Actinides and Rare Earths Focus Topic
Room C124 - Session AC+MI+TH-TuM

Magnetism, Electron Correlation, and Superconductivity in the Actinides/Rare Earths

Moderators: Edgar Buck, PNNL, **Tomasz Durakiewicz**, Idaho National Laboratory, **Krzysztof Gofryk**, Idaho National Laboratory

8:00am **AC+MI+TH-TuM-1 Uranium and Cerium Based Systems Probed with High-Pressure XANES and XMCD***, **Fabrice Wilhelm**, A. Roagelv,* ESRF, France **INVITED**

This talk reviews recent advances in use of polarized x-rays to study local magnetic properties and electronic structure of uranium and cerium based compounds such as the ferromagnetic UGe_2, the heavy-fermion paramagnet UTe_2 and the nanolamellar ferromagnetic Kondo lattice $Mo_4Ce_4Al_7C_3$ system.

8:40am **AC+MI+TH-TuM-3 Searching for New Uranium-Based Arsenides***, **Eteri Svanidze**,* Max Planck Institute for Chemical Physics of Solids, Germany

As new classes of superconducting materials emerge, puzzles of high-temperature superconductivity continue to be one of the pressing issues in condensed matter physics and solid-state chemistry. In particular, iron pnictide superconductors still pose many open questions. Surprisingly, very few actinide-based analogues of iron pnictide high temperature superconductors have been reported so far, perhaps as a result of synthesis complications imposed by toxicity, reactivity, and high vapor pressure of constituent elements. In this work, we revisit the U-Fe-As ternary, in which only one compounds has been reported to exist so far – $UFeAs_2$ (*P*4/*nmm* space group) [1]. By implementing flux synthesis, we were able to grow large single crystals of UFe_5As_3 compound, which adopts UCr_5P_3 structure type [2] ($P2_1$/m, *mP*18) with lattice parameters a = 7.0501(17) Å, b = 3.8582(9) Å and c = 9.6342(13) Å, β = 100.2(8)° [3]. The refined composition agrees well with the elemental ratio established by the EDX analysis – $U_{9.9(2)}Fe_{58.7(2)}As_{31.4(2)}$. The magnetic behavior of UFe_5As_3 was studied by magnetic susceptibility measurements in the temperature range 1.8 - 600 K and an antiferromagnetic ordering below T_N = 56 K was established. The Sommerfeld coefficient g = 138 mJ/mol K^2 indicates enhanced effective electron mass. More in-depth investigations of this and other U-Fe-As ternary compounds are currently underway.

References:

[1] D. Kaczorowski, J. Alloys. Compd. 186, 333-338 (1992).

[2] W. Jeitschko, R. Brink, P.G. Pollmeier, Z. Naturforsch. (1993) 48b, p. 52-57.

[3] N.Zaremba, M. Krnel, Yu. Prots, A. Leithe-Jasper, Yu. Grin, E. Svanidze, in preparation (2023)

9:00am **AC+MI+TH-TuM-4 5*f* Magnetism at an Extreme***, **Ladislav Havela**,* Charles University, Faculty of Mathematics and Physics, Czechia*; V. Buturlim,* Idaho National Laboratory*; F. Honda,* Tohoku University, Japan*; D. Kaczorowski,* Institute of Low Temperature and Structure Research, Wrocław, Poland

Specific features of 5*f* magnetim in U-based systems, namely the strong spin-orbit coupling and very strong magnetic anistropy or giant magnetoresistance, are degraded by low temperatures of magnetic ordering. The variability of T_C or T_N in intermetallics has been explored and it turns out that involvement of magnetic *d*-metals such as Fe or Co does not help, unless very high fraction of the transition metals turns a compound in fact a regular *d*-magnet, in which the unique 5*f* features are suppressed. The reason is the 5*f*-*d* hybridization with a destabilizing action on both *d* and 5*f* moments.

Seeking additional degrees of freedom we turned towards compounds with more polar character of bonding, which drives U to the verge of metallicity. Interesting alternative to intermetallics is provided by Zintl phases, typically ternary compounds with one cation (e.g. an *f*-metal) and a complex covalently bond anion, stabilized by a charge transfer from the cation. An excellent insight is provided by such compounds with layered crystal structures, which leads to strongly anisotropic electronic properties. Our research focuses on Zintl phases with the trigonal $CaAl_2Si_2$ type (*P*-3*m*), formed by alternating cationic (Ca) and anionic (Al-Si) layers. Those without *f*-metals or with 4*f* metals tend to be narrow-gap semiconductors. U-based phases such as UCu_2P_2 are semi-metallic. The prominence of this compound dwells in ferromagnetism with high Curie temperature T_C = 216 K, which is further enhanced by pressure application to the vicinity of room temperature. Ab-initio calculations reveal it this material is actually a half-metal, with spin-split 5*f* band bringing spin-up only states to the Fermi level. The conduction electron states remain hybridized with the 5*f* states, which causes also the non-f electrons to be fully spin polarized. The magnetisms is of local moment type, with magnetic entropy exceeding R*ln2, but arising from 5*f*bands. UCu_2P_2 can be compared with $EuZn_2P_2$. Here the Eu^{2+} moments are organized in an AF structure. The field alignment of the moments impacts the width of the gap seen in transport data, but the material remains semiconducting.

This work was supported by the Grant Agency of the Czech Republic under the grant No. 21-09766S.

9:20am **AC+MI+TH-TuM-5 Valence-to-Core RIXS in Insulating Compounds with 4f and 5f Elements***, **Jindrich Kolorenc**,* Institute of Physics, Czech Academy of Sciences, Czechia

In the first part, we investigate the electronic structure of europium sulfide (EuS) with the aim to understand the valence-to-core resonant inelastic x-ray scattering (RIXS) spectra measured at the Eu L_3 edge. We show that the main part of the observed signal comes from the direct RIXS: an Eu 2p core electron is excited to an empty Eu 5d band above the Fermi level, and then another electron from an Eu 5d state hybridized with the S 3p bands (located below the Fermi level and hence occupied) fills back the core hole. Besides this straightforward channel, the measured RIXS spectra display two satellite features. After considering several candidates (such as excitations of the 4f shell excited by indirect RIXS processes, that is, by the interaction with the core hole in the intermediate state), we arrive at the conclusion that the satellites are excitons formed by a 4f hole and an 5d electron localized at the same Eu atom. Such excitons were suggested in the context of optical absorption a long time ago [1], but the concept is not widely accepted. It was argued that existence of these excitons is incompatible with photoconductivity measurements [2]. Our observations indicate that these arguments may need to be revisited.

In the second part, we simulate valence-to-core RIXS at the actinide M_5 edge in selected actinide oxides starting from the dynamical mean-field electronic structure obtained earlier [3] and using techniques similar to [4]. This investigation is motivated by the recent experimental study of UO_2 and UF_4 [5]. Our preliminary results suggest that the feature observed at an energy loss of roughly 10 eV above the white line is likely a charge-transfer excitation, the intensity of which is sensitive to the hybridization between the actinide 5f states and the ligand 2p states.

This work was supported by the Czech Science Foundation under the grant No. 21-09766S.

[1] T. Kasuya and A. Yanase, Rev. Mod. Phys. 40 (1968) 684, https://doi.org/10.1103/RevModPhys.40.684
[2] P. Wachter and B. Bucher, Physica B 408 (2013) 51, https://doi.org/10.1016/j.physb.2012.09.018
[3] J. Kolorenc, A. Shick, A. I. Lichtenstein, Phys. Rev. B 92 (2015) 085125, https://doi.org/10.1103/PhysRevB.92.085125
[4] J. Kolorenc, Physica B: Condensed Matter 536 (2018) 695, https://doi.org/10.1016/j.physb.2017.08.069
[5] J. G. Tobin et al., J. Phys.: Condens. Matter 34 (2022) 505601, https://doi.org/10.1088/1361-648X/ac9bbd

9:40am **AC+MI+TH-TuM-6 Magnetism of Binary Actinide Oxides***, **Binod Rai**, A. Bretaña,* Savannah River National Laboratory*; G. Morrison,* University of South Carolina, Columbia*; R. Greer,* Savannah River National Laboratory*; K. Gofryk,* Idaho National Laboratory*; H. zur Loye,* University of South Carolina, Columbia

Historically, the bulk of actinide oxide research has focused on the properties of various uranium and plutonium compounds as they impact their use in the nuclear fuel industry. While the fundamental understanding of compounds such as UO_2 has improved, a fundamental grasp of the physical properties of other actinide oxides remains elusive. In actinide systems, the 5*f* electrons experience a uniquely delicate balance of effects and interactions having similar energy scales, which are often difficult to properly disentangle. The interplay of factors such as the dual character of 5*f*-states, competing interactions, and strong spin-orbit coupling results in magnetically unusual and intriguing behavior: multi-*k* antiferromagnetic ordering, multipolar ordering, mixed valence configurations, and more. In this presentation, I will provide an overview of the available synthesis techniques for selected binary actinide oxides. I will also show the current state of knowledge on their crystal structures and magnetic properties.

Moreover, I will talk about the future opportunities that are vital for a fundamental understanding of these systems.

11:00am **AC+MI+TH-TuM-10 N-Point Saddle-Band Model for the Hidden Order Phase of URu$_2$Si$_2$*,*** ***J. D. Denlinger,*** Lawrence Berkeley National Laboratory*; J. Kang,* The Catholic University of Korea*; L. Dudy,* SOLEIL, France*; J. Allen,* University of Michigan*; L. Wray,* New York University*; A. Gallagher, R. Baumbach,* National High Magnetic Field Laboratory*; N. Butch,* University of Maryland*; M. Maple,* University of California, San Diego

The 5f heavy fermion system of URu$_2$Si$_2$ is famous for an unconventional hidden order (HO) phase transition at T$_0$=17.5K and the various related doping phase diagrams explored to elucidate the nature of this unknown transition. A new model of an extended U 5f saddle-point dispersion at the N-point is proposed for the underlying physics of this 35-year old puzzle. With a 10X DFT energy renormalization suggested by angle resolved photoemission (ARPES) measurements in comparison to DMFT calculations [1], this feature lies only a few meV below E$_{F,}$ and thus is thermally active at T$_0$. ARPES reveals a distinct temperature-dependent evolution of incommensurate 5f nesting hotspots lying along Z-N-Z [1], whose origins are found in electronic susceptibility calculations of intraband q-scattering for thermal occupations in the temperature range of T$_0$. Tuning of the N-point region f-band energetics with chemical doping is thus naturally proposed to unify our understanding of the various phase diagrams. ARPES is presented which confirms the existence of N-point spectral and dichroic changes for ferromagnetic Re/Ru-substitution, for (001) antiferromagnetic Fe and Os/Ru-substitution, and for (1/2,1/2,1/2) antiferromagnetic P/Si-substitution, thus further demonstrating experimentally the key relevance of the N-point electronic structure to the HO phase.
[1] J. D. Denlinger et al., Electron. Struct. 4, 013001 (2022).

11:20am **AC+MI+TH-TuM-11 Magnetoelastic Properties of 5*f* Ferromagnet UCu$_2$P$_2$*,*** ***Volodymyr Buturlim,*** Idaho National Laboratory*; P. Doležal, O. Koloskova, J. Prchal,* Charles University, Czechia*; I. Turek,* Charles university, Czechia*; M. Martinez Celis,* CRISMAT Laboratory, France*; F. Honda,* Kyushu University, Japan*; M. Divis,* Charles University, Czechia*; D. Kaczorowski,* Polish Academy of Sciences, Poland*; K. Gofryk,* Idaho National Laboratory*; L. Havela,* Charles University, Czechia

UCu$_2$P$_2$, a Zintl phase with the trigonal CaAl$_2$Si$_2$ structure type, is a 5*f* ferromagnet with a record-high Curie temperature among U compounds, T_C = 216 K [1]. While the size of the magnetic moment 2.0 μ_B/U is not surprising due to U-U spacing exceeding the Hill limit, the reasons for the high T_C are less understood. Ab-initio calculations reveal only very weak hybridization of the U-5*f* states with the 6*d* states as well as with electronic states of Cu and P. It seems that a transfer of U-6*d* states to the P-3*p* states is an important ingredient, which was highlighted by a rapid increase of T_C under hydrostatic pressure so that a room-temperature 5*f* ferromagnetism could be demonstrated. Besides magnetization, transport, and heat capacity studies on single crystals we performed also characterization of a polycrystalline material, which has T_C = 219 K. Thermal expansion study revealed a moderate increase of both lattice parameters just below T_C, so we can exclude that the pressure enhancement of T_C is driven simply by thermodynamics (via the Ehrenfest relation). Hence the reasons have to be attributed to the enhancement of specific U-U couplings upon compression. Indeed, ab initio calculations probing the energy enhancement upon moments reversal gave a semi-quantitative account of the observed tendency of T_C.

[1] D. Kaczorowski, R. Troc, Magnetic and transport properties of a strongly anisotropic ferromagnet UCu$_2$P$_2$, J. Phys. Condens. Matter, 1990, 2, 4185.

*This work was supported by the Czech Science Foundation under the grant No. 21-09766S.

11:40am **AC+MI+TH-TuM-12 Density Functional Theory Calculations of the Phonons in Gamma and Delta Phase Pu*,*** ***Sven P. Rudin,*** Los Alamos National Laboratory

The thermodynamics of plutonium challenges both theory and experiment. The challenge arises from the multiple structural phase transitions, the nature of the 5f electrons, and the effects due to the material's self-irradiation. Density functional theory calculations have made steady progress toward clarifying experimental measurements. Recently, for the delta phase a non-collinear 3Q spin structure was shown to make all structurally equivalent bonds equivalent in their bonding character. This results in elastic constants and phonons with the correct symmetry, and the calculated phonon dispersion agrees well with experiment. Extending the calculations into the gamma phase of Pu now provides a prediction for the phonons of that phase.

12:00pm **AC+MI+TH-TuM-13 The 5f UDOS of the Actinide Dioxides: Why Pu is n = 5 in PuO$_2$*,*** ***James Tobin,*** University of Wisconsin-Oshkosh*; H. Ramanantoanina,* KIT, Germany*; C. Daul,* U. Fribourg, Switzerland*; S. Yu,* LLNL*; P. Roussel,* AWE, UK*; S. Nowak, R. Alonso-Mori, T. Kroll, D. Nordlund, T. Weng, D. Sokaras,* SSRL

The Unoccupied Density of States (UDOS) of ThO$_2$, UO$_2$ and PuO$_2$ have been investigated with a combined experimental and theoretical approach.[1,2]Ligand field density functional theory calculations of the dioxides of thorium, uranium, and plutonium have been combined with high-energy-resolution fluorescence detection (HERFD) in x-ray absorption spectroscopy and inverse photoelectron spectroscopy (IPES) measurements to provide powerful insight into the underlying composition of the unoccupied 5f electronic structure in these 5f localized systems. Fine structure in the 5f$_{5/2}$ transitions in HERFD can be directly correlated with the fine structure in the leading edge of the IPES. The shapes, intensities, and systematics in HERFD and IPES are explained in a consistent and rigorous fashion in terms of the j-specific 5f electronic structure.Additionally, an actinide N$_{4,5}$ branching ratio analysis of PuO$_2$ and UO$_2$ has been performed, including measurements with a scanning transmission electron microscope at the Advanced Light Source and simulation with FEFF. It is shown that the 5f occupation of the Pu in plutonium dioxide is n = 5.

References

1. J. G. Tobin,H. Ramanantoanina, C. Daul, S.-W. Yu, P. Roussel, S. Nowak, R. Alonso-Mori, T. Kroll, D. Nordlund, T.-C. Weng, D. Sokaras, "The Unoccupied Electronic Structure of Actinide Dioxides," *Phys. Rev. B* 2022, **105**, 125129.https://doi.org/10.1103/PhysRevB.105.125129
2. J. G. TobinandS.-W. Yu, "Pu5f Occupation in Plutonium Dioxide," *Inorg. Chem.* 2023, **62**, 6, 2592–2598, https://doi.org/10.1021/acs.inorgchem.2c03202

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