Monday Morning, October 28, 2013

Actinides and Rare Earths Focus Topic
Room: 102 C - Session AC+MI+SA+TF-MoM

Actinides and Rare Earths: Experiment and Electron Correlation
Moderator: T. Durakiewicz, Los Alamos National Laboratory

8:20am AC+MI+SA+TF-MoM1 Our Understanding of the Condensed-Matter Physics of Actinides: What have we Learned in 50 Years?, *G. Lander*, ITU, Karlsruhe, Germany **INVITED**
By 1950 the Manhattan Project and the early nuclear industry had a large legacy of new materials that were poorly understood from a physics perspective. The physics of uranium and plutonium are good examples.

By the mid-1960s progress had been made in applying many physical techniques (many of which, such as sensitive transducers to measure elastic constants, had also been a development of WW II) on the actinide elements and many of their compounds, particularly the simple dioxides. Most theoretical treatments considered the elements and their metallic compounds within the framework of d transition-metals, as many properties seemed to follow these metals, rather than those of the $4f$ lanthanide series.

By the mid-1970s the group at Argonne National Laboratory had shown, *inter alia*, that a large orbital moment existed in the actinides even if many properties followed itinerant-electron behavior, and the first band-structure calculations showed how difficult it was to resolve this dichotomy.

The discovery of so-called heavy-fermion superconductors, such as UBe_{13}, at Los Alamos National Laboratory in the early 1980s brought considerable prominence to the field and was a precursor, although not recognized at the time, to the discovery of high-T_c materials in 1986. The further discovery (in 2001) of superconductivity at 18 K in $PuCoGa_5$, also at Los Alamos, shows the key importance of the electronic ground state of the $5f$ electrons and how this drastically affects the physical properties.

Theory has always been "behind" experiments in the actinides; however, the experimental results have proved a sensitive test to the most advanced electronic-structure calculations, such as dynamical mean-field theory (DMFT) within the local-density approximation, so that in some respects the actinides have become a "test bed" for the newest theoretical models.

60 years after some of the pioneering condensed-matter experiments on these materials, we have a far better picture of the actinides, the importance of the orbital moments, the relevance of intermediate coupling, and the criterion that determine whether the $5f$ states behave as localized or itinerant. However, we do not have *predictive* theories – they are all *reactive*. This implies that we still need to maintain an experimental capability, as these materials will be with us a very long time, even if we abandon nuclear energy.

The challenge today is how to maintain and nurture that experimental capability in a climate where even depleted uranium is regarded with suspicion and its handling demands kilograms of paperwork? Without experiments will theory follow?

9:00am AC+MI+SA+TF-MoM3 5f Electron Localization, *J.L. Smith*, Los Alamos National Laboratory **INVITED**
The light actinide elements show a large number of crystal structures and low-melting points. At the element americium, this $5f$-electron series finally settles down and looks like the rare-earth series. This occurs because the $5f$ electrons have ceased to form energy bands and have localized. The superconductivity of americium proved this. I will review how the tug of war between itinerant and localized behavior leads to all of the interesting properties and touch on such things as quantum critical points. This has impact on the understanding of the other long rows in the periodic table.

9:40am AC+MI+SA+TF-MoM5 Historical Aspects and Perspectives of X-Ray Spectroscopy in Lanthanide and Actinide Materials, *G. Kaindl*, Freie Universität Berlin, Germany **INVITED**
The talk addresses some aspects in the use of tunable x-rays in studies of electronic and magnetic properties of lanthanide and actinide materials by x-ray absorption fine-structure (XANES) and resonant elastic x-ray scattering (REXS), emphasizing related features of these 4f and 5f materials.

Based on early applications of L- and M-edge XANES to lanthanide valence studies, the method was applied to U and Th compounds, exploring XANES at various thresholds (L, M, N, O) [1], and then to the more radioactive actinides Np, Pu, and Am as well as to high-pressure studies. Subsequently, the method has been improved both experimentally (e.g. high-resolution XANES [2]) and theoretically [3], and even compounds of Pa, Cm, and Cf in solid and aqueous environments have been investigated by now.

Resonant magnetic x-ray scattering was first applied to Ho metal, where the magnetic scattering cross-section is enhanced by a factor of 50, when the x-ray energy is tuned across the L_{III} absorption edge of Ho [4]. Subsequently, much larger enhancements up to 5 magnitudes were observed at the M_V edges of U in UAs [5] and of Eu in the antiferromagnetic (AFM) semiconductor EuTe [6]. In the latter, an epitaxial thin EuTe(111) film was studied, and virtually background-free magnetic Bragg-peaks with pronounced Laue oscillations were found. From these, the AFM order in the EuTe(111) film could be derived with atomic-layer resolution. The magnetization of the outermost layer was found to decrease significantly stronger with temperature than that of the bulk layer [6]. In a further pioneering experiment that employed a synchrotron slicing source for the production of tunable soft x-rays with pulse widths as short as 100 fs (probe pulses) and synchronized pump pulses of 400 nm wavelength, the dynamics of the AFM order could be studied by fs soft x-ray diffraction [7].

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11:00am AC+MI+SA+TF-MoM9 High Energy Resolution X-ray Spectroscopy of f-electron Systems, *K.O. Kvashnina*, European Synchrotron Radiation Facility (ESRF), France, *J.G. Tobin*, Lawrence Livermore National Laboratory
This contribution will provide an overview of the possible spectroscopic techniques and experiments that become available for f-electron systems using high energy resolution X-ray emission spectrometer[1]. As an example we will show the studies of the electronic structure of cerium (Ce) and uranium (U) nanostructured materials by means of high energy resolution fluorescence detection (HERFD) and resonant inelastic X-ray scattering (RIXS) via transitions between core levels and between core and valence levels[2–5]. The experimental spectral features will be characterized using a variety of theoretical codes including the LDA+U approximation within DFT[6], atomic multiplet theory[7] and full multiple scattering FEFF[8].

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11:20am AC+MI+SA+TF-MoM10 Signatures of the γ - α Volume Collapse in Cerium, *M.J. Lipp*, Lawrence Livermore National Laboratory

INVITED

High-pressure x-ray emission measurements of the $L\gamma_1$ (L_2N_4) emission line were used to decide the longstanding debate over the nature of the famous iso-structural (γ-α) volume collapse at 0.75 GPa in elemental cerium that ends in a critical point at 1.5 GPa and 480 K. The satellite structure of this line offers direct access to the total angular momentum observable $<J^2>$ as shown by extended local atomic model calculations and experiences a 30% step-like decrease across the volume collapse. This validates the Kondo model in conjunction with previous measurements of the equation of state at high temperature that were also well fit by the Kondo volume collapse model plus a quasiharmonic representation of the phonons - but could also be reproduced within the Hubbard-Mott framework. The remaining satellite in the α -phase after the volume collapse does not change significantly over the pressure range studied. Direct comparison is made with previous predictions by dynamical mean field theory.

Monday Afternoon, October 28, 2013

Actinides and Rare Earths Focus Topic
Room: 102 C - Session AC+MI+SA+TF-MoA

Actinides and Rare Earths: Theory and Electron Correlation
Moderator: L. Havela, Charles University, Czech Republic

2:00pm AC+MI+SA+TF-MoA1 Structural and Electronic Relationships Between the Lanthanide and Actinide Elements, *B. Johansson*, Uppsala University, Sweden **INVITED**
The similarity and difference between the solid state properties of the 4f and 5f transition

metals are pointed out. The heavier 5f elements show properties which have direct

correspondence to the early 4f transition metals, suggesting a localized behaviour of the

5f electrons for those metals. On the other hand, the fact that Pu metal has a 30% lower

volume than its neighbour heavier element, Am, suggests a tremendous difference in the

properties of the 5f electrons for this element relative to the heavier actinides. This change

in behaviour between Pu and Am can be viewed as a Mott transition within the 5f shell

as a function of the atomic number Z. On the metallic 5f side of the Mott transition (i.e.,

early actinides), the elements show most unusual crystal structures, the common feature

being their low symmetry. An analogous behaviour for the lanthanides is found in cerium

metal under compression, where structures typical for the light actinides have been observed

experimentally. A generalized phase diagram for the actinides is shown to contain features

comparable to the individual phase diagram of Ce metal. The crystal structure behaviour of

the lanthanides and heavier actinides is determined by the number of 5d (or 6d) electrons

in the metallic state, since for these elements the f electrons are localized and nonbonding.

For the earlier actinide metals electronic structure calculations – where the 5f orbitals

are treated as part of the valence bands – account very well for the observed ground state

crystal structures. The distorted structures can be understood as Peierls distortions away

from the symmetric bcc structure and originate from strongly bonding 5f electrons occupying

relatively narrow 5f states.

2:40pm AC+MI+SA+TF-MoA3 Signature of Strong Correlations in Actinides and its Compounds: A Dynamical Mean Field Theory Perspective, *G. Kotliar*, Rutgers University **INVITED**
Plutonium is a unique element, poised at the edge of a localization delocalization transition. Its compounds exhibit

remarkable phenomena, ranging from insulating behavior with a topologically non trivial band structure in PuB6 [1]

to high temperature superconductivity PuCoGa5 [2].

In the last decade a new paradigm for understanding, modeling and predicting physical properties of these materials

has emerged based on realistic implementations of dynamical mean eld theory (DMFT) concepts [3][8] [9]. This theory

treats the wave (band-like) and the (particle-like) multicon gurational multiplet aspects of the f-electrons on the same

footing. This theory accounts for the volume of δ Pu in a paramagnetic con guration [6] and predicted its phonon

spectra [7].

In DMFT, an underlying self consistent impurity model can be used to reconstruct local observables of a material.

An illustrative example is the valence histogram, describing the weight of each atomic con guration in the ground

state of the solid. This important concept, and the resulting prediction for Pu can now be probed experimentally

using resonant XES [5] and neutron form factor measurements [11].

There are now many applications by many groups which have extended the reach of this approach to many actinide

based compounds. We will review the basis of the DMFT approach and compare some results with selected experiments

on 5f electron system. We will conclude with some new directions to face the challenge for material design in this

eld [10].

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3:40pm AC+MI+SA+TF-MoA6 Towards a Better Understanding of Low-Energy Excitations in Heavy-Fermion Systems, *G. Zwicknagl*, Technische Universität Braunschweig, Germany **INVITED**
Metals containing lanthanide or actinide ions have been at the focus of interest in condensed matter physics during the past decades. The presence of the partially filled f-shells leads to unexpected "anomalous" behavior such as heavy fermions, unconventional superconductivity, unusual magnetism as well as their co-existence.

The f-electron systems lie at the intersection of a large number of long-standing problems in the physics of metals. In metals containing ions with partially filled inner shells, we immediately face the fundamental question which picture provides the better starting point for theoretical models, a delocalized description in terms of energy bands or a localized representation which accounts for the atomic properties. The answer to the question which of the above-mentioned pictures is the appropriate starting point seems to depend on the physical quantities under consideration. This fact is a consequence of electronic correlations which prevent to describe the influence of the f-states over the entire temperature and energy range in terms of a unique simple model. While the high-temperature (high-energy) properties of lanthanide compounds can be understood in terms of localized f-moments it is generally accepted by now that the f-electrons should also be described in within a band picture as delocalized states as far as the low-energy excitations are concerned.

Concerning the underlying microscopic picture, it is generally accepted that the formation of strongly renormalized 4f-bands in lanthanides is a consequence of the Kondo effect where the degrees of freedom of the 4f-shell form a collective singlet ground state with the conduction electrons. The Kondo model, however, does not apply to actinide compounds where the situation is more complex. In some compounds, experiments suggest the co-existence of both localized atomic-like 5f-degrees of freedom with itinerant 5f-band states at low temperatures/ low energies. Microscopic model calculations suggest that partial localization of 5f-electrons may result from the intra-atomic Hund's rule-type correlations.

In the present talk, I shall give an overview over our present understanding of the "Dual Nature" of f-electrons. I present recent results on the suppression of the Kondo state in YbRh$_2$Si$_2$ [1]. I discuss microscopic

calculations for electron spectroscopies in actinide compounds emphasizing the consequences of strong intra-atomic correlations of the 5f -shell [2,3].

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[2] Gertrud Zwicknagl, MRS Online Proceedings Library, Volume 1444, (2012)

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4:20pm **AC+MI+SA+TF-MoA8 Electronic Structure of EuO under Pressure**, *L. Petit*, *D. Szotek, M. Lueders, W.M. Temmerman,* Daresbury Laboratory, UK, *A. Svane*, Aarhus University, Denmark

We present results of an ab-initio study of EuO under pressure. The calculations are based on a first-principles methodology that adequately describes the dual character of electrons, itinerant versus localized by correcting for the unphysical self-interaction that underpins the local spin density approximation. We find that EuO, which at ambient conditions crystallizes in the NaCl structure, undergoes an isostructural insulator to metal transition around 35 GPa. The transition is associated with a change in the ground state valency configuration from $Eu^{2+}(f^7)$ to $Eu^{3+}(f^6)$. At even higher pressure we observe a transition to the CsCl structure. The ground state valency configuration remains Eu^{3+}, i.e. this latter transition is isovalent. We compare our results to a recent experimental investigation that postulates a reentrant valence transition to a nearly divalent Eu^{2+} configuration at high pressures.

Tuesday Morning, October 29, 2013

Actinides and Rare Earths Focus Topic
Room: 102 C - Session AC+AS+SS-TuM

The Surface Science of Actinides and Rare Earths
Moderator: D. Shuh, Lawrence Berkeley National Laboratory

8:00am **AC+AS+SS-TuM1 From Berkeley to Bristol: Defect Structures in Actinide Oxides**, *G.C. Allen*, University of Bristol, UK **INVITED**

The first generation of British gas-cooled reactors used natural uranium metal as fuel but UO_2 is far and away the most important fuel in use today. It is in fact the first in a complex family of oxides, initially based on the fluorite UO_2 unit cell (U_4O_9 and U_3O_7) but giving way to layered-type oxides as the O/U ratio increases (U_3O_8 and UO_3). Oxidation in UO_2 is known to occur via accumulation of point oxygen interstitials and defect aggregates such as Willis, cuboctahedral and split-interstitial clusters. Spectroscopic evidence is used to demonstrate that the link between defect clusters and the U_4O_9 and U_3O_7 structures can be rationalised in terms of multiple Willis, cuboctahedral and split-interstitial clusters. DFT models have been used to examine the stability of different defect clusters in UO_2 supercells. The formation energy of each cluster is calculated along with the variation of their concentrations with increasing the temperature. All interstitial clusters are found to be charge compensated by U^{5+} ions, suggesting this is the highest uranium oxidation state reached amongst the fluorite based structure.

8:40am **AC+AS+SS-TuM3 Covalent Interactions in Metal Oxides**, *P.S. Bagus*, University of North Texas, *E.S. Ilton*, Pacific Northwest National Laboratory, *C.J. Nelin*, Consultant

The covalent character of ionic metal compounds, in particular oxides, may lead to substantial departures from nominal oxidation states. [1, 2] Since this covalent character changes the effective charge of the cation, it contributes to the chemical and physical properties of these compounds. We present a new and novel method of determining the degree of the covalent mixing by projection of cation and ligand orbitals [2, 3] on the total wavefunctions for clusters used to model the electronic structure of these compounds. An important advantage of this method is that it provides estimates of the uncertainties of the assignments of effective charges to the cations and anions. Such estimates of the uncertainty directly reflect the overlap of cation and anion orbitals and, hence, their potential for chemical bonding; estimates of the uncertainty of charge assignments are not generally available. There is evidence that the properties of the spectra from X-Ray photoemission spectroscopy, XPS, [2] and X-Ray Adsorption spectroscopy, XAS, [4] reflect the extent of the covalent mixing of the cation and anion orbitals. We will consider how the covalent character changes between the initial and final state configurations in these spectroscopies, which arise from the screening of the core-hole, affect the interpretation of the core-level spectroscopies.

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9:00am **AC+AS+SS-TuM4 Historical Perspective on Studies of the Surface Reactivity of Actinides at the AWE, UK**, *D.A. Geeson*, AWE, UK **INVITED**

Actinides play an important role in the business of the AWE.

The corrosion behaviour of uranium- and plutonium-based systems is of particular interest with a view to considering material stability during long-term storage as well as aspects of surface segregation and fundamental electronic structure.

The historical use of modern surface science techniques to investigate many aspects of the actinide gas-solid interface is reviewed with emphasis on the development of in-house capabilities and their adaptation for use in a nuclear environment studying highly hazardous materials. Key conclusions from several aspects of corrosion phenomena are presented together with strategies for continuing studies. Examples are drawn from; the corrosion of uranium in dry and moist atmospheres, the mechanism of initiation of hydriding on uranium surfaces, the oxidation of plutonium alloys, americium segregation in plutonium and inverse photoemission studies of actinide surfaces.

AWE's engagement with the wider UK and international community, as part of a broad strategy to collaboratively support our work in areas of more novel aspects of actinide surface phenomena, is described.

The discussion concludes with consideration of the future direction of studies at AWE supported by the provision of enhanced capabilities to explore surface and bulk phenomena.

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11:00am **AC+AS+SS-TuM10 Exploring Plutonium Electronic Structure Using a Unique Photoemission Capability**, *J.J. Joyce*, Los Alamos National Laboratory **INVITED**

The understanding of complex materials has made remarkable advances in recent years. Much of this understanding has been realized through new spectroscopy capabilities at synchrotron facilities. While the vast majority of materials can take advantage of public synchrotrons, transuranic materials are excluded when multiple containment barriers are incompatible with the chosen spectroscopy. Photoemission requires no physical barrier between photons, sample surface and the electron analyzer, thus photoemission on Pu materials is generally not allowed at public synchrotrons.

The Laser Plasma Light Source has been developed at Los Alamos for transuranic photoemission. Using several different variants of photoemission we have explored a range of Pu materials which has lead to a significant improvement in our understanding of transuranic electronic structure. Examples of these successes will be given along with details of the unique facility. Using the capabilities of our transuranic photoemission system we exploit opportunities in angle-resolved photoemission (ARPES) providing insight into the details of both the energy and crystal momentum for a material. Additional information is obtained using tunable photons used to isolate the 5f electron contribution to the valence electronic structure. Between ARPES and tunable photoemission, we construct a fairly detailed picture of the bonding and hybridization for transuranic materials. By adding temperature-dependent photoemission to the experimental tools, we cross over phase transition boundaries as well as quantify electron-phonon coupling. We also have the capability for 1.5 and 3 keV core-level spectroscopy using a monochromatized x-ray source.

By combining the above photoemission tools with a variety of surface preparation capabilities including cleaving, laser ablation, and thermal desorption, we have a flexible photoemission facility that provides unique insight into the electronic structure of transuranic materials. We will show photoemission results for $PuCoGa_5$, $PuCoIn_5$, PuO_2, PuTe and Pu metal that span the range of materials from Mott insulators to heavy fermion superconductors. The latest developments in Pu electronic structure combine a multivalent configuration for Pu with ongoing efforts to quantify the localized/delocalized 5f electron boundary. We will discuss details of Pu electronic structure in light of both valence configurations and localization.

Work supported by the U.S. DOE Basic Energy Science, Materials Sciences and Engineering; LANL LDRD program, and Science Campaign 2.

Actinides and Rare Earths Focus Topic
Room: 102 C - Session AC+AS+EN-TuA

Actinides and Rare Earths: The Nuclear Fuel Cycle and Critical Materials
Moderator: L. Petit, Daresbury Laboratory, UK

2:00pm **AC+AS+EN-TuA1 Prospects for Accident Tolerant Fuels in Light Water Reactors**, *S.J. Zinkle*, K.A. Terrani, L.L. Snead, Oak Ridge National Laboratory **INVITED**
Further enhancement of safety margins in current and next generation commercial fission reactors in general requires an integrated engineering systems design approach. However, tangible gains in safety margin (and performance) may be achievable by utilizing one or more materials science modifications to the fuel system. In this paper the specific attributes of what would constitute *accident tolerant* (or *enhanced safety margin*) fuels will be presented. There are four key metrics to be considered for such a fuel under transient accident conditions: reduced enthalpy production, reduced hydrogen production, improved resistance to clad ballooning and rupture (maintaining coolability of the core), and suppressed fission product release. There are a variety of materials science approaches that can be considered to address one or more of these four metrics for accident tolerant fuels, ranging from relatively incremental modifications to the cladding material to dramatic alternatives to the historical monolithic UO_2 ceramic fuel pellets surrounded by seamless Zr alloy tubing. For example, solute modifications and/or highly adherent coatings that improve the high temperature steam oxidation resistance of Zr alloy cladding would directly lead to reduced enthalpy and hydrogen production. For extended high temperature transient conditions, deployment of high thermal-creep strength, oxidation-resistant cladding (e.g. advanced steels, coated molybdenum, or SiC/SiC) would maintain the coolant channel geometry and significantly suppress the rate of enthalpy and hydrogen production in the core compared to current Zr alloy cladding. This will effectively delay the threshold for fission product release from the fuel while providing longer time periods for emergency core cooling systems to become activated to halt core degradation processes. In addition, the critical heat removal limit in the core to prevent severe degradation would be lowered. Utilization of microencapsulated fuel forms (i.e., triple-encapsulated fuel kernels) within a high thermal conductivity matrix (i.e. SiC) would reduce the stored energy under normal operating conditions compared to standard fuels, resulting in suppressed fuel temperature increase under loss of coolant accident conditions that could limit fuel cladding ballooning and burst. Improved fission product retention within the fuel during high temperature accidents would also be anticipated. This presentation will review several potential fuel system options and outline key feasibility challenges that need to be resolved, along with briefly discussing potential impact on reactor neutronics and overall electricity production costs.

2:40pm **AC+AS+EN-TuA3 Photoelectron Spectroscopy Study of Uranium Materials**, *S. Fujimori*, Japan Atomic Energy Agency, Japan **INVITED**
Electronic structure of uranium materials have been studied by means of photoelectron spectroscopy (PES) as well as angle-resolved PES (ARPES) using synchrotron radiations. The results on the nuclear fuel material UN as well as uranium heavy Fermion superconductors UPd_2Al_3 will be presented.

Uranium monoride (UN) is a promising fuel material for the generation-IV advanced nuclear reactors since it has high melting point, a very good thermal conductivity at high temperatures as well as a high fuel density. We have revealed its electronic structure by ARPES, and found that they are well explained by the band structure calculation based on local density approximation (LDA) [1].

UPd_2Al_3 is a heavy Fermion superconductor. It shows transitions into the antiferromagnetic phase at T_N=14 K and into the superconducting phase at T_{SC}=2 K. Since U 5f electrons in these compounds show both pronounced localized and delocalized characters, the nature of U 5f electrons have been not well understood. Their detailed electronic structure was derived by ARPES by synchrotron radiation as well as very high resolution PES by leaser. It was found that quasi-particle bands with strong U 5f character form Fermi surface at low temperatures, suggesting that U 5f electrons have itinerant nature in this compound. Furthermore, we have succeeded to observe the superconducting gap of this compound by PES [2]. This is the first observation of the superconducting states of actinide materials by PES.

[1] Shin-ichi Fujimori *et al.*, Phys. Rev. B **86**, 235108 (2012).

[2] Y. Ohta *et al.*, in preparation.

4:00pm **AC+AS+EN-TuA7 Interaction of γ-U alloys with Hydrogen**, *L. Havela*, I. Tkach, S. Maskova, Z. Matej, Charles University, Czech Republic, *N.-T.H. Kim-Ngan*, Pedagogical University Cracow, Poland, *A.V. Andreev*, Academy of Science of the Czech Republic
Uranium metal absorbs H readily at low pressures, forming a fine highly pyrophoric powder of β-UH_3, which is ferromagnetic with $T_C \approx$175 K. More technologically important than the orthorhombic α-U is the *bcc* γ-U, known as existing at high temperatures or stabilized by doping to low temperatures.

In the course of the study of fundamental properties of Mo-stabilized *bcc* U alloys [1] we have been testing their resistance to H. There was no interaction with H_2 at ambient pressure and room temperature. However, increasing pressure over approx. 4 bar a slow hydrogenation was observed after several days if incubation. Increasing the H_2 pressure makes the hydrogenation faster. The product, in which the H concentration corresponds to the 1U-3H ratio, does not turn into powder, but consist of large brittle fragments with metallic luster. X-ray diffraction indicates that the hydride is amorphous, with a basic structure pattern corresponding to β-UH_3, while the grain size is ≈1 nm only.

The hydrides obtained were subjected to studies of magnetic properties, electrical resistivity, and specific heat. The most striking fact is that the Curie temperature can be higher than in β-UH_3. It reaches T_C = 200 K for $UH_3Mo_{0.18}$, for both lower and higher Mo concentrations it weakly decreases. Also the magnetization values increase from 0.93 μ_B/f.u. to 1.2 μ_B/f.u. (both in μ_0H = 14 T). At low temperatures a striking high coercivity, reaching 4 T, is seen from magnetization loops. It can be understood as due to a high anisotropy randomly distributed over spatial directions.

The Sommerfeld coefficient of electronic specific heat γ = 29.2 mJ/mol K^2 is similar to β-UH_3 values (29-33.2 mJ/mol K^2 by various authors) and higher that pure $UMo_{0.18}$ (18.8 mJ/mol K^2). Electrical resistivity exhibits the weakly negative slope known from the *bcc* U-Mo alloys [2] and other strongly disordered systems with a cusp-like anomaly at 200 K superimposed. The absolute values about 1 mΩcm are about an order of magnitude higher than for $UMo_{0.18}$, and even higher than that of UH_3, which exceeds 600 μΩcm at room T [3]. The most surprising fact is that the 5f magnetism, which is normally suppressed by disorder, is supported in the case of UH_3Mo_x, probably due to enhanced U-U spacing due to Mo included in the lattice.

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4:20pm **AC+AS+EN-TuA8 The Effect of U and Fe Cations on the Reduction of CeO_2 for Thermal Water Splitting to Hydrogen**, *Y. Al Salik*, SABIC, Saudi Arabia, *I. Al Shankiti*, SABIC and University of Colorado, *H. Idriss*, SABIC, Saudi Arabia **INVITED**
Thermal water splitting to hydrogen on reducible materials is one of the promising methods to secure renewable energy vectors for the future. the process relies on a redox cycle whereby steam is introduced to a prior reduced CeO_2 to generate hydrogen which is consequently oxidized. However to achieve this cycle CeO_2 needs be reduced at elevated temperatures (> 1500ºC) [1, 2]. Mixing CeO_2 with metal cations can lower the energy needed for the reduction process. Among the methods of changing CeO_2 are the incorporation of metal cations smaller in size than Ce^{4+} cations such as Zr^{4+} [3] or the addition of a metal cation that can transfer electrons to Ce^{4+} [4, 5]. In this work we present a core and valence level study of the extent of reduction of Ce^{4+} cations by the addition of Fe and U cations. We compare XPS Ce3d, Ce4d of stoichiometric CeO_2 to those of $Ce_xFe_{1-x}O_2$ and $Ce_xU_{1-x}O_2$ (x<1). We also investigate the reduction of these materials upon Ar ions sputtering. We find that the addition of Fe or U cations in any proportions increases the reduction of Ce^{4+} cations. In particular considerable enhancement of the reduction of CeO_2 with Ar ions was noticed (compared to CeO_2 alone) when x>0.5 in both $Ce_xFe_{1-x}O_2$ and $Ce_xU_{1-x}O_2$ series of the oxide materials. The reasons for the enhancement of CeO_2 reduction by Fe cations can be linked to both size and electron transfer effect while in the case of U cations it is mainly due to electron transfer from the U5f to Ce4f levels. Tests for hydrogen production by thermal water splitting for both series were conducted and indicated the enhancement of the activity of the mixed oxide when compared to CeO_2 alone.

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5:00pm AC+AS+EN-TuA10 Soft X-ray Investigations of Covalent Orbital Mixing in Metal Oxides, *S. Minasian*, Lawrence Berkeley National Lab (LBNL), *J. Keith, E. Batista, K. Boland*, Los Alamos National Lab (LANL), *J. Bradley*, Lawrence Livermore National Laboratory (LLNL), *S. Daly*, George Washington Univ., *S. Kozimor*, LANL, *W. Lukens*, LBNL, *R.L. Martin*, LANL, *D. Nordlund*, SLAC National Accelerator Lab, *G. Seidler*, Univ. of Washington, *D. Shuh*, LBNL, *D. Sokaras*, SLAC National Accelerator Lab, *T. Tyliszczak*, LBNL, *G. Wagner*, LANL, *T.-C. Weng*, SLAC National Accelerator Lab, *P. Yang*, Pacific Northwest National Lab

Developing a clear understanding of how metal oxide electronic structure changes for a range compounds and materials will greatly benefit a variety of existing and emerging energy technologies. Many of the technologically desirable chemical, magnetic, electronic, and thermal properties of metal oxides are derived from strongly covalent metal–oxygen multiple bonds (metal oxos). Among approaches explored previously, ligand K-edge X-ray absorption spectroscopy (XAS) has emerged as an effective method for quantitatively probing electronic structure and orbital mixing. The presence of covalent mixing is observed as a pre-edge feature in the ligand K-edge XAS, which only has transition intensity if the final state metal orbital contains a component of ligand p orbital character. Recent advances have shown that insights regarding the nature of orbital mixing in metal oxides can be obtained at the K-edge for oxygen through a combination of XAS with a scanning transmission X-ray microscope (STXM), non-resonant inelastic X-ray scattering (NIXS), and hybrid density functional theory calculations (DFT). The spectroscopic work in this study was performed at the ALS Molecular Environmental Sciences beamline 11.0.2 (STXM), beamline 6.2 at SSRL (NIXS), and the LERIX facility at the APS (NIXS).

Herein, a new effort is discussed that employs these techniques to understand bonding interactions in d- and f-block oxides. Oxygen K-edge XAS measurements and DFT studies began with a series of six tetrahedral oxyanions, MO_4^{2-} and MO_4^{1-} (M = Cr, Mo W and Mn, Tc, Re). Despite the similarities of the isoelectronic d^0 MO_4^{2-} and MO_4^{1-} anions, unexpected differences in metal oxo orbital mixing were observed for adjacent metals in the periodic table. The lanthanide dioxides and sesquioxides, LnO_2 and Ln_2O_3 (Ln = Ce, Pr, Tb), were chosen for subsequent work because their electronic structures are well-established from hard X-ray spectroscopies. Features in the O K-edge XAS follow anticipated trends based on 4f and 5d orbital energies and occupancies. Taken together with L_3-edge intensities determined previously, a detailed picture of the electronic structure in lanthanide oxides emerges. Overall, the research shows that orbital composition is influenced by a complex interplay between periodic changes in both orbital energy and radial extension.

5:20pm AC+AS+EN-TuA11 The Microstructure of Cerium Hydride Growth Centres, *M. Brierley, J. Knowles, N. Montgomery*, AWE, UK, *M. Preuss, A. Sherry*, University of Manchester, UK

Considerable work has been undertaken into the hydriding of rare earth metals and actinides [1]; specifically into the reaction rate of various hydrides on the surface of these materials [2]. Cerium is a reactive rare-earth metal and quickly forms a semi-protective oxide layer in air. Upon exposure of an oxide-covered sample to hydrogen, hydride is formed as discrete sites on the surface, often termed 'Growth Centres', which then grow radially across the surface [3]. In the present study, the emphasis was to investigate the microstructure of the cerium growth centres with the intention of understanding any hydriding nucleation and growth mechanisms which may occur. The samples were prepared to 1 μm finish before being exposed to ultra-pure hydrogen at pressures between 10 mbar and 300 mbar, for sufficient time to have nucleated a number of hydride Growth Centres. Post-test analysis was performed using Secondary Ionisation Mass Spectrometry (SIMS), Scanning Electron Microscopy (SEM) and Optical Microscopy (OM) to determine the microstructure of the hydride growth centres. SIMS confirmed that the Growth Centres were comprised of cerium hydride, and that the hydrogen exists specifically within the features. The morphology of individual hydride Growth Centres was examined using OM and SEM and the data reported demonstrates that the hydride-metal interface has a discrete boundary between two distinct phases; a region of deformed metal surrounds the Growth Centres; the microstructure within the Growth Centres indicates that the microstructure of the parent metal was retained by the hydride product.

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