

Actinides and Rare Earths

Room 123 - Session AC+MI-FrM

Actinide and Rare Earth Chemistry and Physics

Moderators: Edgar Buck, PNNL, Krzysztof Gofryk, Idaho National Laboratory, Gertrud Zwicknagl, Technical University Braunschweig

8:15am **AC+MI-FrM-1 Structure, Stability, and Chemistry of Actinide Nanoparticles**, Ping Yang, G. Wang, E. Batista, Los Alamos National Laboratory **INVITED**

Nanoscale materials bearing heavy elements have a wide range of applications from the nuclear fuel cycle to environment and health. Nanocrystals (NCs) with size and shape dependent properties are a thriving research field and remarkable progress has been made in the controlled synthesis and characterization of NCs composed of stable elements in the past three decades. In this context, interfacial chemistry of nano-sized materials is critical for controlling the morphology that drives their unique associated chemical and physical properties. The understanding of NCs containing f-elements is comparatively limited due to difficulties in handling them both experimentally and theoretically. In this talk, I will share some recent progress in understanding the interplay between surface energy, surfactant ligands, and the chemistry in determining the morphology of 5f-element nanoparticles. Quantum simulations provide a molecular-level picture of the relevant driving forces and dynamic properties. To push for larger lengthscale, we recently developed the density functional theory tight-binding (DFTB) parameters for actinide systems, that enabled the microsecond quantum MD simulations of actinide nanoparticle systems.

[1] G Wang, ER Batista, P Yang, *Phys Chem Chem Phys* **2018**, *20*, 17563

[2] G Wang, ER Batista, P Yang, *J. Phys Chem C*, **2019**, *123*, 30245

[3] RK Carlson, MJ Cawkwell, ER Batista, P Yang, *J. Chem. Theor. Compt* **2020**, *16*, 3073

[4] NF Aguirre, J Jung, P Yang, *Phys Chem Chem Phys* **2020**, *22*, 18614

[5] G Wang, ER Batista, P Yang, *Appl Sci* **2020**, *10*, 4655

[6] D G Gonzalez, G Wang, ER Batista, P Yang, *Inorg Chem* **2023**, *in press*

8:45am **AC+MI-FrM-3 The Use of Ligand Modified Electrodes as Electrocatalysts for Actinide Redox Chemistry**, Christopher Dares, Florida International University; T. Grimes, Idaho National Laboratory; J. McLachlan, University of California at Berkeley; X. Hou, University of Utah; A. Ruiz Reyes, Florida International University **INVITED**

The lanthanides are most stable in the trivalent oxidation state, and with few exceptions, are difficult to generate in higher or lower oxidation states. In contrast the early actinides are redox active and can be generated and studied in a variety of oxidation states ranging from +7 to +2. This variety can complicate separations processes since oxidation state and can have a profound influence on ligand binding and solvent extraction. Separations schemes can also exploit the differences in binding preferences in different oxidation states to make selective extraction more efficient. In an aqueous acidic environment, the Am(IV/III) couple is at 2.6 V vs. the standard hydrogen electrode (SHE). This is nearly at the limit of what is possible in an aqueous solution where the 1-electron oxidation of water to hydroxyl radical is only about 0.3 V more positive. The subsequent potentials to generate penta- and hexavalent americium are lower though the high Am(IV/III) couple renders Am effectively redox-inert. Ligand coordination can be used to reduce the Am(IV/III) couple and/or facilitate the proton-coupled electron transfer (required to make the americium cation). These can be organic ligands including N-donors or inorganic ligands such as lacunary polyoxometalates. Ligands anchored to metal oxide electrodes serve as good electrocatalysts to generate Am(V) or Am(VI) and operate at potentials as low as 1.6 V vs. SCE (nearly 1 V below the Am(IV/III) couple). Ligands are attached to the surface using either organic functional groups like phosphonic acids, or, through a combination of attractive interactions including hydrogen-bonding. They form well-packed monolayers on mesoporous thin layers of conductive oxides. The development of these ligand modified electrodes (LMEs) will be introduced along with characterization of their ability to adjust actinide oxidation states.

9:15am **AC+MI-FrM-5 Observation of Flat Bands in Rare-Earth Based Kagome Metals**, Madhab Neupane, University of Central Florida **INVITED**
Quantum materials with kagome lattice – comprised of corner-sharing triangles forming a hexagon in the crystal structure – have been studied as the potential playgrounds for exploring the interplay among parameters

such as geometry, topology, electronic correlations, magnetic, and charge density orders. Recent report on a family of kagome metals of the form ReTi_3Bi_4 (Re = rare-earth) has generated interest due to the combination of highly anisotropic magnetism and a rich electronic structure. We use angle-resolved photoemission spectroscopy measurements in combination with density functional theory calculations to investigate the electronic structure of newly discovered kagome metals ReTi_3Bi_4 . Our results reveal multiple van Hove singularities (VHSs), some of which are in the vicinity of the Fermi level. We clearly observe multiple flat bands, which originate from the destructive interference of wave functions within the Ti kagome motif. These flat bands and VHSs originate from Ti d-orbitals and are very responsive to the polarization of the incident beam. These results demonstrate that of Ti based kagome materials system is an excellent material platform for studying kagome induced flat band physics and its connection with magnetism.

9:45am **AC+MI-FrM-7 Kinetics and Mechanism of Plutonium Oxycarbide Formation**, Paul Rousset, AWE plc, UK

Plutonium is both electropositive and highly reactive, such that an oxide film of varying thickness is always present on metal samples. It is of interest from a safety point of view (reduced handling/processing) to investigate methods that either prevent or slow down the rate of corrosion reaction of the metal. Plutonium oxycarbide, $\text{PuC}_{1-x}\text{O}_x$, surface films on plutonium metal have shown the ability to slow the rate of oxidation [1]. Favart *et al.* have reported the rate of plutonium oxycarbide formation at 350 °C [2] as measured using X-ray Diffraction. In the theoretical study reported by Qiu *et al.* the authors proposed four different mechanisms for the formation of plutonium oxycarbide [3]. Two of the proposed mechanisms involved the reaction of a gas with plutonium sesquioxide, Pu_2O_3 , and the other two involved a solid state reaction of this oxide to form plutonium oxycarbide. Using a combination X-ray Photoelectron Spectroscopy, Secondary Ion Mass Spectrometry and X-ray Diffraction the kinetics and mechanism of plutonium oxycarbide formation have been investigated and will be presented.

[1] Retardation of plutonium oxidation by a PuO surface film, D. T. Larson, D. L. Cash, *J. Vac. Sci. Technol.* **9**, 800 (1972).

[2] Characterization of PuO/PuCO phase and its influence on the oxidation kinetics of d-plutonium, N. Favart, B. Ravat, L. Jolly, B. Oudot, L. Berlu, F. Delaunay, I. Popa, S. Chevalier, *Oxid. Met.*, **96**, 271 (2021)

[3] Thermodynamical stability of plutonium monoxide with carbon substitution, R. Qiu, X. Wang, Y. Zhang, B. Ao, K. Liu, *J. Phys. Chem. C* **122**, 22821 (2018).

10:00am **AC+MI-FrM-8 Layered f-Metal Zintl Phases - EuZn_2P_2 and UCu_2P_2** , LADISLAV HAVELA, Charles University, Czech Republic; V. Buturlim, Idaho National Laboratory; O. Koloskova, Charles University, Prague, Czechia; D. Legut, J. Prchal, Charles University, Czech Republic; J. Kolorenc, J. Kastil, M. Misek, Institute of Physics CAS, Prague, Czechia

Zintl phases consisting of an electropositive element, cation, and covalently bonded polyanion, offer a large variability of electronic structure, bridging the gap between semiconducting and metallic behavior and offering interesting functionalities. In case of magnetic cation, properties can be further tuned by magnetic fields. Here we compare compounds based on lanthanide (Eu) and actinide (U) cations. We selected layered compounds, crystallizing in the trigonal structure CaAl_2Si_2 , which exhibit pronounced magnetic anisotropy. EuZn_2P_2 is a narrow band-gap semiconductor. Antiferromagnetic ordering of Eu^{2+} moments sets in at $T_N = 23$ K. Rapid increase of T_N with applied pressure, which reaches 43 K at $p = 9.5$ GPa, can be associated with reduction of the band gap, indicated by transport properties as well as by ab-initio calculations. Ferromagnetic alignment of Eu moments, achieved in fields of several Tesla, can reduce electrical resistivity by several orders of magnitude, which is classified as Colossal Magnetoresistance Effect. At $p = 18$ GPa (still within the same structure type), EuZn_2P_2 becomes semi-metallic. The compression by hydrostatic pressure is anisotropic, with soft c-axis direction. UCu_2P_2 with a smaller unit-cell volume is semi-metallic (and probably half-metallic) at ambient conditions. Also here the magnetic order (ferromagnetic) is supported by applied pressure, reaching 290 K at 6 GPa. The situation of 5f states is dramatically different comparing with the 4f states in the Eu counterpart. The indications given by large spontaneous magnetostriction, softer a-axis direction (nearest U-U links), or extremely strong uniaxial magnetocrystalline anisotropy point to an involvement of the 5f states in bonding, i.e. delocalization, although they do not contribute to the Fermi level, located in a pseudo-gap. Tuning by composition changes is not

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straightforward for single crystals grown by Chemical Vapor Transport method, nevertheless certain routes have been attempted with a positive outcome and properties of doped UCu_2P_2 will be discussed.

10:30am **AC+MI-FrM-10 Experimental Electronic Structure Measurements of Actinide-Containing Samples Using Scanning Tunneling Spectroscopy**, Benjamin Heiner, M. Beaux, Los Alamos National Laboratory

The many difficulties performing experiments on plutonium-containing samples makes the prospect of studying them using computational methods enticing. The lag in collection of experimental data using modern techniques, especially related to electronic structure, has made validating computational methods challenging. With the establishment of a scanning tunneling microscope at Los Alamos National Laboratory with the capacity to study plutonium and other radioactive samples, the ability to probe electronic structure seamlessly across the Fermi energy is now possible. In a first of its kind experiment, scanning tunneling spectroscopy data on plutonium-containing samples, especially gallium-stabilized δ -phase plutonium, has been collected. The spectra reveal a surface with semimetal characteristics instead of a computationally predicted semiconductor band gap.

LA-UR-24-24274

10:45am **AC+MI-FrM-11 Unconventional Superconductivity in UBe_{13} - Investigation via Variation of Impurity Level - and Comparison to the Conventional Superconductor LuBe_{13}** , Greg Stewart, J. Kim, University of Florida

We have prepared and characterized down to $T=0.40$ K three arc-melted samples each of MBe_{13} , $M = \text{Lu}, \text{U}$, using three different purities (99.999%, 99.96%, and 99.8%) of Be but with the same high purity M (Lu or U) for all three. The measurements down to 0.40 K allow the detection of the maximum in the specific heat in all three LuBe_{13} samples. The resulting superconducting properties **strongly** depend on impurity level in UBe_{13} (40% decrease in $\Delta C/T_c$, 15% decrease in T_c mid) while the three LuBe_{13} samples exhibit significantly smaller changes (10% and 5% respectively) with purity. The comparison of properties at the first two levels of purity (99.999% vs 99.96%) is even more disparate: 12% decrease in T_c mid in UBe_{13} vs no change in LuBe_{13} . These results are consistent with previous results that argue for unconventional superconductivity in UBe_{13} , and are consistent with assignment of LuBe_{13} as a conventional, BCS superconductor. As will be discussed in more detail, this example of comparing superconducting properties vs controlled gradations in impurity levels with two compositionally and structurally “matched” superconducting compounds (one conventional and one of to-be-determined coupling behavior) offers a new method - versus the already existing ones - for determining unconventional superconducting behavior.

11:00am **AC+MI-FrM-12 Strong Magnetoelastic Interactions in HoSb Probed by High-Resolution Dilatometry and X-Ray Diffraction**, Volodymyr Buturlim, Glenn T. Seaborg Institute, Idaho National Laboratory; N. Poudel, Idaho National Laboratory; D. Kaczorowski, Polish Academy of Sciences, Poland; M. Jaime, Physikalisch Technische Bundesanstalt, Germany; Z. Islam, Argonne National Laboratory; K. Gofryk, Center for Quantum Actinide Science and Technology, Idaho National Laboratory

Rare-earth (RE) mononictides, which crystallize in a cubic structure similar to NaCl have drawn considerable interest due to their diverse transport, magnetic, and structural properties. The non-magnetic compounds are known for the transition from topological to trivial electronic states (e.g. LaPn where $\text{Pn} = \text{Bi}$ and As [1]). Magnetism of the compounds with long-range order brings complexity to their topological properties. However, the topological nature of these materials undergoes intense debates and investigation. HoSb is a topologically trivial semimetal, which orders antiferromagnetically below $T_N = 5.7$ K [2]. Application of magnetic field leads to the change of its magnetic structure from MnO-type antiferromagnetic (AFM) arrangement to HoP-type arrangement, then to ferromagnetic (FM) arrangement. There are also reports which suggest a transition to tetragonal structure taking place at T_N [3]. The variety of the low-temperature phenomena makes HoSb a good platform to investigate the role of magnetic ordering and the strength of spin-phonon coupling on the crystal structure of this system. We will present the results of low-temperature high-resolution dilatometry as well as X-ray diffraction studies performed at static and pulsed magnetic fields. Heat capacity studies and the presence of latent heat agree with the structural distortion that occurs at T_N . The lowering of the symmetry is further supported by detailed low-temperature X-ray diffraction measurements under magnetic fields. Strong spin-lattice coupling in HoSb results in giant magnetostriction of the order of 1500 ppm. Furthermore, our detailed dilatometry studies allow us to

construct a magnetic phase diagram of HoSb. We will discuss the implications of these results in the context of the strong magnetoelastic properties in HoSb and other rare-earth mononictides.

[1] H. Y. Yang et al., Phys. Rev. B **98**, 045136 (2018).

[2] M. M. Hosen et al., Sci. Reports 2020 101 **10**, 1 (2020).

[3] F. Lévy, Phys. Kondens. Mater. **10**, 85 (1969).

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11:15am **AC+MI-FrM-13 Electronic Structure in a Rare-Earth-Based Intermetallic System TbNi_3Ga_9** , Sabin Regmi, V. Buturlim, Idaho National Laboratory; B. Rai, Savannah River National Laboratory; T. Durakiewicz, K. Gofryk, Idaho National Laboratory

Rare-earth-based intermetallics provide flexibility to study the electronic, magnetic, superconducting, and topological properties by tuning the crystal structure, composition, and spin-orbit coupling. Recently, $\text{RNi}_3(\text{Ga}/\text{Al})_9$ intermetallic materials have been studied for their richness in broad range of exotic crystal, magnetic, heavy fermion, and quantum criticality behaviors. However, momentum-resolved electronic structure studies are lacking. Here, we present results of the angle-resolved photoemission spectroscopy measurements to reveal the underlying electronic structure and topology in TbNi_3Ga_9 , both above and below the Néel temperature. This study will open up exciting avenues towards exploration of electronic properties in the chiral family of $\text{RNi}_3(\text{Ga}/\text{Al})_9$ materials with wide range of intriguing properties.

11:30am **AC+MI-FrM-14 Catalytic Activities of Defected Actinide Dioxide AnO_2 Surface: A First Principles Study**, Shukai Yao, G. Wang, E. Batista, P. Yang, Los Alamos National Laboratory

Actinide dioxides AnO_2 play an important role as nuclear fuels in commercial nuclear reactors. Understanding the surface chemistry of AnO_2 is crucial in various aspects such as safe operations, recycling, and storage of nuclear fuels. Actinide materials have shown to be highly efficient catalyst for the activation of H_2 , CO , NH_3 , etc., mainly due to valent 5f electrons of actinides characterized by strong electron correlations and various oxides states. However, experimental studies of actinide systems are limited by their high safety requirement associated with radioactivity. In this computational study, we employed first principles electronic structure calculations based on density functional theory (DFT) to reveal the catalytic behavior of AnO_2 surface with O vacancies. We will show that O vacancies significantly change the electronic structure of AnO_2 surfaces, and act as the active sites of small molecules adsorption. As a result, defected AnO_2 surface leads to an enhanced reactivity compared to the pristine AnO_2 surface.

11:45am **AC+MI-FrM-15 Thin Film Synthesis of Rare Earth and Actinide Nitrides Using Molecular Beam Epitaxy**, Keivn Vallejo, B. May, Z. Cresswell, V. Buturlim, S. Regmi, K. Gofryk, Idaho National Laboratory

Lanthanide- and actinide-based nitride compounds are an understudied group of materials compared to their oxide counterparts, which provide new avenues for nuclear reactor designs. Their 4f and 5f electron shell gives rise to a variety of interesting physics such as magnetism and unconventional superconductivity. Samarium nitride (SmN) has been recently identified as a material where ferromagnetic order and potential p-type superconductivity coexist. Our team will present results on the growth conditions in a molecular beam epitaxy chamber of pure and doped SmN using molecular beam epitaxy, and its electronic transport properties as a function of temperature and magnetic field. CeN and UN thin films are also explored. The presence of $\text{SmN}(111)$ peaks on (001) substrates indicates an orientation-preference for some material systems. The electrical resistivity and magnetic susceptibility studies have shown a range of magnetic behaviors, including paramagnetic and ferromagnetic. With a potential superconductive transition around ~ 10 K, SmN and its doping effects on crystal structure and electronic properties are characterized.

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