Monday Morning, November 10, 2014

Actinides and Rare Earths Focus Topic
Room: 301 - Session AC+AS+MI+SA+SS-MoM

Spectroscopy, Microscopy and Dichroism of Actinides and Rare Earths

Moderator: David Shuh, Lawrence Berkeley National Laboratory

8:20am **AC+AS+MI+SA+SS-MoM1 Novel Synthetic and Spectroscopic Techniques in Actinide Materials Chemistry**, *Stefan Minasian*, Lawrence Berkeley National Laboratory, *E. Batista,* Los Alamos National Laboratory, *C.H. Booth,* Lawrence Berkeley National Laboratory, *D. Clark,* Los Alamos National Laboratory, *J. Keith,* Colgate University, *W. Lukens,* Lawrence Berkeley National Laboratory, *S. Kozimor, R.L. Martin,* Los Alamos National Laboratory, *D. Nordlund,* SLAC National Accelerator Laboratory, *D. Shuh, T. Tyliszczak,* Lawrence Berkeley National Laboratory, *D. Sokaras,* SLAC National Accelerator Laboratory, *X.-D. Weng,* Los Alamos National Laboratory, *T.-C. Weng*, SLAC National Accelerator Laboratory **INVITED**

The development of a detailed, quantitative understanding of electronic structure and bonding for a broad range actinide materials remains a significant scientific challenge. Recent advances have shown that the 1s to np transition intensities measured by Cl and S K-edge X-ray absorption spectroscopy (XAS) directly relate to coefficients of covalent orbital mixing in M–Cl and M–S bonds. The scientific progress associated with these Cl and S XAS studies suggests that using synchrotron-generated radiation to quantify covalency for ligands beyond Cl and S would have a wide impact. The nature of chemical bonds between actinides and light atoms such as oxygen, nitrogen, and carbon is of particular interest because these interactions control the physics and chemistry of many technologically important processes in nuclear science. However, obtaining accurate light atom K-edge XAS spectra on non-conducting compounds is notoriously difficult, because the measurement is highly sensitive to surface contamination, self-absorption, and saturation effects. Fortunately, recent upgrades at synchrotron facilities, advancements in beamline instrumentation, and sample preparation methods suggest that these insights are now within reach. Specifically, comparing XAS spectra measured in transmission with a scanning transmission X-ray microscope (STXM) with those from non-resonant inelastic X-ray scattering (NIXS) and time-dependent density functional theory provides a sound basis for validation of bulk-like excitation spectra.

Herein, a new effort is discussed that employs these techniques to understand bonding interactions in two well defined series of f-element materials. The actinide sandwich complexes, "actinocenes," $(C_8H_8)_2An$ (An = Th, Pa, U, Np, Pu) have played a central role in the development of organoactinide chemistry. Results showed two contrasting trends in actinide–carbon orbital mixing, and evidence that covalency does not increase uniformly as the actinide series is traversed. Additionally, the C K-edge XAS spectrum of thorocene represents the first experimental evidence of a ϕ-type orbital interaction. Oxygen K-edge XAS measurements and DFT studies began the lanthanide dioxides LnO_2 (Ln = Ce, Pr, Tb), because their electronic structures are well-established from hard X-ray spectroscopies. Preliminary efforts to use lanthanide oxides and lanthanide organometallics as experimental benchmarks for quantitative determinations of covalency in d-block and f-block materials will also be discussed.

9:00am **AC+AS+MI+SA+SS-MoM3 X-ray Magnetic Circular Dichroism of Actinides**, *Andrei Rogalev*, *F. Wilhelm*, European Synchrotron Radiation Facility (ESRF), France **INVITED**

Actinides compounds, which are straddling the magnetic properties of rare-earths and transition metals, have been the subject of increasing interest due to their very different properties, such as Pauli paramagnets, localized and itinerant ferromagnets, and heavy fermion superconductors. The key parameter responsible for the large variety of magnetic properties is obviously degree of localization of the 5f states which are indeed involved in both the chemical bonding and the magnetism. To unravel the details of the electronic structure and magnetic properties of these 5f states, polarization dependent X-ray spectroscopy at the $M_{4,5}$ edges appears as the most suitable experimental tools. At the third generation synchrotron radiation facilities, small x-ray beam with flexible polarization sized down to few microns can be routinely achieved. This technique is thus perfectly suited for studying minute samples (a few micrograms) of transuranium materials. This talk reviews recent advances in use of polarized x-rays to study local magnetic properties and electronic structure of actinides compounds.

The magnetic properties are mostly studied with X-ray Magnetic Circular Dichroism (XMCD). The great advantage of this technique is its capability to probe the orbital and spin magnetization of 5f states separately. XMCD experiments have been reported for a great number of uranium compounds and have permitted to understand, at least qualitatively, which is the ground state despite the difficulty over assigning a valency. It has also revealed differences between localized and itinerant systems that are not yet fully understood. To our knowledge there are very few reports on XMCD measurements on other trans-uranium materials. This is unfortunate, as the questions of localization of 5f states become more interesting as the 5f count increases. In order to improve our understanding of the magnetism of actinides, which is based up to now solely on uranium compounds, and thus better to describe the differences between localized and itinerant 5f systems, we report a thorough XMCD study of a series of ferromagnetic $AnFe_2$ Laves-phase compounds. Moreover, we show that additional information regarding exchange interaction between neighboring actinides atoms can be extracted from the XMCD measurements performed at absorption edges of other "nonmagnetic" atoms in the compounds.

Finally, we demonstrate that the study of the branching ratio in $M_{4,5}$ absorption spectra can bring valuable information regarding the coupling scheme, within which to discuss the electronic and magnetic properties of actinides atoms.

9:40am **AC+AS+MI+SA+SS-MoM5 Magnetic Circular Dichroism Measured with Transmission Electron Microscope**, *Jan Rusz*, Uppsala University, Sweden **INVITED**

X-ray magnetic circular dichroism (XMCD; [1]) is an established experimental probe of atom-specific magnetic properties of lanthanides and actinides. In XMCD, a photon of well-defined energy and polarization is absorbed by an atom in the sample with a probability that is proportional to the number available unoccupied states with an energy that allows fulfilling the energy conservation and selection rules. An essential element of XMCD are so called sum rules [2,3], which relate the XMCD spectra to the spin and orbital angular momenta, respectively.

Recently, a new experimental method has been developed that is closely related to XMCD. It was named electron magnetic circular (or chiral) dichroism (EMCD) and it is measured with a transmission electron microscope (TEM) instead of a synchrotron beam-line. We will review the short history of this method starting from its proposal in 2003 [4], first experimental proof-of-the-concept in 2006 [5], formulation of the theory [6] and sum rules [7,8] in 2007 to the present state-of-the-art and early applications, for example [9-12]. Yet, despite intense efforts, EMCD is still in its development phase, particularly from the point of view of quantitative studies. On the other hand, qualitative EMCD experiments have reached resolutions below 2nm [13].

The primary advantages of the EMCD, when compared to XMCD, are costs, availability and lateral resolution. Even a state-of-the-art TEM is a device considerably cheaper than a synchrotron beam-line and as such it can be available locally to a research group. TEM is also a very versatile instrument that combines diffraction experiments, elemental analysis, local electronic structure studies via electron energy loss spectroscopy [14] and now also magnetism via EMCD.

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10:40am AC+AS+MI+SA+SS-MoM8 The Microstructure of Plutonium Hydride Growth Sites, *Martin Brierley*, *J.P. Knowles,* AWE, UK*, M. Preuss, A.H. Sherry*, University of Manchester, UK

Under certain conditions plutonium is able to form plutonium hydride during long term storage [1]. Plutonium is radioactive, decaying via release of an alpha particle. Alpha particles are particularly damaging within the body and every attempt should be made to limit the distribution of loose material. Plutonium hydrides have been shown to be pyrophoric when exposed to oxygen; a reaction that could potentially liberate loose particulate outside of suitable containment.

Previous work into the hydriding rate of plutonium has investigated the reaction rate of various hydrides on the surface of these materials; specifically the nucleation rate, the lateral growth rate and the specific hydriding rate [2, 3]. Plutonium is a reactive metal and quickly forms a semi-protective oxide layer in air. Upon exposure of an oxide-covered sample to hydrogen, hydride is formed at discrete sites on the surface, which then grow radially across the surface [1]. Recent work has suggested a grain boundary enhanced growth rate [4].

In the present study, the microstructure associated with selected plutonium hydride growth sites was studied to provide information regarding the nucleation and growth mechanisms that govern the formation of plutonium-hydride. The samples were ground to 600 grit and evacuated before being exposed to ultra-pure hydrogen at pressures between 10 mbar and 1000 mbar for sufficient time to have nucleated a number of hydride sites.

Post-test analysis was performed using Scanning Electron Microscopy (SEM) and Optical Microscopy (OM) to determine the microstructure of the hydride growth sites. The morphology of individual hydride growth sites indicates that the hydride-metal interface has a highly discontinuous boundary, resulting from enhanced grain boundary diffusion and spears of transformed material; the microstructure within the plutonium hydride growth sites indicates that a preferred growth habit was adopted by the hydride product.

References

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11:00am AC+AS+MI+SA+SS-MoM9 Hydrides of U-Mo and U-Zr Alloys: Structure and Electronic Properties, *Ladislav Havela, M. Paukov, I. Tkach, D. Drozdenko, M. Cieslar, Z. Matej*, Charles University, Czech Republic

When U metal (α-U) is exposed to H gas, it forms a stable hydride β-UH_3. The lattice expansion stabilizes the ferromagnetic order with the Curie temperature around 170 K. The metastable form, α-UH_3, could not be synthesized as a pure phase, and the admixture of β-UH_3 did not allow to determine reliably its intrinsic magnetic properties. We have been testing the reaction to H exposure of γ-U (bcc), which was synthesized as a single phase by combination of Mo or Zr doping into U and ultrafast cooling. We found that such alloys need high H_2 pressure and long exposure to absorb hydrogen. The products can be characterized by the formula $UH_3Mo(Zr)_x$. The hydrides with Mo have a structure corresponding to β-UH_3 with grain size around 1 nm, i.e. almost amorphous. Its ordering temperatures increase to 200 K for $UH_3Mo_{0.18}$ and then decrease for higher Mo concentrations. The hydrides UH_3Zr_x exhibit the UH_3 structure (bcc U lattice filled with H atoms). Their Curie temperature weakly decreases with increasing Zr concentration and the extrapolation to Zr-free state indicates T_C = 170 K, i.e. identical to β-UH_3. The results can be compared with numerous hydrides obtained by hydrogenation of U_6X compounds (X = Mn, Fe, Co, Ni), all probably having similar magnetic properties. We present a detailed study of magnetic properties, electrical resistivity and specific heat. The structure characterization of initial alloys and the hydrides has been done by means of XRD, SEM with EBSD and TEM. The hydrides represent and new class of U materials, which exhibit, irrespective of details of composition or crystal structure, strong ferromagnetism with relatively very high ordering temperatures, quite surprising at materials at which the inter-U spacing does not exceed appreciably the Hill limit 340-360 pm. At last, the variations using double doping (both Mo and Zr) will be presented.

11:20am AC+AS+MI+SA+SS-MoM10 Unraveling the Mystery of Reactively-Sputtered UO(4+x), *David Allred, R.S. Turley, B.S. McKeon, A. Diwan, E.A. Scott, R.R. Vanfleet*, Brigham Young University

We recently found EDX and XPS evidence in reactive sputtered uranium oxide thin films of higher oxygen-to-uranium ratios than the 3-to-1 allowed by stoichiometry. We used reactive, DC-magnetron sputtering in 100% oxygen to prepare uranium-oxide thin films on silicon wafer with the highest possible oxygen content to investigate this. Both EDX & XPS showed that the ratio of oxygen-to-uranium in freshly samples was at least 4-to-1, with compositions approached 5 to 1. The potential explanations are uranates or peroxides. Detecting hydrogen- and an element difficult to detect in thin films-is crucial in understanding what is happening chemically. Uranates require cations. The only one possible in our films would be hydrogen. Similarly, bulk uranium peroxides without water/ hydrogen peroxide of hydration are not known. (We have found evidence of uranium trioxide being weekly hygroscopic and stored samples in a dry environment, nonetheless these samples show high oxygen contents as prepared.) We report our chemistry and structural (TEM and XRD) attempts to solve this mystery. We also report are measurement of extreme ultraviolet reflectance of this material. (ALS-beamline 6.3.2)

11:40am AC+AS+MI+SA+SS-MoM11 Cathodoluminescence and Band Gap Studies of Single Crystal $U_xTh_{1-x}O_2$ (x = 0.00, 0.01, 0.22), *David Turner*, Oak Ridge Institute for Science and Education, *J. Reding, R. Hengehold, T. Kelly,* Air Force Institute of Technology, *J.M. Mann,* Air Force Research Laboratory, *J. Kolis,* Clemson University, *J. Petrosky*, Air Force Institute of Technology

Analyses of depth- and temperature-resolved cathodoluminescence experimental techniques have identified many previously unobserved spectral characteristics in $U_xTh_{1-x}O_2$ compounds grown using a slow growth hydrothermal method. Three $U_xTh_{1-x}O_2$ (x = 0.00, 0.01, 0.22) hydrothermally grown, single crystals were examined using cathodoluminescence. Unique luminescence features were identified as a function of uranium concentration. In the undoped and x = 0.01 $U_xTh_{1-x}O_2$, an electronic phase transition is observed as a 20 nm (0.21 eV) red-shift in the wavelength of maximum emission. This red-shift appears when the crystals are heated during both 5 and 10 keV electron beam irradiation. Conversely, a similar phase transition is not observed in the $U_xTh_{1-x}O_2$ alloy (x = 0.22). Instead, the wavelength of maximum emission remains constant at 305 nm (4.07 eV). Ultimately, the addition of uranium to the ThO_2 lattice increases the band gap of the material which is identified as a 10 nm (0.13 eV) blue shift if the luminescence. Finally, a quadrupole transition is observed in the uranium-containing crystals (O 2p to U 5f) at approximately 600 nm (2.07 eV).

Monday Afternoon, November 10, 2014

Actinides and Rare Earths Focus Topic
Room: 301 - Session AC+AS+MI+SA+SS-MoA

Theoretical Modeling of f Electron Systems
Moderator: Ladislav Havela, Charles University, Czech Republic

2:00pm **AC+AS+MI+SA+SS-MoA1 Nonmagnetic Ground State of PuO₂**, *Jindrich Kolorenc*, Academy of Sciences of the Czech Republic **INVITED**

The correlated band theory implemented as a combination of the local density approximation with the dynamical mean-field theory is applied to PuO_2. We obtain an insulating electronic structure consistent with the experimental photoemission spectra, and a nonmagnetic ground state that is characterized by a noninteger filling of the plutonium f shell ($n_f \approx 4.4$). Due to a sizable hybridization of the f shell with the p states of oxygen, the ground state is more complex than the four-electron Russell–Saunders $^5I_4$ manifold split by the crystal field. The dynamical mean-field theory, which in the present case can be schematically viewed as an extension of the crystal-field model with hybridization terms, improves the agreement between the theory and experiment for the magnetic susceptibility [1]. Encouraged by the good accuracy achieved for PuO_2, we apply the theory to several other tetravalent actinide oxides.

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2:40pm **AC+AS+MI+SA+SS-MoA3 DMFT Modeling of Electronic Spectral Properties in Pu-based Actinides**, *Jian-Xin Zhu*, Los Alamos National Laboratory **INVITED**

Plutonium-based materials have been studied for many years due to their importance in nuclear energy applications. Scientifically, these materials exhibit highly complex properties. Pu metal shows a significant volume expansion and anomalous magnetic properties; while Pu-115 (like $PuCoGa_5$) are found to be superconductors. These intriguing phenomena originate from the special location of Pu in the Periodic Table, which is at the boundary between the light actinides that have itinerant 5f electrons and the heavy actinides with localized 5f electrons. They call out the notion of strong correlation of 5f electrons. In this talk, I will present a study of the electronic structure of Pu metals and its 115 compounds in the framework of the combination of local density functional approximation and dynamical mean-field theory. In particular, the results on momentum-resolved spectral functions will be presented and be compared with those based on the LDA only. In addition, the effect of Pu 5f electron occupancy on the electronic structure of these systems will also be discussed. The test of these results by future angle-resolved photoemission spectroscopy measurements will give a stringent constraint on the theoretical approach.

3:40pm **AC+AS+MI+SA+SS-MoA6 The Evolution in Pu Nanocluster Electronic Structure: From Atomicity to Three-Dimensionality**, *James Tobin, S.W. Yu, B.W. Chung*, Lawrence Livermore National Laboratory, *M.V. Ryzhkov*, Russian Academy of Science-Urals, *A. Mirmelstein*, Russian Federation Nuclear Lab (VNIITF)

The development of electronic structure in solid systems as a function of size has long been a subject of great interest and extensive scientific investigation. Experimentally, the transition, from nanoscale or mesoscopic to bulk behavior in metal clusters, was reported in 1981 by Mason and co-workers. Similarly, the evolution from two-dimensional to three-dimensional band structure in metal overlayers and the manifestation of nanoscale effects in compound semiconductor have also observed. In the area of actinide materials, the progress has been slowed by the limitations imposed by the highly radioactive, chemically toxic and pyrolytic nature of these materials. Havela and Gouder and colleagues performed investigations upon Plutonium (Pu) ultra-thin films, deposited in situ by means of a discharge-plasma, and Trelenberg and co-workers developed an approach using laser ablation of Uranium (U). Gas phase studies of actinides have also been pursued including atoms, molecules and reactions. Recent theoretical studies include UO_2 molecules, solid actinide oxides, and actinide carbide clusters. A new approach to cluster calculations has been taken in this study. Past cluster calculations were arranged in such a way that the central atom would exist in a bulk like environment. In calculations herein, it is expected that the central atom will be in the most bulk-like environment as well. However, just as in any finite size object, there will be variation of potential at the positions of symmetry non-equivalent atoms within the simulated cluster. Hence, averaging over all of the atoms in the cluster will give a measure of the effect of size. We will use this aspect of

cluster calculations to investigate size related effects. Here, we report the result of the calculation of the electronic structure of clusters of Pu and their comparison to bulk spectroscopic results. Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract No. DE-AC52- 07NA27344. Work at the RAS and VNIITF was supported in part by Contract B590089 between LLNL and VNIITF. The Advanced Light Source (ALS) in Berkeley and the Stanford Synchrotron Radiation Laboratory are supported

by the DOE Office of Science, Office of Basic Energy Science. For more detail see:M.V. Ryzhkov, A. Mirmelstein, S.-W. Yu, B.W. Chung and J.G. Tobin, "Probing Actinide Electronic Structure through Pu Cluster Calculations," Intl. J. Quantum Chem. **113**, 1957 (2013); COVER ARTICLE .

4:00pm **AC+AS+MI+SA+SS-MoA7 First-Principles Density Functional Theory Simulation on Rare-Earth-Based Oxides as Fast Oxygen Ion Conductors**, *Mamoru Sakaue, M. Alaydrus, H. Kasai*, Osaka University, Japan, *T. Ishihara*, Kyushu University, Japan

Development of novel fast ion conductors is a crucial issue for realizing solid oxide fuel cells (SOFCs) which can operate in low temperatures. While yttria-stabilized zirconia (YSZ) had been well-studied both by experiments and theories, exploration of other types of materials retaining high ionic conductivities in lower temperatures is still desired. Experimental studies in the recent twenty years have found some rare-earth-based oxides having higher ionic conductivities to be promising for operation below 600°C, and first-principles simulation studies on the materials have begun.

We studied atomic and electronic properties on oxygen-ionic conduction of $LaGaO_3$-, La_2GeO_5-, Pr_2NiO_4- and CeO_2-based materials by first-principles calculations based on density functional theory (DFT). We analyzed stable structures, electronic densities of states, oxygen migration paths and activation energies in the paths of pure and doped materials in order to evaluate their capabilities in application to electrolytes or electrodes. The obtained results of the activation energies showed good agreements with experiments in several aspects. However, for Pr_2NiO_4- and CeO_2-based materials that contain lanthanoid elements, there remains an open question about theoretical treatment of $4f$ electron states. The strong localization was found to affect oxygen ion motions fundamentally as well as electronic/magnetic properties. Then the strong electron-electron correlation modifies simple trends in activation energies found for the lanthanoid series within an approximation in which the correlation effects were neglected [1].

While fundamental reproduction of the strong electron-electron correlation in localized states by DFT is extremely difficult, empirical corrections by Hubbard U terms enable a practical solution to this problem. Here, the U value can be determined only by comparison with experiments in most cases because the value is affected by environment of the lanthanoid atoms. However, a theoretical study based on an empirical model demonstrated that the environment effects on $4f$ orbitals can be small if its strong localization is maintained [2]. In the presentation, we confirm this rule based on the results by the DFT first-principles calculations with Hubbard U corrections and discuss possibilities of computational materials design of lanthanoid-doped ceria ($Ce_{1-x}Ln_xO_{2-x/2}$) as electrolyte materials.

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4:20pm **AC+AS+MI+SA+SS-MoA8 Electronic Structure, Magnetic Properties, and Magneto-Structural Transformations of Rare Earth Magneto-Caloric Materials**, *Durga Paudyal*, Ames Laboratory, *V.K. Pecharsky, K.A. Gschneidner, Jr.*, Ames Laboratory and Iowa State University **INVITED**

We present first principles modeling of structural and magnetic properties of Gd_5Ge_4 based magneto-caloric materials. The total energy as a function of the shear displacement of slabs confirms stability of experimentally observed crystal and magnetic structures. Small substitutions of the Gd by Y and Lu lead to a catastrophic loss of ferromagnetism, but the substitutions by La have no effect on the magnetism. Furthermore, substitutions of the Ge by Si exert chemical pressure and transform the antiferromagnetic O(II) to the ferromagnetic O(I) ground state. In addition, we present a pathway for estimating the magnetic entropy change in the room temperature giant magnetocaloric compounds, i.e. $Gd_5Si_2Ge_2$, by coupling first principles outputs with the established magneto-thermodynamic models. The theoretical values of the magnetic entropy change compare well with experimental results.

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.

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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 U236 presents a special case because of interference from the U235 hydride ion that is removed by peak-stripping. The effect of the hydride on the uncertainty in the U236 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 U236 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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