (SAXS) was used to determine the nanoparticle form factor (for size and polydispersity) in a globally-averaged manner. Scanning transmission X-ray microscopy (STXM) was used to probe micron-scale morphology and to evaluate composition with X-ray absorption spectroscopy at the B, C, and O K-edges. Finally, X-ray absorption fine structure (XAFS) spectroscopy was used to determine composition and structure because it does not require long-range crystallographic order, and because it is capable of probing the nanoparticles selectively despite the substantial background from the organic host. This presentation will also discuss our efforts to show how 4f and 5f-electron behavior changes with variations in size and composition at the nanometer level.

11:00am **AC+AS+LS-TuM10 Multiple Forms of Uranium Hydrides and their Electronic Properties, Ladislav Havela, V. Buturlim, E. Chitrova, O. Koloskova, P. Minarik, M. Cieslar, M. Dopita, L. Horak, M. Divis, I. Turek, Charles University, Prague, Czech Republic; *D. Legut*, VSB-Technical University of Ostrava, Czech Republic; *T. Gouder*, European Commission - Joint Research Centre, Germany**

Although the published U-H binary phase diagram contains only the UH_3 phase, a recent progress in sputter deposition synthesis led to the discovery of UH_2 , which is with its CaF_2 structure type analogous to e.g. PuH_2 or YH_2 [1]. In addition, a high pressure synthesis yielded several U hyper-hydrides (as UH_8), which are predicted to be a high-temperature superconductors [2]. As both UH_3 (appearing in two structure modifications, α - and β - UH_3) and UH_2 allow alloying with selected transition metals, we have a whole spectrum of U-H hydrides and certain general features can be deduced, which have a serious implications for our understanding of actinides in general.

The striking fact that both UH_3 phases have, despite very different crystal structure, practically identical size of U moments and magnetic ordering temperature $T_C \approx 165$ K, which do not change even in the nanostructured state (grain size several nm) is underlined by the fact that both parameters only weakly depend on substantial alloying with Mo and other d-metals. UH_2 with substantially larger U-U spacing is a ferromagnet, as well, its $T_C \approx 125$ K. Structure of all those forms contains identical building blocks, H atoms inside U tetrahedra of invariable size, which are only set up into different patterns. The U-H bonding seems to be therefore an ingredient, which is more important than the conventional U-U spacing. The nature of the bonds is revealed by ab-initio calculations. One general feature is the U-6d hybridization with the H-1s states, which leads to an electron transfer towards H. However, unlike rare-earth trihydrides, UH_3 remains metallic, UH_2 naturally, too. The 5f states largely released from the 5f-6d hybridization can therefore develop a strong ferromagnetism despite low U-U spacings. The transfer could be traced even in the real space using the Bader analysis.

The ab-initio techniques, which are successful in capturing the equilibrium volumes and U magnetic moments, are so far less successful in description of photoelectron spectra close to the Fermi level, which indicates importance of electron-electron correlations.

This work was supported by the Czech Science Foundation under the grant No. 18-02344S.

[1] L. Havela et al., Inorg. Chem. 57 (2018) 14727.

[2] I.A. Kruglov et al., Sci. Adv. 4 (2018) eaat9776.

Tuesday Morning, October 22, 2019

11:20am **AC+AS+LS-TuM11 Hafnium L-Edge X-ray Absorption Near Edge Structure Spectra Reveals Crystal Field Splitting**, *David Shuh, D. Caulder*, Lawrence Berkeley National Laboratory; *L. Davis*, Pacific Northwest National Laboratory; *M. Mara*, University of California at Berkeley; *C.H. Booth*, Lawrence Berkeley National Laboratory; *J. Darab, J. Icenhower, D. Strachan*, Pacific Northwest National Laboratory

One method for the safe disposal of actinides currently under consideration by the U.S. Department of Energy is immobilization of radionuclides in a glass or ceramic wasteform that will subsequently be stored in a geological repository. To develop successful, stable wasteforms, it is necessary to acquire an understanding of the fundamental chemistry of the actinides (U, Pu, etc.) and neutron absorbers (B, Gd, Hf) that will be incorporated into the glass or ceramic matrix. The X-ray absorption near edge structure (XANES) at the hafnium L_3 and L_1 absorption edges has been investigated to elucidate the local structure of Hf in wasteform glasses that are currently being considered as candidates for the immobilization of radionuclides. During our investigations of the structure of Hf, a neutron absorber and potential Pu(IV) surrogate, we noted an unusual feature at the white line maximum at the L_3 absorption edge: The examination of a variety of Hf model compounds demonstrates that the second derivative of the Hf L_3 XANES displays structure characteristic of crystal field splitting of the empty d-manifold. The peralkaline glasses studied exhibit L_3 XANES spectra typical of Hf in an octahedral crystal field. The L_1 XANES data corroborate these results, as the L_1 spectra of the glasses also resemble that of an octahedral Hf siloxane model compound, distinct from spectra of other standards measured.

11:40am **AC+AS+LS-TuM12 Electrical Resistivity in Uranium-based Thin Films**, *Evgeniya Tereshina-Chitrova, L. Havela, M. Paukov, M. Dopita, L. Horak, M. Cieslar*, Charles University, Prague, Czech Republic; *Z. Soban*, Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic; *T. Gouder, F. Huber, A. Seibert*, Joint Research Center, European Commission, Germany

Metallic 5f materials have a very strong coupling of magnetic moments and electrons mediating electrical conduction. It is caused by strong spin-orbit interaction together with involvement of the 5f states in metallic bonding. In this work we investigate the electrical resistivity $\rho(T)$ of various uranium-based thin films using the Van der Pauw method. Thin film samples of U-Mo and their hydrides were prepared by reactive sputter deposition [1]. The basic in-situ diagnostics was performed using a photoelectron spectroscopy (XPS). The films were further characterized using x-ray diffraction (XRD) methods and Transmission Electron Microscopy (TEM). The $\rho(T)$ of the films studied correspond to known bulk systems of equivalent composition but provide much more variability of concentrations and geometries.

We studied superconductivity in the U-Mo films by measuring low-temperature resistivity down to 0.4 K. The 100 nm-thick $U_{0.79}Mo_{0.21}$ film shows a transition to the superconducting state at 0.55 K. The transition is wide and extends to 0.4 K. The upper critical field for the thin U-Mo film is ~ 1 T, i.e. much lower than that for the bulk U-Mo obtained by splat cooling [2].

The hydrides of the U-Mo films had to be prepared using a cooled substrate (≈ 177 K). The study of the $(UH_3)_{0.74}Mo_{0.26}$ of estimated thickness 210 nm showed that it is a ferromagnet with the Curie temperature of ≈ 165 K, i.e. equivalent to bulk UH_3 , which underlines the general insensitivity of U hydrides to structure modifications. Overall temperature dependence is very weak and the absolute value of 2 m Ω cm, estimated from the nominal thickness, is very high for a metallic system.

The net negative resistivity slope in the U-Mo films and hydrides can be attributed to the randomness on atomic scale, yielding very strong scattering of electrons and weak localization. In the hydrides it is supported also by random anisotropy, randomizing local directions of U moments.

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[1] Gouder, R. Eloirdi, F. Wastin, E. Colineau, J. Rebizant, D. Kolberg, F. Huber, Phys.Rev. B **70**, 235108 (2004).

[2] N.-T. H. Kim-Ngan, S. Sowa, M. Krupska, M. Paukov, I. Tkach and L. Havela, Adv. Nat. Sci: Nanosci. Nanotechnol. **6**, 015007 (2015).

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