

## Actinides and Rare Earths Focus Topic Room 202C - Session AC+MI+SA-FrM

### Actinide and Rare Earth Theory and Related Measurements

**Moderators:** Paul S. Bagus, University of North Texas, David Shuh, Lawrence Berkeley National Laboratory

8:20am **AC+MI+SA-FrM-1 Periodic Boundary Condition and Embedded Cluster DFT Calculations of Water Adsorption on  $\text{AnO}_2$  ( $\text{An} = \text{U}, \text{Pu}$ ) Surfaces, *Nikolas Kaltsoyannis*, University of Manchester, UK, United Kingdom of Great Britain and Northern Ireland **INVITED****

Over half of the World's stockpile of civil plutonium (c. 126 tonnes) is stored at Sellafield in the UK as  $\text{PuO}_2$  powder in sealed steel cans. There is evidence of gas generation in some of these cans. Many routes to gas production have been suggested, several of which involve complex, interconnected and poorly understood  $\text{PuO}_2/\text{H}_2\text{O}$  interactions.

We have an ongoing project to study computationally the interaction of  $\text{AnO}_2$  ( $\text{An} = \text{U}, \text{Pu}$ ) surfaces with water. Standard periodic boundary condition (PBC) implementations of DFT using generalized gradient approximation (GGA) functionals can fail to reproduce key features of actinide solids, e.g. predicting metallic properties in systems known to be insulating. This failure stems from incorrect description of the strongly correlated 5f electrons, which are overly delocalized by the GGA, and the standard solution to this problem is to correct the GGA functionals with an onsite Coulomb repulsion term known as the Hubbard  $U$ . An alternative solution is to employ hybrid DFT, in which some of the exact exchange energy of Hartree-Fock theory is incorporated into the Hamiltonian. Such functionals typically produce more localized 5f electrons, and recover insulator behavior. They are, however, extremely expensive to employ in PBC calculations, and hence are rarely used. We have therefore sought a model which allows the routine use of hybrid DFT in  $\text{AnO}_2$ /water systems, and have adopted the periodic electrostatic embedded cluster method (PEECM), in which a quantum mechanically treated cluster is embedded in an infinite array of point charges. We treat a cluster of  $\text{AnO}_2$  and adsorbing water molecules using hybrid DFT (PBE0) whilst the long-range electrostatic interactions with the bulk are modelled *via* embedding in point charges.

In this presentation, I shall describe the results of both PBC and PEECM studies of the interactions of water with both stoichiometric and reduced (oxygen vacancy) {111}, {110} and {100} surfaces of  $\text{UO}_2$  and  $\text{PuO}_2$ . The geometries and energetics of single and multiple layers of water will be presented, together with our calculations of water desorption temperatures, from which we propose an alternative interpretation of experimental data.

[1] J.P.W. Wellington, A. Kerridge, J.P. Austin and N. Kaltsoyannis *J. Nuc. Mat.* **482** (2016) 124

[2] B.E. Tegner, M. Molinari, A. Kerridge, S.C. Parker and N. Kaltsoyannis *J. Phys. Chem. C* **121** (2017) 1675

9:00am **AC+MI+SA-FrM-3 Understanding the Role of Oxidation States on the Chemistry of Actinides through Integration of Theory and Experiment, *Wibe de Jong, J Gibson***, Lawrence Berkeley National Laboratory; *R Abergel*, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**  
Fundamental insights into the role of 5f electrons in the redox chemistry of actinides is essential for predicting the fate and controlling the behaviour of nuclear materials in the ecosystem, as well as for developing new advanced applications in energy, medicine and forensics. In recent years computational chemistry has become a key pillar of multidisciplinary actinide research, advancing the fundamental understanding of actinide chemistry through strong synergies between experiment and simulations. We will present some recent multidisciplinary gas-phase thermochemistry and spectroscopy efforts focused on understanding the role of metal-ligand interactions on the oxidation states of actinides across the series.

9:40am **AC+MI+SA-FrM-5 An Experimentalist's Viewpoint: The Tremendous Strengths and Occasional Weaknesses of Actinide Cluster Calculations, *James G. Tobin***, University of Wisconsin-Oshkosh

Over the course of the last several years, cluster calculations have been used in a myriad of ways to analyze spectroscopic results from actinide systems and gain insight into the electronic structure of these actinide systems. For example, the calculated 6d Unoccupied Density of States (UDOS) in Uranium Tetrafluoride and Uranium Diode were probed using U

L3 (2p) X-ray Absorption Near Edge Structure (XANES) as well as U N7 (4d) X-ray Absorption Spectroscopy (XAS). [1-3] Cluster calculations have also been used successfully to study the development from atomic to bulk electronic structure in Pu [4,5] and issues associated with the 2p Occupied Density of States (ODOS) in Uranium Tetrafluoride. [6, 7] However, there now appear to be some interesting discrepancies between what has been observed experimentally and the predictions of cluster theory. In particular, the F 1s XAS of Uranium Tetrafluoride [8] and the U 4d XAS branching ratio (BR) predictions for oxidized uranium. [1] These issues will be addressed in the talk.

### References

[1] J. G. Tobin, S.-W. Yu, C. H. Booth, T. Tyliczszak, D. K. Shuh, G. van der Laan, D. Sokaras, D. Nordlund, and T.-C. Weng, and P. S. Bagus, *Phys. Rev. B* **92**, 035111 (2015).

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[3] A. Yu. Teterin, Yu. A. Teterin, K. I. Maslakov, A. D. Panov, M. V. Ryzhkov, and L. Vukcevic, *Phys. Rev. B* **74**, 045101 (2006).

[4] M. V. Ryzhkov, A. Mirmelstein, S.-W. Yu, B. W. Chung, [c] and J. G. Tobin, *International Journal of Quantum Chemistry* **113**, 1957 (2013).

[5] M.V. Ryzhkov, A. Mirmelstein, B. Delley, S.-W. Yu, B.W. Chung, J.G. Tobin, *Journal of Electron Spectroscopy and Related Phenomena* **194**, 45 (2014).

[6] J.G. Tobin, S.-W. Yu, R. Qiao, W.L. Yang, and D.K. Shuh, "F1s X-ray Emission Spectroscopy of  $\text{UF}_4$ ," *Progress in Nuclear Science and Technology*, submitted 2017.

[7] Elisabeth Thibaut, Jean-Pol Boutique, Jacques J. Verbist, Jean-Claude Levet and Henri Noel, *J. Am. Chem. Soc.* **104**, 5266-5273 (1982).

[8] J. G. Tobin, S.-W. Yu, R. Qiao, W. L. Yang, C. H. Booth, D. K. Shuh, A. M. Duffin, D. Sokaras, D. Nordlund, and T.-C. Weng, *Phys. Rev. B* **92**, 045130 (2015).

10:00am **AC+MI+SA-FrM-6 Ligand and Metal XAS Edges in Heavy Metal Compounds, *Paul S. Bagus***, University of North Texas; *C Nelin*, Consultant

In previous work, [1] it has been shown that the magnitude and character of the covalent mixing in representative lanthanide and actinide oxides depends strongly on the nominal oxidation state of the oxide. In the present work, ab initio theoretical wavefunctions, WF, have been determined and have been used to obtain the energies and dipole intensities for different Near Edge X-Ray Absorption (XAS) Fine Structure, NEXAFS edges. The theoretical NEXAFS spectra have been examined in order to determine the extent to which the features of these edges can be used to infer the character and extent of the covalent bonding. An important and novel feature of the theory is that the angular momentum coupling of the open shell electrons is taken into account and the multiplets, both resolved and unresolved, associated with the various NEXAFS features are identified. Furthermore, different sets of variationally optimized orbitals are used for the initial, ground state, and the final, excited state, configurations. Thus, the relaxation and screening in response to the core-hole are taken into account. The systems examined are Ce(III) and Ce(IV) in  $\text{CeO}_2$  and U(IV), U(V), and U(VI) in  $\text{UO}_2$ . For these systems, cation p and d edges are used to distinguish excitations to the frontier nf and (n+1)d orbitals, especially since it has been shown that both of these cation orbitals have significant covalent mixing with the ligands. The O K-edge NEXAFS is presented and the relative excitation energies and intensities into the cation nf and (n+1)d orbitals are compared to the covalent character of the different systems. The WFs are solutions of the Dirac-Coulomb Hamiltonian. [2] Comparisons are made with experiment to demonstrate the accuracy of the theoretical treatments used.

Support for this work by the Geosciences Research Program, Office of Basic Energy Sciences, U.S. DOE, is acknowledged.

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10:20am **AC+MI+SA-FrM-7 Thermal Expansion and Conductivity of Th and Ac from First Principles Calculations, *Dominik Legut, L Kyvala***, VSB-Technical University of Ostrava, Czech Republic; *U Wdowik*, Pedagogical University, Poland

We investigate electronic structure, lattice dynamics, and thermophysical properties of elemental thorium and made a prediction for actinium as

here the experimental data are scarce. The results were obtained within density function calculations. Recently, Actinium (Ac) shows excellent potential in radiotherapy and Thorium (Th) appears to be a suitable substitution for uranium in novel nuclear fuels. Therefore, we determined the effect of spin-orbit interaction (SOI) for the electronic, elastic, phonon and thermodynamic properties of number of Ac phases (hcp, bcc, fcc, and sc). Similarly, in the case of Th in addition to SOI we investigated also localized versus itinerant behavior of the f electrons. Therefore we applied so-called Hubbard parameter U in the range of 0.5-2 eV for the Th 5f electrons. Next, we calculated the elastic tensor by the linear-response method as implemented in VASP code [1] to determine elastic constants (Cij). Subsequently, the criteria of stability based on Cij were evaluated. Next, we calculated vibrational properties using the direct force-constant method as implemented in the PHONOPY code [2]. Actinium phase transition is discussed within the quasi-harmonic approximation under temperature and pressure to draw different conclusion than in Ref. [3]. We advance our knowledge to predict the thermal conductivity Using the Boltzman transport code [4] we address contribution to the thermal conductivity not only from phonons but also from free electrons. Our determined mechanical and thermodynamical properties of Th show very good agreement with experimental data and give us a high confidence to be able to predict similar properties of Ac and to explain the highest know thermal conductivity of Th among actinides.

#### References

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10:40am **AC+MI+SA-FrM-8 XANES Investigation into the Electronic Structure of Ce Coordination Complexes, Liane Moreau, C Booth, Lawrence Berkeley National Laboratory; Y Qiao, E Schelter, University of Pennsylvania**

Cerium is of particular interest among the lanthanide elements for its stability in both the Ce(III) and Ce(IV) oxidation states. This provides unique redox properties, making Ce a promising candidate for advanced energy materials. To this end, chemistries to control the Ce oxidation state have been widely developed. More interestingly, Ce-ligand bonding has in some cases shown intermediate behavior between Ce(III) and Ce(IV), which is indicative of a multiconfigurational ground state. This phenomenon results in low-energy ligand-to-metal charge transfer in addition to its magnetic behavior, such as temperature independent paramagnetism. In order to understand the effects of Ce electronic structure on compound chemical and physical properties, it is imperative to develop methods to accurately probe the fractional occupancy between  $4f^1$  and  $4f^0$  configurations.

Ce L<sub>3</sub> edge X-ray absorption near edge structure (XANES) measurements provide detailed information concerning the density of states from varying Ce-ligand bonding configurations. In particular, XANES spectra of Ce(IV) imido, Ce(III/IV) guanidinate-amide and Ce(IV) anilide complexes are presented and related to their specific coordination chemistry. From XANES, lanthanide-ligand bonding covalency is explored. We also consider the effects of varying the alkali metal species in metal-capped Ce(IV) imido. Results from the Ce(IV) complexes exhibit characteristic double white line absorption, indicative of significant 4f orbital participation in metal-ligand bonding. The extent to which covalency is observed is highly dependent on the specific ligand chemistry. In combination with DFT and magnetism results, XANES is used to study the effects of such chemistries on the orbital configurations and relate them to the observed novel properties of Ce coordination complexes.

11:00am **AC+MI+SA-FrM-9 Structure and Properties of Reactively Deposited Uranium Hydride Coatings Studied by the X-ray Scattering Methods, Milan Dopita, L Havela, L Horák, E Chitrova, Charles University, Prague, Czech Republic; D Legut, VSB-Technical University of Ostrava, Czech Republic; M Cieslar, Charles University, Prague, Czech Republic; Z Matěj, MAX-IV, Lund, Sweden**

A series of Uranium hydride coatings was prepared using a reactive sputtering method. The samples were sputtered with different Mo doping levels as well as at different hydrogen pressure and various substrate temperature. Fused silica and Si single-crystals were used as substrates for deposited coatings. The structure and the real structure (i.e. the deviations of the structure from the ideal 3D crystal periodicity) of the samples were investigated using the x-ray scattering methods. The x-ray reflectivity yielded the information on the coatings thickness, roughness and electron density. The key results of our work were the determination of the phase composition and its evolution, the description of the coherently diffracting domains - crystallite size and defects distributions, the description of the residual stress, strains and preferred orientation of crystallites - textures and its depth profiles in the coatings.

The sample sputtered on the fused silica substrates crystallized in the  $\beta$ -UH<sub>3</sub> structure (stable uranium hydride phase) with the stress free lattice parameter  $a = 0.6703 \pm 0.0004$  nm. The coating exhibited strong 001 preferred orientation of crystallites and compressive residual stress  $\sigma = -5.1 \pm 0.1$  GPa. Additionally, the coating revealed a bimodal distribution of crystallite sizes with two components having the mean crystallite size  $D_1 = 200$  nm and  $D_2 = 3.6$  nm with volume fractions of 60:40, respectively, and huge microstrain in both components. Contrary, the coating sputtered on cooled Si single-crystal substrate showed totally different behavior. It did not form nor the stable  $\beta$ -UH<sub>3</sub> neither the meta-stable  $\alpha$ -UH<sub>3</sub> structure. The measured diffraction pattern revealed the fluorite fcc structure, analogous to e.g. PuH<sub>2</sub>. This is highly interesting result, since to our best knowledge such form of uranium hydride has not been so far reported in the literature. The polycrystalline coating exhibited tilted *hhh* texture, stress free lattice parameter  $a = 0.53598 \pm 0.00014$  nm, compressive residual stress  $\sigma = -1.54 \pm 0.09$  GPa and mean crystallite size of 82 nm. Besides, the coating contains pronounced microstrain caused by the crystal lattice defects and significant fraction of the stacking faults. The results of the x-ray scattering studies were correlated with data obtained from HRTEM. Additionally, the possibility of formation of uranium hydride with fcc fluorite structure was confirmed by the ab-initio theoretical calculations (LDA+U).

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11:20am **AC+MI+SA-FrM-10 Ligand Induced Shape Transformation of Thorium Dioxide Nanocrystals, Gaoxue Wang, E Batista, P Yang, Los Alamos National Laboratory**

Nanocrystals (NCs) with size and shape dependent properties are a thriving research field. Remarkable progress has been made in the controlled synthesis of NCs of stable elements in the past two decades; however, the knowledge of the NCs of actinide compounds has been considerably limited due the difficulties in handling them both experimentally and theoretically. Actinide compounds, especially actinide oxides, play a critical role in many stages of the nuclear fuel cycle. Recently, a non-aqueous surfactant assisted approach has been developed for the synthesis of actinide oxide NCs with different morphologies, but an understanding of its control factors is still missing to date. Herein we present a comprehensive study on the low index surfaces of thorium dioxide (ThO<sub>2</sub>) and their interactions with relevant surfactant ligands using density functional calculations. A systematic picture on the thermodynamic stability of ThO<sub>2</sub> NCs of different sizes and shapes is obtained employing empirical models based on the calculated surface energies. It is found that bare ThO<sub>2</sub> NCs prefer the octahedral shape terminated by (111) surfaces. Oleic acid displays selective adsorption on the (110) surface, leading to the shape transformation from octahedrons to nanorods. Other ligands such as acetylacetone, oleylamine, and trioctylphosphine oxide do not modify the equilibrium shape of ThO<sub>2</sub> NCs. This work provides atomic level insights into the anisotropic growth of ThO<sub>2</sub> NCs that was recently observed in experiments, and thus may contribute to the controlled synthesis of actinide oxide NCs with well-defined size and shape for future applications.

# Friday Morning, October 26, 2018

11:40am AC+MI+SA-FrM-11 Perspectives on the Synthesis, Characterization and Applications of Upconversion and Downconversion Nanomaterials, *Martin Ntwaaborwa*, University of the Witwatersrand, South Africa

Luminescent nanomaterials incorporating one or more active ions (usually lanthanides) have many uses today in applications such as information displays, light emitting diodes, theft prevention, advertising, medical imaging, photodynamic therapy and photovoltaic cells. In the past few decades, there has been an upsurge of research interest in the synthesis of luminescence down-conversion and up-conversion nanomaterials with different particle morphologies, and their characterization using different optical techniques. The use of lanthanide ions to convert photons either by down-conversion or up-conversion process to different and more useful wavelengths is an interesting research phenomenon for a wide range of applications. For example, the use of down-conversion and up-conversion nanomaterials to improve the power conversion efficiency of crystalline silicon solar cells and for treatment of tumour cells, respectively, have been demonstrated. While efficient down-conversion has been demonstrated from a combination of many rare-earths ions, the most efficient up-conversion has been demonstrated from only a few combination of rare-earths ions such as erbium ( $\text{Er}^{3+}$ ) – ytterbium ( $\text{Yb}^{3+}$ ), thulium ( $\text{Tm}^{3+}$ ) –  $\text{Yb}^{3+}$ , and holmium ( $\text{Ho}^{3+}$ ) –  $\text{Yb}^{3+}$  incorporated in different host lattices with low phonon energies. Different mechanisms of luminescence down-conversion and up-conversion will be discussed. In addition, a few selected methods used to synthesise luminescence down-conversion and up-conversion nanomaterials will be discussed.

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