

# Wednesday Morning, October 21, 2015

**Actinides and Rare Earths Focus Topic**  
**Room: 230A - Session AC+AS+MI-WeM**

## **Magnetism, Complexity and Superconductivity in the Actinides and Rare Earths**

**Moderator:** Tomasz Durakiewicz, Los Alamos National Laboratory

8:00am **AC+AS+MI-WeM1 The Valence-Fluctuating Ground-State of  $\delta$ -Pu**, *Marc Janoschek*, Los Alamos National Laboratory **INVITED**

Plutonium (Pu) is arguably the most complex elemental metal known because its 5f electrons are tenuously poised at the edge between localized and itinerant configurations. This complex electronic structure leads to emergent behavior—all a direct consequence of its 5f electrons—including six allotropic phases, large volumetric changes associated with these transitions of up to 25%, and mechanical properties ranging from brittle  $\alpha$ -Pu to ductile  $\delta$ -Pu. Pu also exhibits a Pauli-like magnetic susceptibility, electrical resistivity and a Sommerfeld coefficient of the specific heat that are an order of magnitude larger than in any other elemental metal. Finally, while experiments find no sign for static magnetism in Pu, most theories that use the correct volume predict a magnetically ordered state. This discrepancy might be reconciled by recent Dynamical Mean Field Theory (DMFT) calculations that suggest that the electronic ground state of  $\delta$ -Pu is a quantum-mechanical admixture of localized and itinerant valence configurations. The question whether the ground state of  $\delta$ -Pu is indeed a true quantum-mechanical superposition may only be answered via observation of the associated virtual valence (charge) fluctuations among the distinct 5f<sup>6</sup>, 5f<sup>7</sup>, and 5f<sup>8</sup> configurations. The characteristic energy scale for the associated spin fluctuations is expected to  $T_K \approx 800$  K ( $E_{sf} \approx 70$  meV) that will result in a dynamical spectral response centered at this energy for  $T < T_K$ . We have performed high-energy inelastic neutron spectroscopy at room temperature using a large polycrystalline sample of  $\delta$ -<sup>242</sup>Pu with a total mass of  $m \approx 21$  g at the Lujan Center and at the Spallation Neutron Source. Our measurements demonstrate the existence of high energy magnetic fluctuations centered at  $E_{sf} = 84$  meV, in good agreement with the DMFT calculations. In addition, they allow us to extract the magnetic form factor of  $\delta$ -Pu, yielding critical information about its valence state. These unprecedented results place show that the magnetism in Pu is not "missing" but dynamic, but dynamic, and is driven by virtual valence fluctuations. Our measurements provide a straightforward interpretation of the microscopic origin of the large, Pauli-like magnetic susceptibility of  $\delta$ -Pu and associated Sommerfeld coefficient. Furthermore, because the various valence configurations imply distinct sizes of the Pu ion, the valence-fluctuating ground state of Pu also provides a natural explanation for its complex structural properties and in particular the large sensitivity of its volume to small changes in temperature, pressure or doping.

8:40am **AC+AS+MI-WeM3 Exchange Bias in Heterostructures Based on  $\text{UO}_2$** , *Evgeniya Tereshina*, Institute of Physics ASCR, Czech Republic, *Z. Bao*, PANalytical B.V., Netherlands, *L. Havela*, Charles University in Prague, Czech Republic, *R. Springell*, University of Bristol, UK, *S. Danis*, Charles University in Prague, Czech Republic, *A. Mackova*, Nuclear Physics Institute ASCR, Czech Republic, *T. Gouder*, *R. Caciuffo*, Institute for Transuranium Elements (ITU), Germany **INVITED**

Interfacial exchange interaction in bilayers consisting of two dissimilarly ordered magnetic materials (e.g. an antiferromagnet (AF) and a ferro- or ferrimagnet (F)) may give rise to a phenomenon called the magnetic exchange bias (EB) effect [1]. The EB manifests itself as a shift of a magnetic hysteresis loop along the field direction when the bilayer is field-cooled below the Néel temperature ( $T_N$ ) of the AF. This property is of great value for magnetic recording applications. Despite the conceptual simplicity, a generally accepted theory that predicts the EB behavior for an apt pair of materials is still missing. The reason for that might be in poorly defined interface structure in both magnetic and crystallographic aspects.

Critical dependence of EB on magnetic anisotropy brings us the possibility to use actinides with strong spin-orbit interaction as the key ingredient. Here we report exchange bias studies in magnetic bilayers consisting of a stoichiometric  $\text{UO}_2$  film grown epitaxially on different substrates and covered with polycrystalline metallic ( $\text{Ni}_{10}\text{Fe}_{20}$  and Fe) and highly textured oxide ( $\text{Fe}_3\text{O}_4$ ) layers of variable thickness. Large longitudinal exchange bias  $\sim 2.6$  kOe is found in  $\text{UO}_2/\text{Fe}_3\text{O}_4$  bilayers [3] while  $\text{UO}_2$  combined with metallic ferromagnets displays perpendicular exchange coupling with an order of magnitude smaller EB. Interestingly, unusual effects in  $\text{UO}_2/\text{Fe}_3\text{O}_4$  were observed, namely, exchange bias did not vanish at  $T_N$  of  $\text{UO}_2$ . Apart from the fact that single layers of magnetite were showing some EB (not

more than 25 % of the total effect in  $\text{UO}_2/\text{Fe}_3\text{O}_4$ ), the EB in  $\text{UO}_2/\text{Fe}_3\text{O}_4$  bilayers exceeded notably that of the single  $\text{Fe}_3\text{O}_4$ 's to approx. 70 K that was attributed to possible proximity effects of  $\text{Fe}_3\text{O}_4$  on  $T_N$  of  $\text{UO}_2$  and/or to the magnetic anisotropy of  $\text{UO}_2$  preserved locally above  $T_N$ . The effects were observed for the samples of quality controlled by different methods such as X-ray Photoelectron Spectroscopy, conventional X-ray Diffraction, Transmission Electron Microscopy and Rutherford Backscattering Spectroscopy. The work has been supported by the Czech Science Foundation, grant No. 13-25866P.

[1] W. H. Meiklejohn and C. P. Bean, "New magnetic anisotropy", Phys. Rev. B 102, 1413 (1956).

[2] V. Sechovsky, L. Havela, in: Magnetic Materials, K.H.J. Buschow (Ed.), Elsevier, Amsterdam, 1998, Vol. 11, p. 1.

[3] E. A. Tereshina et al., Appl. Phys. Lett. 105, 122405 (2014).

9:20am **AC+AS+MI-WeM5 Transport and Magnetism of 4f and 5f Systems: What we can Learn from Thermoelectric Power**, *Krzysztof Gofryk*, Idaho National Laboratory **INVITED**

The interplay between different electronic ground states, especially magnetism and superconductivity, has evolved in a climate of discovery in which many of the fundamental rules of condensed matter physics are questioned by materials with unexpected properties. These "emergent properties," such as complex magnetism, heavy-fermion superconductivity, the coexistence of magnetism and superconductivity, and/or Kondo physics emerge from complex materials in which quasiparticles develop different states of organization and correlation. The majorities of these bizarre electronic ground states are encountered in *f*-electron systems and are linked to the hybridization between the *f*-states and ligand electrons. How these properties evolve with the progressive filling of the *f*-shells remains an open question, but it is a key ingredient for their understanding. The 4*f* and 5*f* strongly correlated electron systems at the border of magnetism are of active current interest, particularly because the accompanying quantum criticality provides a route towards both strange-metal, non-Fermi-liquid behavior, and unconventional superconductivity. In spite of large theoretical and experimental efforts the nature of the electronic behaviors is still unclear. One way to address the electronic properties of these fascinating materials is to perform extensive transport studies such as Hall, Nernst, or Seebeck effects. In particular, the latter one has gained importance in recent years in thermoelectric materials as potential solutions for applications, such as spot cooling of electronic components, waste heat recovery system and/or remote power generation in space stations and satellites. In addition, the Seebeck coefficient is a sensitive probe of energy relative to the Fermi level, it can therefore be used as a tool to characterize the electronic structure of materials, especially in the vicinity of the narrow gap or pseudo-gap. During the talk I will provide a general introduction to the magnetic and transport characteristics of 4*f* and 5*f* electron systems. Then, I will present thermoelectric properties of selected 4*f* and 5*f* materials and give an overview on how the thermoelectric power studies can be used to probe electronic properties in this class of materials. I will discuss implications of the results, and their limitations.

11:00am **AC+AS+MI-WeM10 Magnetic Properties of 2-2-1 Rare-earth and Uranium Compounds and their Interaction with Hydrogen**, *Silvie Maskova*, Charles University, Prague, Czech Republic, *R.V. Denys*, Institute for Energy Technology, Kjeller, Norway, *I. Halevy*, Nuclear Research Center Negev, Beer-Sheva, Israel, *K. Miliyanchuk*, *L. Akselrud*, Ivan Franko National University of Lviv, Lviv, Ukraine, *A. Kolomiets*, Lviv Polytechnic National University, Lviv, Ukraine, *V. Yartys*, Institute for Energy Technology, Kjeller, Norway, *M. Giovannini*, University of Genova, Genova, Italy, *L. Havela*, Charles University, Czech Republic

We have been studying some members of large family of  $\text{A}_2\text{T}_2\text{X}$  (A = Rare-Earth (RE) or actinide, T = transition metal, X = *p*-metal) compounds crystallizing in the  $\text{Mo}_2\text{FeB}_2$  structure type (space group  $P4/mbm$ ).  $\text{U}_2\text{T}_2\text{X}$  interact with  $\text{H}_2$  only at high pressure ( $\approx 100$  bar) reaching 2 H/f.u. The H absorption produces a lattice expansion, while the tetragonal structure is preserved. The H atoms presumably enter the 8*k* position inside the  $\text{U}_3\text{T}$  tetrahedra occupied randomly up to 50%. On the other hand, it was found that some  $\text{RE}_2\text{T}_2\text{X}$  compounds can absorb more hydrogen compared to their U-counterparts in much lower H pressures. The amorphization of the structure upon hydrogenation (4 H/f.u.) was found for  $\text{RE}_2\text{Pd}_2\text{In}(\text{Sn})$  with light RE (La, Nd).  $\text{RE}_2\text{Pd}_2\text{In}(\text{Sn})$  with heavy RE behave similar way as  $\text{U}_2\text{T}_2\text{X}$  compounds (2 H/f.u., crystal structure type not changed). For the isostructural indide  $\text{Nd}_2\text{Ni}_2\text{In}$  the hydrogen absorption of 7 H/f.u. leads to the orthorhombic distortion of the crystal structure.

Recently, we have been studying several isostructural  $\text{RE}_2\text{T}_2\text{Mg}$  (T = Ni, Pd). The H absorption in these compounds depends on the type of transition

metal. The compounds with Ni tend to absorb up to 8 H/f.u. The crystal structure is changed to monoclinic (space group  $P21/c$ ). If the transition metal is Pd, the hydrogen absorption is lower, reaching approx. 6 H/f.u. and the crystal structure is modified in different way. The  $Tb_2Pd_2Mg$ -hydride crystallizes in a new ternary structure type ( $Fmmm$ ). In the case of Mg-compounds, the hydrogen absorption is not reversible. Upon desorption of H the initial crystal structure is not restored.

We have found that in U-compounds the ordering temperatures increase upon hydrogenation contrary to the RE-compounds where the ordering temperatures are dramatically reduced. Magnetic properties of U-compounds strongly depend on the inter-U distances. Hydrogen intrusion modifies the lattice by expanding it without changing the crystal-structure type leading to a band narrowing. As a consequence doping of U intermetallics by interstitial hydrogen leads to stronger magnetic properties. On the other hand, the hydrogen absorption has opposite effect on magnetic properties of  $RE_2T_2X$  compounds. For RE compounds, hydrogenation affects mainly the  $4f$ -magnetic moments and their ordering. The exchange coupling is reduced presumably by reducing the concentration of conduction electrons.

11:20am **AC+AS+MI-WeM11 Structural, Electronic, and Magnetic Characteristics of  $Np_2Co_{17}$  and Analogue Compounds Under Pressure.** *Itzhak Halevy*, Nuclear Research Center Negev, Israel, *A. Hen*, Institute for Transuranium Elements (ITU), Germany, *I. Orion*, Ben Gurion University, Israel, *E. Colineau*, *R. Eloirdi*, *J.C. Griveau*, ITU, Germany, *F. Wilhelm*, *A. Rogalev*, ESRF, France, *N. Magnani*, *A.B. Shick*, *R. Caciuffo*, ITU, Germany

A previously unknown neptunium-transition-metal binary compound  $Np_2Co_{17}$  has been synthesized and

characterized by means of powder x-ray diffraction,  $^{237}Np$  Mössbauer spectroscopy, superconducting-quantum-interference-device magnetometry, and x-ray magnetic circular dichroism. The compound crystallizes

in a  $Th_2Ni_{17}$ -type hexagonal structure with room-temperature lattice parameters  $a=8.3107\text{\AA}$  and  $c=$

$8.1058\text{\AA}$ . Magnetization curves indicate the occurrence of ferromagnetic order below  $T_C>350$  K. Mössbauer

spectra suggest a  $Np^{3+}$  oxidation state and give an ordered moment of  $\mu_{Np}=1.57\mu_B$  and  $\mu_{Co}=1.63\mu_B$

for the Np atoms located, respectively, at the  $2b$  and  $2d$  crystallographic positions of the  $P6_3/mmc$  space group.

Combining these values with a sum-rule analysis of the XMCD spectra measured at the neptunium  $M_{4,5}$  absorption

edges, one obtains the spin and orbital contributions to the site-averaged Np moment [ $\mu_S=-1.88\mu_B$ ,

$\mu_L=3.48\mu_B$ ]. The ratio between the expectation value of the magnetic-dipole moment and the spin magnetic

moment ( $m_{md}/\mu_S=1.36$ ) is positive as predicted for localized  $5f$  electrons and lies between the values

calculated in intermediate-coupling (IC) and  $jj$  approximations. The expectation value of the angular part of

the spin-orbit-interaction operator is in excellent agreement with the IC estimate. The ordered moment averaged

over the four inequivalent Co sites, as obtained from the saturation value of the magnetization, is  $\mu_{Co}\sim 1.6\mu_B$ .

The experimental results are discussed against the predictions of first-principles electronic-structure calculations

based on the spin-polarized local-spin-density approximation plus the Hubbard interaction. The structural behavior of  $Np_2Co_{17}$  is investigated by means of high pressure diamond-anvil compression measurements and is compared with that of the isostructural compounds  $Lu_2Co_{17}$  and  $Lu_2Ni_{17}$ . The  $Th_2Ni_{17}$ -type hexagonal crystal structure is preserved with no measurable discontinuous volume collapses up to the highest achieved pressure,  $p=43$  GPa. For  $Np_2Co_{17}$ , fits to the Birch-Murnaghan and Vinet equations of state give values of the isothermal bulk modulus and

its pressure derivative of  $B_0=286$  GPa and  $B_0=3$ , revealing that this Np compound is a highly incompressible solid with stiffness comparable to that of superhard covalently bonded materials. The isothermal equation of state for the studied compounds are in excellent agreement with the results of *ab initio* fully-relativistic, full potential local spin-density functional calculations. Theoretical estimates of the bulk modulus are given also for  $Np_2Ni_{17}$ , for which  $B_0$  is predicted to assume values intermediate between those measured for  $Lu_2Ni_{17}$  and  $Np_2Co_{17}$ .

11:40am **AC+AS+MI-WeM12 Alloying  $UH_3$  as a Probe into the  $5f$  Magnetism.** *Ladislav Havela*, *M. Paukov*, *I. Tkach*, *M. Cieslar*, *Z. Matej*, *D. Kriegner*, *D. Drozdenko*, *I. Turek*, *M. Divis*, Charles University, Czech Republic, *N.-T.H. Kim-Ngan*, Pedagogical University, Poland

Several routes of preparation of alloyed U trihydrides,  $UH_3$ , were discovered. Starting from the  $U_6T$  compounds, hydrogenation leads to T atoms embedded in the  $\beta-UH_3$  structure, with transition-metal atoms T occupying one of the U sites. We have been hydrogenating  $\gamma-U$  alloys, using various transition metals helping (together with ultrafast cooling) to retain the bcc U structure down to low temperatures. As such alloys are much more resistant to hydrogen attack, high pressures of  $H_2$  gas had to be applied. The H absorption corresponds to approx. 3H/atoms per 1 U atom. In none of the cases the alloying metals segregate and two different structures were obtained. The hydrides  $(UH_3)_{1-x}Zr_x$  form the  $\alpha-UH_3$  structure, i.e. the bcc structure expands and fills by H. Hence basic electronic properties of  $\alpha-UH_3$  could be established. Starting from  $U_{1-x}Mo_x$ , we obtained  $(UH_3)_{1-x}Mo_x$ , which tends to be  $\beta-UH_3$  like, but has the grain size is 1 nm only, i.e. practically amorphous. This amorphous phase also easily accepts additional dopants, as Zr, Fe, Ti, V...however magnetic properties remain only weakly affected. It is quite remarkable that all such materials are ferromagnets with the Curie temperature in the range 160-205 K, even if the active U sublattice is diluted by more than 30% of other metals. In this respect the hydrides are different than conventional band ferromagnets, sensitive to inter-atomic spacings and alloying. Albeit all are metallic, the U-H interaction, which can have a partly ionic character, plays clearly important role. Electronic structure calculations (performed for the  $\alpha-UH_3$  structure and in ferromagnetic or Disordered Local Moment state, with possible random Zr occupancy) suggest a transfer of U-6d and 7s electrons into H-1s states, reducing the hybridization of 5f and non-f states, supporting thus magnetism even if the U-U spacing is below the Hill limit [1].

[1] I. Tkach et al. Phys.Rev. B 91, 115116 (2015).

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