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, **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 (Δm/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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2. J. G. Tobin, H. Ramanantoanina, C. Daul, S.-W. Yu, P. Roussel, S. Nowak, R. Alonso-Mori, T. Kroll, D. Nordlund, T.-C. Weng, D. Sokaras, "The Unoccupied Electronic Structure of Actinide Dioxides," Phys. Rev. B 105, 125129 (2022)
3. J. G. Tobin, S. Nowak, C.H. Booth, E.D. Bauer, S.-W. Yu, R. Alonso-Mori, T. Kroll, D. Nordlund, T.-C. Weng, D.Sokaras, "Separate Measurement of the 5f5/2 and 5f7/2 Unoccupied Density of States of UO2," J. El. Spect. Rel. Phen. 232, 100 (2019).
4. J. G. Tobin, S. Nowak, S.-W. Yu, P. Roussel, R. Alonso-Mori, T. Kroll, D. Nordlund, T.-C. Weng, D. Sokaras, "The Underlying Simplicity of 5f Unoccupied Electronic Structure," J. Vac. Sci. Tech. A 39, 043205 (2021).
5. J. G. Tobin, S. Nowak, S.-W. Yu, P. Roussel, R. Alonso-Mori, T. Kroll, D. Nordlund, T.-C. Weng, D. Sokaras, "Comment on The Underlying Simplicity of 5f Unoccupied Electronic Structure," J. Vac. Sci. Tech. A 39, 066001 (2021).
6. J. G. Tobin, S. Nowak, S.-W. Yu, P. Roussel, R. Alonso-Mori, T. Kroll, D. Nordlund, T.-C. Weng, D. Sokaras, "The Thorium Model and Weak 5f Delocalization," J. Vac. Sci. Tech. A 40, 033205 (2022).

9:00am **AC+MI-FrM-4 Room Temperature H_2 Dosing on Polished α-Pu Surfaces with XPS*, Daniel Rodriguez*[1]*,*** *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 (α) 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 α-Pu.

Here we investigated the effect of hydrogen (H_2) gas dosing of α-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 α-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 α-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 α-Pu surface.

9:15am **AC+MI-FrM-5 Ab Initio Modeling of Hydrogen Interaction with the Surface of α-Pu*, Raymond Atta-Fynn,*** *Sarah Hernandez,* Los Alamos National Laboratory

Hydrogen (H) reacts strongly with plutonium (Pu) metal, with the reaction primarily initiated on the metal surface. However very little is known theoretically about H dynamics on the surface of the ambient temperature phase of Pu, namely α-Pu. In this regard, we carried out calculations on H interactions with the α-Pu(020) surface using density functional theory-based geometry optimizations and *ab initio* molecular dynamics at 300 K. Molecular H_2 dissociated spontaneously on the metal surface at room temperature, resulting in atomic H chemisorption. The energy barriers to diffusion of the chemisorbed H from the surface into the subsurface and bulk layers were modeled using accelerated *ab initio* molecular dynamics. The magnitudes of the energy barriers to H diffusion in relation to hydride formation will be discussed.

9:30am **AC+MI-FrM-6 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

[1] **JVST Highlighted Talk**

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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