

Tuesday Morning, November 11, 2014

Actinides and Rare Earths Focus Topic

Room: 301 - Session AC+AS+MI+SA+SS-TuM

Synchrotron Radiation and Laboratory Based Investigations of Actinides and Rare Earths

Moderator: David Geeson, AWE

8:00am AC+AS+MI+SA+SS-TuM1 **The Role of the 5f Band and Partial Occupancy in Actinide L3-edge XANES and RXES Measurements**, *Corwin Booth, S.A. Medling, Y. Jiang*, Lawrence Berkeley National Laboratory, *J.G. Tobin*, Lawrence Livermore National Laboratory, *P.H. Tobash, J.N. Mitchell, D.K. Veirs*, Los Alamos National Laboratory, *M.A. Wall, P.G. Allen*, Lawrence Livermore National Laboratory, *J.J. Kas*, University of Washington, *D. Sokaras, D. Nordlund, T.-C. Weng*, SLAC National Accelerator Laboratory, *E.D. Bauer*, Los Alamos National Laboratory

INVITED

Although actinide (An) L3-edge x-ray absorption near-edge structure (XANES) spectroscopy has been very effective in determining An oxidation states in insulating, ionically-bonded materials, such as in certain coordination compounds and mineral systems, the technique fails in systems featuring more delocalized 5f orbitals, especially in metals. Recently, actinide L3-edge resonant x-ray emission spectroscopy (RXES) has been shown to be an effective alternative. This technique is further demonstrated here using a parametrized partial unoccupied density of states method to quantify both occupancy and delocalization of the 5f orbital in alpha-Pu, delta-Pu, PuCoGa5, PuCoIn5, and PuSb2. These new results, supported by FEFF calculations, highlight the effects of strong correlations on RXES spectra and the technique's ability to differentiate between f-orbital occupation and delocalization. Potential temperature-dependent spectral changes in the hidden order compound URu2Si2 and the superconductor PuCoGa5 will be discussed.

8:40am AC+AS+MI+SA+SS-TuM3 **Actinide Research with Hard Synchrotron Radiation**, *Roberto Caciuffo*, European Commission, JRC-ITU, Germany

INVITED

Advanced x-ray synchrotron radiation techniques, addressing spatial and temporal fluctuations of structural and electronic degrees of freedom, hold outstanding scientific promises for the future of actinide research [1]. Indeed, by probing hidden order parameters and elementary electronic excitations with high sensitivity and resolution, element- and edge-specific (resonant and non-resonant) x-ray scattering experiments provide the bricks for building the novel conceptual frameworks necessary to unravel the complexity of actinides. Here, I will present selected results from these experiments and discuss what they tell us.

Whereas resonant x-ray diffraction (RXD) with photon energies tuned to the $M_{4,5}$ absorption edges of actinide ions are used to study the order of electric quadrupole moments in oxides and intermetallics [2-4], resonant x-ray emission spectroscopy (RXES) and non-resonant inelastic X-ray scattering (NIXS) are applied to study the bulk electronic configuration in solids, liquids and gases [5,6]. In particular, the high penetration depth of hard X-rays employed in NIXS enables flexible containment concepts, facilitating investigations of radioactive materials in the liquid phase or under extreme conditions. Finally, inelastic x-ray scattering (IXS) can be used to map phonon dispersion branches with an energy resolution comparable to the one afforded by inelastic neutron scattering, but using crystal samples with sizes orders of magnitude smaller than those required by neutrons.

In the first example, I will show how a combination of diffraction, RXES, and absorption near-edge spectroscopy experiments at high-pressure can be used to study the correlation between polymorphism, mixing of different electronic configurations, and hybridization effects in elemental americium [7]. The potential of RXD in elucidating the nature of "hidden order" will be illustrated by the examples of the low-temperature phases in NpO_2 [8] and URu_2Si_2 [9]. Then, I will present NIXS results interrogating the $O_{4,5}$ absorption edges of uranium and plutonium materials, and results of IXS studies of the vibrational dynamics in $PuCoGa_5$ and NpO_2 .

[1] R. Caciuffo, E. C. Buck, D. L. Clark, G. van der Laan, *MRS Bulletin* **35**, 889 (2010)

[2] P. Santini et al., *Rev. Mod. Phys.* **81**, 807 (2009)

[3] H. C. Walker et al., *Phys. Rev. Lett.* **97**, 137203 (2011)

[4] Z. Bao et al., *Phys. Rev. B* **88**, 134426 (2013)

[5] T. Vitova et al., *Phys. Rev. B* **82**, 235118 (2010)

[6] R. Caciuffo et al., *Phys. Rev. B* **81**, 195104 (2010)

[7] S. Heathman et al., *Phys. Rev. B* **82**, 201103(R) (2010)

[8] N. Magnani et al., *Phys. Rev. B* **78**, 104425 (2008)

[9] H. C. Walker et al., *Phys. Rev. B* **83**, 193102 (2011)

9:20am AC+AS+MI+SA+SS-TuM5 **Lumps, Bumps and Pyrophoric Powders - Nuclear Waste Viewed in a New Light**, *Tom Scott*, University of Bristol, UK, *C.A. Stitt, M. Hart*, Diamond Light Source Ltd., UK, *J. MacFarlane, A. Banos, H. Paraskevoulakos, K. Hallam*, University of Bristol, UK

INVITED

How do you look inside a nuclear waste package without breaking it open? This question is important when the contained corrosion products are potentially flammable and radioactive. Synchrotron x-rays have been used to perform micro-scale in situ observation and characterisation of uranium entrapped in grout; a simulation for some intermediate level waste. Using specially designed analysis cells X-ray tomography and x-ray diffraction have been used to generate both qualitative and quantitative data from a grout encapsulated uranium sample before, and after, deliberately constrained H_2 corrosion. Tomographic reconstructions determined the extent, rates and mechanisms of the oxidation reaction by assessing the relative densities between the materials and the volume of corrosion products. The oxidation of uranium in grout was shown to follow the anoxic $U + H_2O$ oxidation regime, and the pore network within the grout was observed to influence the induction period for the initiation of uranium hydride formation across the surface of the metal. Powder diffraction analysis identified the corrosion products UO_2 and UH_3 , and permitted measurement of corrosion induced stress. Together, x-ray tomography and diffraction provide a means of accurately determining the types and degree of uranium corrosion occurring, thereby offering a future means for studying the reactions occurring in real full-scale waste package systems.

11:00am AC+AS+MI+SA+SS-TuM10 **Isotopic Measurements of Uranium in Particles by SIMS**, *David Simons*, National Institute of Standards and Technology (NIST)

INVITED

Secondary ion mass spectrometry (SIMS) has become a primary tool for the International Atomic Energy Agency (IAEA) and its Network of Analytical Laboratories (NWAL) to monitor activities at uranium enrichment sites. IAEA inspectors collect samples by wiping surfaces within facilities with cloth wipes that are later distributed to the NWAL for analysis. At the laboratories particles are extracted from the wipes and searched by various means to find those that contain uranium. The uranium-bearing particles are analyzed by mass spectrometry for their isotopic composition that is the key signature to be compared with the declared use of the facility. Large-geometry (LG) SIMS instruments based on magnetic sector mass spectrometers with multicollector array detectors are used by five members of the NWAL to both search for the uranium particles and analyze those that are found. We have characterized the performance of this type of instrument and found that it can be set up with a mass resolving power that excludes nearly all mass spectral interferences from uranium isotopes while maintaining high instrument transmission and high abundance sensitivity. The total efficiency for uranium detection has been measured with monodisperse microspheres and found to exceed 1%. Detection of U^{236} presents a special case because of interference from the U^{235} hydride ion that is removed by peak-stripping. The effect of the hydride on the uncertainty in the U^{236} abundance determination has been modeled for different uranium enrichments and hydride-to-parent ratios, and the effect of the particle substrate on hydride production has been investigated. The performance of LG-SIMS instruments for isotopic measurements of uranium in particles was recently demonstrated in the NUSIMEP-7 study organized by the Institute of Reference Materials and Measurements in which these instruments were able to detect and measure all uranium isotopes in particles smaller than 400 nm, including U^{236} at an isotopic abundance of 8×10^{-6} .

11:40am AC+AS+MI+SA+SS-TuM12 **X-ray Excited Auger Transitions of Pu Compounds**, *Art Nelson, W.K. Grant, J.A. Stanford, W.J. Siekhaus, W. McLean*, Lawrence Livermore National Laboratory

X-ray excited Pu NOO Auger line-shapes were used to characterize differences in the oxidation state of Pu compounds. The Auger line-shapes were combined with the associated chemical shift of the Pu $4f_{7/2}$ photoelectron line, which defines the Auger parameter and results in a reliable method for definitively determining oxidation states independent of binding energy calibration. Results show that PuO_2 , Pu_2O_3 , $PuH_{2.7}$ and Pu have definitive Auger line-shapes. These data were used to produce a chemical state (Wagner) plot for select plutonium oxides. This Wagner plot allowed us to distinguish between the trivalent hydride and the trivalent oxide, which cannot be differentiated by the Pu $4f_{7/2}$ binding energy alone.

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