Actinides and Rare Earths
Room 207 A W - Session AC+MI-FrM

Spectroscopy, Spectrometry, 5f Behavior and Forensics

Moderators: Ladislav Havela, Charles University, Czech Republic, **Gertrud Zwicknagl**, Technical University Brauschweig, **Eteri Svanidze**, Max Planck Institute for Chemical Physics of Solids, **Alison Pugmire**, LANL

8:15am **AC+MI-FrM-1 Exploring the Surface Chemistry of Plutonium using ToF-SIMS*, Sarah Hernandez,*** Los Alamos National Laboratory **INVITED**

Plutonium metal is highly reactive by immediately forming an oxide layer when exposed to air and quickly forming a hydride when exposed to hydrogen. The fundamental understanding of the impact of impurities and defects on the effect of oxidation and corrosion of Pu is limited in both experimental and theoretical studies. Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) is a unique surface science technique that is highly sensitive to the first 1-2 monolayers of the surface (<1nm) and can detect all isotopes (including hydrogen) at parts-per-million levels, which gives a comprehensive survey of surface constituents. This technique also provides a structural and reactivity, chemisorption versus physisorption, information and complements other surface science techniques, such as X-ray photoelectron spectroscopy (XPS). In general, ToF-SIMS may provide a more in-depth analysis of surface constituents that otherwise might not be detected or deconvolute from a complex XPS spectra. A newly installed ToF-SIMS nanoToF 3 at LANL uses a 30 kV Bi_3^{++} liquid metal ion gun as the primary ion source and has a mass resolution of 12,000 ($\Delta m/m$), thus providing a new level of mass resolution and sensitivity on Pu surfaces that was not previously achieved. I will show recently collected ToF-SIMS results of hydrogen and oxygen gas reactions on alpha-Pu and 2 at. % Ga stabilized δ-Pu surfaces and how they compare with other.

8:45am **AC+MI-FrM-3 HERFD vs XAS: The Case for Equivalence*, J G Tobin,*** U. Wisconsin - Oshkosh

The advent of new, powerful, highly efficient, multi-component, X-ray monochromators used in the detection of tender x-rays has revolutionized spectroscopic investigations of the 5f electronic structure. All of the new experiments are, in essence, variants of X-ray Emission Spectroscopy (XES), where the improved monochromatized detection, applied to novel specific decay pathways, plays a key role. In HERFD (High Energy Resolution Fluorescence Detection) a type of Resonant Inelastic X-Ray Scattering (RIXS), the monochromatized XES detection allows the performance of a scattering experiment with vastly improved resolution.It is argued here that HERFD devolves into a higher resolution version of X-Ray Absorption Spectroscopy (XAS). It has been shown that the M_4 and M_5 spectra are essentially direct measurements of the j-specific ($5f_{5/2}$ and $5f_{7/2}$) Unoccupied Density of States (UDOS), which can be directly correlated with the UDOS from Inverse Photoelectron Spectroscopy (IPES) and Bremsstrahlung Isochromat Spectroscopy (BIS). [1-3] Furthermore, a remarkable level of agreement is achieved between a model based upon the UDOS of Th and a series of HERFD and IPES/BIS results with various 5f occupation levels. [4-6] Finally, the historical record of XAS will be examined, demonstrating the success of various resonant decay schemes as measures of the underlying XAS.

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9:00am **AC+MI-FrM-4 Combinatorically Estimating the Orbital Occupancy of Actinides using an Entropic Approach*, Miles Beaux,*** *Benjamin Heiner,* Los Alamos National Laboratory

Predicting material properties in *f*-block elements, especially actinides, is complicated by their complex electronic structures, such as multiconfigurational ground states and strong correlation effects. These structures arise from large electron degrees of freedom, posing challenges in modelling their behavior. A non-integer orbital occupancy representation describes the superposition mixing of multiple near-energy degenerate configurations. This representation generalizes by approximation to established ground states in elements with simpler electronic structures and enables an over-approximation of entropy for multiconfigurational ground state structures. A complementary combinatorial approach applies Hund's rule constraints to establish an under-approximation of entropy. Together, these methods bracket entropy limits, providing insights into electronic configurations that most significantly contribute to the multiconfigurational ground states of actinide elements to a low order approximation. Under an energy degeneracy assumption weighted by configuration permutations, calculations iteratively refine the contributing configurations, yielding low-order orbital occupancy estimates that align with experimental data and theoretical models. (LA-UR-25-22711)

9:15am **AC+MI-FrM-5 Soft X-Ray Spectroscopy of Americium Oxides*, David Shuh,*** Lawrence Berkeley National Laboratory*; Sergei Butorin,* Uppsala University, Sweden

Americium oxides are an integral part of the existing nuclear fuel cycle and are important considerations in future mixed-oxide (MOX) fuel cycles that involve the minor actinides for recycling. Knowledge of the chemical bonding and physical properties of the Am oxides is increasingly important for these envisioned future nuclear cycles. Synchrotron radiation soft x-ray spectroscopy complemented by theoretical calculations were utilized to characterize the electronic structure of americium dioxide (AmO_2) and americium sesquioxide (Am_2O_3). For the sesquioxide, this included x-ray absorption near-edge structure (XANES) spectroscopy studies at the Am $O_{4,5}$- and the $N_{4,5}$ -edges (Am $5d_{5/2,3/2}$; Am $5d_{5/2,3/2}$; respectively) and resonant inelastic x-ray scattering (RIXS) measurements at the Am $O_{4,5}$-edges. For the dioxide, XANES investigations conducted at the $N_{4,5}$-edges were compared to spectra obtained from the sesquioxide as well as a $U_{0.9}Am_{0.1}O_2$ specimen. Experiments were performed at beamlines of the Advanced Light Source at the Lawrence Berkeley National Laboratory and at MAXlab, (Lund, Sweden).

The results of the synchrotron radiation experiments were compared to theoretical calculations performed with several methods. These included the Anderson Impurity Model (AIM) with full multiplet structure to account for the 5f electrons, and progressively employing crystal-field multiplet theory when appropriate (Am_2O_3) starting with an atomic multiplet formulation. The results of the XANES and RIXS experiments combined with theory show that AmO_2 can be classified as a charge-transfer compound with a 5f occupation of 5.73 electrons with significant covalence in the Am 5f - O 2p bonds. Contrasting to this behavior, Am_2O_3 can be well-represented by a Mott-Hubbard system with a 5f occupation of 6.05 electrons. The RIXS result suggest that Am_2O_3 possesses weak Am 5f - O 2p hybridization. A recent development by Tobin et al. has utilized FEFF to identify the spectral shape on the higher energy side the Am $N_{4,5}$-white lines as arising scattering features.

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9:30am **AC+MI-FrM-6 Theory of Valence-to-Core RIXS Measured at the Uranium M_5 Edge: Comparison of UO_2 and UF_4*,*** *Ondrej Stejskal,* ***Jindrich Kolorenc,*** Institute of Physics, Czech Academy of Sciences, Czechia

Motivated by a recent experimental study [1], we model the valence-to-core resonant inelastic x-ray scattering (RIXS) measured at the uranium M_5

edge in insulating compounds UO$_2$ and UF$_4$. We employ the Kramers–Heisenberg formula in conjunction with the Anderson impurity model extracted from the corresponding LDA+DMFT electronic-structure calculations [2], in which the double-counting correction is adjusted to best reproduce the experimental valence-band XPS spectra [3,4]. In our simulations, we find two sets of excited states. One group is formed by excitations of the 5f^2 shell that appear at energy losses $\lesssim 4$ eV. These excitations are not well resolved in the experimental data [1] as they are largely obscured by the elastic peak. The other group of excited states is formed by the charge-transfer excitations corresponding to a transfer of an electron from the oxygen/fluor 2p states to the uranium 5f shell. We identify these excitations with the spectral feature experimentally observed at an energy loss of roughly 8–10 eV, in agreement with other closely related investigations [5,6]. Our model estimates the intensity, with which the charge-transfer excitations appear in the RIXS spectra, to be larger in UO$_2$ than in UF$_4$, just like it is observed in the experiment [1]. We analyze in some detail how this intensity depends on the strength of the metal-ligand hybridization and on other parameters of the model, such as the magnitude of the core-valence interaction acting in the intermediate state of the RIXS process.

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9:45am **AC+MI-FrM-7 Room Temperature H$_2$ Dosing on Polished ɑ-Pu Surfaces with XPS***, **Daniel Rodriguez**, Timothy Gorey, William Ponder, Alessandro Mazza, Raymond Atta-Fynn, Sarah Hernandez,* Los Alamos National Laboratory

Plutonium (Pu) is a complex element with an interesting electronic structure, and it is also a material of great importance for both nuclear energy and security. To better understand its interaction with gases, surface analysis of the alpha (ɑ) variant provides valuable insight when coupled with a technique such as X-ray photoelectron spectroscopy (XPS). Different core electron orbitals may be probed, and binding energies from emitted electrons provide information on the local chemical state, i.e., degree of oxidation, reduction, or carbonization within the ɑ-Pu.

Here we investigated the effect of hydrogen (H$_2$) gas dosing of ɑ-Pu surfaces, which reacts and forms plutonium hydride (PuH$_2$) at temperatures >100 °C. By slowing the kinetics at room temperature, we may witness H$_2$ dynamics on native ɑ-Pu surfaces, and view how Pu materials such as oxidized and carbonized forms evolve with H$_2$ exposure. In addition, we present our findings from density functional theory (DFT) validating experimental observation. To provide an example, **Fig. 1** shows a plot of various Pu 4f spectra. In red, metal ɑ-Pu is observed after having been sputtered to remove both surface contaminants and the native oxide layer. The defining metal feature in the 4f$_{7/2}$ peak is seen at ~422.2 eV. Next, the sample was dosed with H$_2$ gas for 198 Langmuir (L) (blue line), and then the exposure was increased (green line) until reaching 396 L. A clear reduction in the signal's intensity is seen in both the 5/2 and 7/2 metal peaks. Secondly, the 7/2 satellite shows an increase in signal, which is indicative of surface passivation. Clearly, more is needed to know what these H$_2$ induced changes signify, and this presentation will show additional spectra from the O 1s, C 1s, and the Pu valence band, along with DFT to contextualize the on-going mechanisms of H$_2$ with the ɑ-Pu surface.

10:00am **AC+MI-FrM-8 Discovering Persistent Morphological and Chemical Signatures from Oxidation and Corrosion of Plutonium and Uranium Metals***, **Brandon Chung**, Alexander Baker, Scott Donald, Tian Li, Rachel Lim, Uday Mehta, Debra Rosas, Donya Servando-Williams,* Lawrence Livermore National Laboratory*; Alexander Ditter, S. Olivia Gunther, David Shuh,* Lawrence Berkeley National Laboratory

Much is known about various process pathways that can produce purified plutonium (Pu) and uranium (U) metals. In addition to material signatures imparted by their source materials (e.g., spent fuel), some signatures will be propagated by their separation processes and processing conditions to extract and form Pu and U metals. Once fabricated, both Pu and U metals are highly susceptible to environmental corrosion. Later, these metals may be calcined at high temperatures to convert them to more stable oxides for long-term storage or disposal. Relatively unexplored are the relationship between the oxide and corrosion products to their starting metal itself (e.g., trace element impurity). Our multiplatform characterization experiments (e.g., focused ion beam-scanning electron microscopy, transmission electron microscopy, and X-ray synchrotron spectromicroscopy) have provided spatially resolved material signatures in Pu and U metals and their products. We highlight the relationship between product morphological and chemical features of both oxide and corrosion products to their starting metal characteristics and exposure environments.

10:30am **AC+MI-FrM-10 A Novel Lexan-Aerogel Detector for Fission Track Analysis for Advancing Nuclear Forensics***, **Itzhak Halevy**, Rami Babayew, Yaacov Yehuda-Zada,* Ben Gurion University Be'er Sheva, Israel*; Galit Bar,* Soreq Nuclear Research Center, Israel*; Noam Elgad, Mark Last,* Ben Gurion University Be'er Sheva, Israel*; Jan Lorincik,* Research Centre Řež, Czechia*; Itzhak Orion,* Ben Gurion University Be'er Sheva, Israel*; Shay Dadon,* Nuclear Research Center Negev, Israel*; Aryeh M. Weiss,* Bar Ilan University, Israel*; Galit Katarivas Levy,* Ben Gurion University Be'er Sheva, Israel

Fission track analysis is a technique employed in nuclear forensics to identify and examine fission isotopes. This technique is specific for small samples in the range of a few picograms or to analyze bigger samples and check for homogeneity.

In the old Lexan detector, the tracks are pretty close, and that limits much the ability to count the tracks and analyze the length of the tracks. The main target of the fission track is to locate the fission ions in between a lot of other isotopes. The located fission ions could be transferred to other techniques like ICP-MS for further analysis. Better separation between tracks and analysis could lead to showing the yield of fission products, which is specific to every fission isotope. The yield fission products are two humps on the graph that are equal in area. One hump is around A=95, 135; in the length of the track histogram, the two humps look different due to the difference in dE/dx of the different energies. The light elements hump looks narrow, and the heavy elements hump looks wide; still, the area of those humps is equal. We created a novel detector for fission track analysis with the Lexan-modified detector.

This innovative detector exhibits more dispersion of fission tracks. In this innovative approach, we adhered aerogel to the Lexan. The aerogel has a low absorption coefficient; hence, it does not substantially obstruct the fission products in the detector. The incorporation of aerogel modifies the geometric configuration, enlarges the dimensions of the fission track stars, and increases the separation between individual tracks, as seen in Fig. 1 in the supplement. A fission track star of a size of 150 microns can reach 350 microns with the aerogel configuration. Given that the fission products are distributed isotopically while the aerogel is two-dimensional, it is necessary to employ stereoscopic projection to facilitate their integration. An illustration of this enhancement of the fission track star is seen in Fig. 1, where the dimensions of the fission track star are greater and the tracks are widely spread. The newly developed analytical program, **Finder**, may utilize a 2D representation of the fission track star. Whether an actual star or a simulated star, of a fission track to conduct analysis and provide 3D evaluations, therefore illustrating the fission yield of the fission isotope. The analysis of the fission track star is shown in Fig. 2, supp. The fission track analysis of ^{235}U star in that software is depicted in Fig. 3 supp.

Fission track length before the detector and in it are shown in that figure of the fission track analysis of ^{235}U star.

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