Intermetallic Compounds with Thorium and Uranium

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A large number of exotic physical phenomena has been observed in actinide-based materials, which ensures a perpetual interest in the discovery of novel systems. Below, we outline a number of targeted explorative methods, that resulted in discoveries of several new materials: heavy fermion $U_{11}Hg_{43}$, uniaxial ferromagnet UBeGe, and $ThPt_{3+x}Be$. Additionally, a comprehensive sample quality analysis has allowed to establish novel ground state and non-Fermi liquid behavior in $U_2Cu_{17-x}Ga_x$, as well as strong crystal-size and annealing dependence of superconducting UBe_{13}.

It is well-known that materials containing *5f* elements display peculiar physics – unconventional super-conductivity, complex magnetic order, heavy-fermion, and non-Fermi liquid behaviors. However, their comprehensive understanding remains unclear, calling for new systems. Additionally, while known systems are typically well-investigated, sample quality issues often result in conflicting reports. With that in mind, we present below two unique avenues that will contribute significantly to the fundamental understanding of unique properties of actinide-based materials.

Discovery of Novel U- and Th-based Materials: $U_{11}Hg_{43}$, $ThPt_{3+x}Be$, and UBeGe

During the last three years, we have been searching for novel heavy fermion materials. We have noticed that U-based compounds with the highest Sommerfeld coefficient γ (UCd_{11}, U_2Zn_{17}, and UBe_{13}) all host U atoms with high coordination numbers (CN). An extensive search of compounds with $CN_U \geq 9$, has resulted in the discovery of $U_{11}Hg_{43}$ – a heavy fermion antiferromagnet with $\gamma = 630$ mJ/mol K^2 and $T_N = 2.3$ K (Fig. 1(a)) [1]. Its crystallographic structure (inset of Fig. 1(a)) is composed of four types of polyhedra, with $14 \leq CN_U \leq 16$. The antiferromagnetic order of $U_{11}Hg_{43}$ is suppressed with magnetic field (H_c = 11.6 T). However, the application of pressure does not change the transition up to p = 1 GPa.

Another novel material is UBeGe, which has been identified as a uniaxial ferromagnet with T_C = 157 K (Fig. 1(b) and (c)) [2]. The temperature-dependent XANES spectra confirm local scenario, suggested by the U-U distances exceeding the Hill limit. Interestingly, this is the first observation of temperature-dependent spectral intensities, which, according to the DFT calculations, are driven by ferromagnetic ordering of the U moments.

Based on the fruitful physical properties of Ce-based perovskite and antiperovskite compounds such as $CePt_3Si$ and $CePt_3Si$, we have been investigating their Th-based analogues. This resulted in a discovery of a new compound - $ThPt_{3+x}Be$ (Fig. 1(d)), which crystallizes in its unique body-centered tetragonal structural arrangement, related to the cubic Ru_3Sn_7 and $W_2Cr_{21}C_6$ structure types [3]. An extensive bonding analysis reveals that $ThPt_{3+x}Be$ is stabilized by strong Pt-Th bonding with an additional supporting Be-Pt bonding framework (see report Kohout).

Improving Sample Quality of Known U-based Materials: $U_2Cu_{17-x}Ga_x$ and UBe_{13}

The $U_2Cu_{17-x}Ga_x$ system is derived from an antiferromagnetic heavy fermion U_2Zn_{17} by replacing

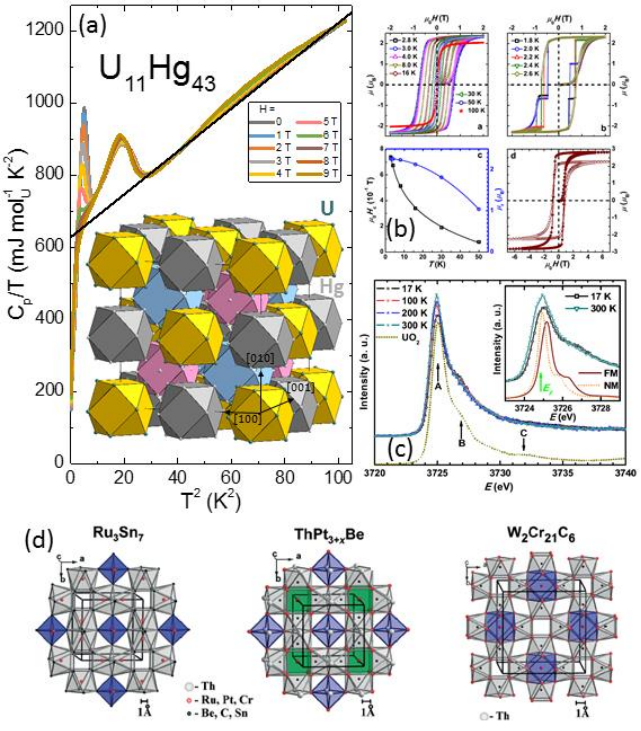

Fig.-1: (a) Novel heavy fermion compound $U_{11}Hg_{43}$ displays γ = 630 mJ/mol K^2, which can likely be attributed to the high CN_U (inset). (b) UBeGe is a uniaxial ferromagnet, with XANES spectra (c) indicating ^{+4}U configuration. (d) $ThPt_{3+x}Be$ (center panel) crystallizes in its own structure type, related to Ru_3Sn_7 (left panel) and $W_2Cr_{21}C_6$ (right panel).

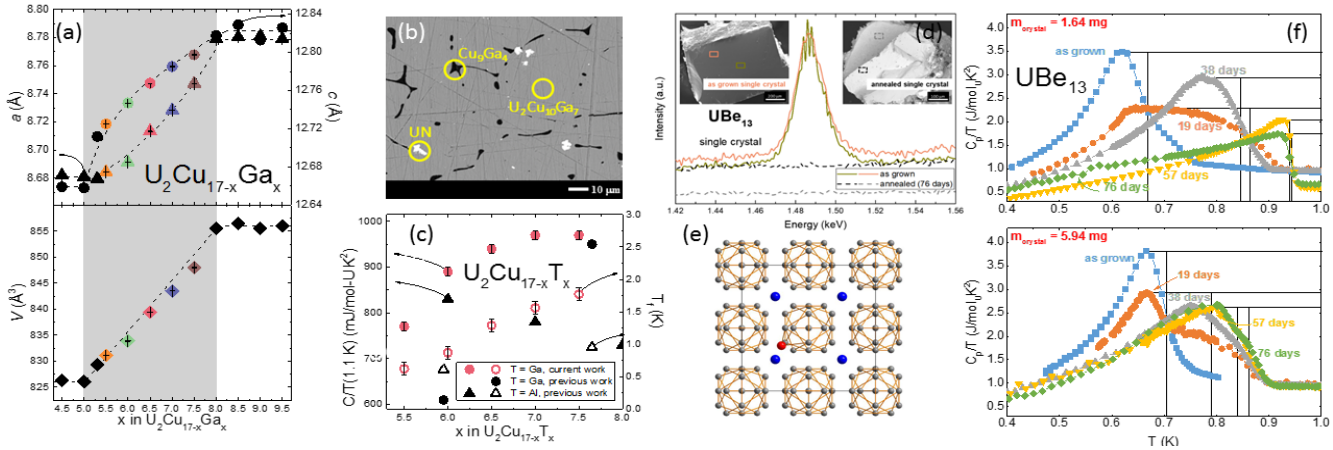

Fig.-2: (a) Crystallographic parameters a (top panel, left axis), c (top panel, right axis), and V (bottom panel) show that the $U_2Cu_{17-x}Ga_x$ system has a limited composition range ($5 \leq x \leq 8$). (b) EDX micrograph of the $x = 7$ sample. (c) The values of the Sommerfeld coefficient γ (left axis) and freezing temperature T_f (right axis) are significantly higher than in previous reports. (d) In the UBe_{13} system, WDX spectra detect Al impurities in as-grown single crystals. (e) Possible lattice defects created by Al substitution. (d) UBe_{13} shows crystal size (top vs. bottom panels) and annealing (various colors) dependence.

all of the Zn atoms with a combination of Cu and Ga. While it has been previously noted that this leads to an effective mass enhancement, proximity to several other binary and ternary heavy fermion compounds has made proper analysis of this system nearly impossible. By implementing a careful crystallographic and EDX analysis, it was possible to establish that this material only exists in a limited composition range, with clean samples only achievable for $5.5 \leq x \leq 7.5$ (Fig. 2(a)) [4]. Furthermore, we have shown that the value of the Sommerfeld coefficient γ is more than doubled compared to U_2Zn_{17}. This, along with non-Fermi liquid behavior, can likely be attributed to the disorder brought on by Cu and Ga mixing as well as twinning.

The UBe_{13} compound has been known for over thirty years with its unusual physical properties suggesting unconventional superconductivity and atypical scenario of non-Fermi liquid behavior. Although single crystals of this material, prepared *via* Al flux method, have been available from early on, it has taken a long while to notice its influence on the physical properties. The amount and even presence of Al impurities in UBe_{13} is not easily detected, calling for an arsenal of techniques, ranging from atomic scale to bulk characterization [5]. Moreover, the Al atoms diffuse and leave the crystal upon annealing. This scenario is further corroborated by the WDX spectroscopy (Fig. 2(c)) - which shows both the incorporation of Al, as well as its elimination upon annealing. The HRTEM (see report Simon) allows to see lattice defects such as Be vacancies, Al substitution as well as sample degradation effects, brought on by long-term annealing. These microscopic effects lead to a drastic variation of the specific heat anomaly, which differs in size, shape, and position, both as a function of crystal size and annealing time (Fig. 1(f)). This comprehensive study provides a long sought after understanding of puzzling properties of UBe_{13}, and the effect Al inclusions have on them.

Outlook

We will extend our coordination-based heavy fermion search to ternary systems. A simultaneous effort in synthesis of single crystalline $U_{11}Hg_{43}$ and UBeGe is underway. We will introduce disorder in UCd_{11} in hopes of enhancing the effective mass even more, as well as comparing the effect of disorder on local *vs.* itinerant systems. The Al inclusions in UBe_{13} will be eradicated using several novel synthesis methods (high temperature and pressure), as well as microstructuring of single-domain devices using focused ion beam. So far, we were able to reproduce both low- and high-temperature behavior of the bulk UBe_{13} crystals. Therefore, we plan to look for quantum oscillations, which have so far been impeded by low single crystalline quality.

External Cooperation Partners

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