Heavy Fermion Behavior in the New Antiferromagnetic Compound UIr$_4$Al$_{15}$

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Abstract. We report the synthesis, crystal structure, and physical properties on the new compound UIr$_4$Al$_{15}$ which crystallizes with the NdRh$_4$Al$_{15.4}$ structure type in the tetragonal space group $P4_{2}/nmc$. From single crystal X-ray diffraction, the compound was found to have unit cell parameters $a = b = 9.0239(6)$ Å and $c = 15.513(2)$ Å. The compound has been synthesized from the flux growth method using an excess of Al metal. UIr$_4$Al$_{15}$ undergoes antiferromagnetic order at approximately 20 K which is consistent with kink-like features in both electrical resistivity and specific heat measurements. Electrical resistivity under hydrostatic pressure shows that the antiferromagnetic ordering temperature is slightly shifted to higher temperatures which is suggestive of the very little pressure dependence and the localized nature of the U 5f electrons. Electronic structure calculations indicated that the Fermi surface of UIr$_4$Al$_{15}$ was quasi two-dimensional.

1. Introduction

Since the discovery of the first heavy fermion (HF) superconductor, CeCu$_2$Si$_2$ [1], the list of additional compounds showing similar properties continues to grow and is detailed very nicely in a review by Pfleiderer [2]. The search continues to be carried out to understand the origin of unconventional superconductivity in this special class of intermetallic compounds. One avenue which is proving to be significant is defining a list of necessary “ingredients” a compound should display so that superconductivity may manifest itself. Two of these qualities which seem promising are crystal systems having tetragonal symmetry and also highly layered systems. As discussed by Lonzarich and co-workers [3], tetragonal systems have a crystal symmetry which is ideal for d-wave overlap and Bauer et al. have shown the correlation of layered systems in the “115” family of compounds as a function of $T_C$ [4]. By far, the number of tetragonal Ce-based HF superconductors dominates the known compounds so far. The isostructural URu$_2$Si$_2$ [5], which shows a superconducting transition at 1.5 K along with a hidden order transition at 17.5 K, is an example of how this crystal chemistry and physics can be extrapolated to actinide-containing compounds. This list of uranium HF superconductors remains small which means that better understanding the dual nature of the 5f electrons in the actinides and how this unconventional superconductivity is mediated can only be carried out by discovering new U compounds. In our search for novel examples of lanthanide and actinide-based binary and ternary HF compounds, we have recently found a new tetragonal antiferromagnet, UIr$_4$Al$_{15}$. We discuss its crystal structure, electronic structure, and usual basic physical properties of magnetization, heat capacity, and electrical resistivity at both ambient pressure and applied hydrostatic pressures up to 6 GPa.
2. Experimental Details

The compound was prepared from its respective elements using an excess of Al. All starting elements were used as received (U: Ames, Ir: Alfa Aesar, Al: Alfa Aesar). Initially, the elements were loaded in 2 cm³ alumina crucibles in the stoichiometric ratio 1:4:15 which were then encapsulated in evacuated quartz tubes. These vessels were then placed in a high temperature furnace that was programmed according to the profile: heated to 800 °C (rate ca. 100 °C/h) where it dwelled for 12 h, heated to 1050 °C (rate ca. 100 °C/h) where it dwelled for 12 h, cooled to 900 °C (rate ca. 60 °C/h) and dwelled for 1 day, and finally cooled to 700 °C (rate ca. 5 °C/h). At this temperature, the reactions were removed and the molten Al flux was isolated through centrifugation resulting in small irregular-shaped crystals corresponding to the title compound. The crystal had shiny facets and the majority of them measured 2-4 mm in length. In the case of the non-magnetic analogue, ThIr₄Al₁₅, which was prepared using an identical recipe, the crystals were typically smaller in size and usually formed aggregates or clusters of small crystallites. Single crystal X-ray and powder diffraction on the flux-grown crystals revealed that the crystal structure of the compound was tetragonal with unit cell parameters \(a = b = 9.0239(6) \, \text{Å}\) and \(c = 15.513(2) \, \text{Å}\) for UIr₄Al₁₅. A detailed summary of the data collection and crystallographic parameters can be found in Table 1. In some cases, small irregular-shaped crystals corresponding to Ir₂Al₉ were found in the reaction and could also be seen being attached to the crystals of UIr₄Al₁₅. The magnetization studies were done on a Quantum Design MPMS in the temperature range 350 K down to 2 K. The raw magnetization data was corrected for the holder contribution and subsequently converted to molar susceptibility. Specific heat measurements were completed on a Quantum Design PPMS with a He3 option. The electrical leads for resistivity measurements were made by spot welding 25 μm Pt wires on a polished face of the crystals. The measurements were then made using an excitation current of 300 μA. Hydrostatic pressures to 6 GPa were generated in a miniature clamped toroid-type anvil cell, equipped with an alumina-epoxy gasket. A sample was placed in a Teflon capsule 2 mm in diameter and filled with a glycerol-water mixture. Pressure was determined by a superconducting transition of Pb.

Table 1. Single crystal X-ray Diffraction data collection parameters.

| Parameter                      | Value                  |
|-------------------------------|------------------------|
| Empirical formula             | UIr₄Al₁₅               |
| Formula weight                | 1411.53 g/mol          |
| Collection temperature        | 273 K                  |
| Radiation, wavelength (λ)     | 0.71073                |
| Crystal system                | Tetragonal             |
| Space group                   | \(P4_2/mmc\)           |
| Unit cell dimensions          | \(a = 9.0239(6) \, \text{Å}\) \(c = 15.513(2) \, \text{Å}\) |
| Unit cell volume, Z           | 1263.2(2) Å³          |
| Density (\(\rho_{\text{calc}}\)) | 7.422 g cm⁻³       |
| Absorption coefficient (μ)    | 55.774 mm⁻¹           |
| Reflections collected         | 11884                  |
| Unique reflections            | 870                    |
| GOF on F²                     | 1.155                  |
| Final R indices (I>2σ(I))     | \(R_1 = 0.0198\)       |
|                               | \(wR_2 = 0.0413\)      |

Figure 1. The crystal structure of UIr₄Al₁₅ with the unit cell outlined in red. The arrow points to the isolated U atom with the coordination atoms around it.

3. Results and Discussion

The crystal structure for UIr₄Al₁₅ is shown in Figure 1. From X-ray single crystal and powder diffraction analysis, it was determined that the compound crystallized with the NdRh₄Al₁₅.₄ structure type [6] in the tetragonal space group \(P4_2/mmc\). More recently, two new rare-earth quaternary phases adopting this type were reported and are described with the formula RE₉Fe₄Al₉Si₀. Since the crystal structure is complex and has already been detailed very nicely in the aforementioned phases, only a brief description will be given here. The structure contains 10 crystallographic sites, one U, two Ir, and seven Al atoms. The structure can be envisioned as being constructed from full and empty polyhedral of U atoms located in the center of a cage made up of Ir and Al atoms. A closer view of this coordination environment is
shown in Figure 1 as an isolated polyhedron. The U atom is surrounded by 20 nearest neighbours with a coordination environment similar to that found in cubic skutterudite structures.

The paramagnetic band-structure for UIr$_4$Al$_{15}$ has been calculated with the augmented plane-wave Wien2k code [8] in the GGA approximation [9]. The unit cell contains four formula units and has a total of 80 atoms. The calculations were converged with on a k-point mesh of 17 X 17 X 10 using R$_m$ = 7 and G$_{max}$ = 20. The muffin-tin radii were 2.5 a$_0$ (Bohr radius) for U, 2.46 a$_0$ for Ir, and 2.19 a$_0$ for Al. Spin-orbit coupling was included using a second-variational method [8]. The total density of states (DOS) and the Fermi surface for three representative bands that cross the Fermi surface are presented in Figure 2. The main features in the DOS are a broad Ir $d$ band that is mainly between -5 eV and 0 eV (where energies are plotted relative to the Fermi energy, which is set to 0 eV), and a very narrow spin-orbit split set of U $f$ bands with bandwidths between about 0.3 to 0.5 eV and a spin-orbit splitting of approximately 0.7 eV. Lying partially

below and also hidden beneath the Ir-$d$ and U-$f$ peaks are broad Al $s$-$p$ bands. The total DOS reflects the relative weighting of the atomic projected DOS by 15 Al atoms and 4 Ir atoms per every U atom (i.e., the Al and Ir contributions to the total DOS are enhanced by these atomic ratios). In the paramagnetic phase, the DOS at the Fermi energy is dominated by very narrow U-$f$ ($J=5/2$) bands. The total DOS at the Fermi energy is about 115 states/(eV cell), and corresponds to a band-structure contribution to the specific heat gamma of about 68 mJ/(mol K$^2$). With so many atoms per unit cell and such flat U-$f$ bands, the number of electronic energy bands that cross the Fermi energy is large (approximately 10 bands; although at least 4 of these bands are marginal in that the crossing occurs at the very top or very bottom of these bands, and small numerical inaccuracies could cause them to miss; in fact, increasing the mesh size from 11 X 11 X 6 to 17 X 17 X 10 increases the number of these crossing bands from 8 to 10). Some representative Fermi surface sheets are presented in Figure 2. Most of the bands have almost vertical sheets indicating a high degree of two-dimensional character.
Figure 3 displays the magnetic susceptibility $\chi(T)$ normalized per mol U atom in the formula unit. The $\chi(T)$ data show Curie-Weiss behaviour down to ca. 20 K where an anomaly is observed which is of antiferromagnetic origin. A linear fit to the data, plotted as $\chi^{-1}(T)$ (shown in the inset of Figure 3), using $\chi(T) = C/(T - \theta_{CW})$, where $C = N_A^2/3k_B$ is the Curie constant and $\theta_{CW}$ is the Curie-Weiss temperature, yields an effective moment of 2.65 $\mu_B$ which is slightly lower for that expected for U$^{3+}$/U$^{4+}$ and a negative Curie-Weiss temperature of -54 K that is consistent with an antiferromagnetic ground state.

The specific heat results are provided in Figure 4. The heat capacity was measured on flux-grown crystals of UIr$_4$Al$_{15}$. As consistent with the cusp-like feature in $\chi(T)$, $C/T$ vs. $T$ for UIr$_4$Al$_{15}$ shows a sharp peak at ca. 20 K with a heat capacity reaching nearly 1 J/mol-K$^2$ in the ordered state as shown in Figure 4a. The nonmagnetic counterpart was also successfully synthesized and was used for suitable phonon subtraction to the specific heat. The Sommerfeld coefficient, gamma, obtained by extrapolation of the data below the ordering temperature is on the order of 86 mJ/mol-K$^2$, indicating moderately heavy fermion-like behaviour. The top inset in Figure 4a, shows a fit to the data in order to determine the gap $\Delta_T$ in the magnon spectrum. According to the equation delta $C(T) = \gamma T + C_{mag}(T)$, where $C_{mag}(T)$ is defined by an equation taken from Perdew [9] and de Medeiros [10], the specific heat data was fit and it was determined that the value of the gap was 29 K. By taking into account the phonon contribution to the specific heat by subtraction of ThIr$_4$Al$_{15}$, results in the total entropy of the magnons being slightly smaller than Rln2 for UIr$_4$Al$_{15}$, suggesting a doublet ground state for U as displayed in Figure 4b.

The electrical resistivity, $\rho(T)$, measured on the same flux-grown crystals as the specific heat measurements for UIr$_4$Al$_{15}$ is provided in Figure 5. The $\rho(T)$ data was typical of a metallic system and remains fairly temperature independent down to 150 K, where a broad coherence peak is observed. The kink in $\rho(T)$ is attributed to the onset of long range antiferromagnetic order. The $\rho(T)$ data were also fit using a gap equation proposed by Continentino [11] to determine the gap in the magnon spectrum. The $\rho(T)$ data were first subtracted from the electrical resistivity data for ThIr$_4$Al$_{15}$ and the value of the gap was determined to be 24 K, close to that determined from the specific heat data. $\rho_0$ was found to be 94 $\mu\Omega$-cm which would result in a RRR value of nearly 3. The derivative plots in Figure 5c indicate clearly that the antiferromagnetic ordering temperature smoothly moves to higher temperature for increasing pressure. The small dependence on the applied hydrostatic pressure suggests that the U magnetic moments can be thought of as being more localized than itinerant.

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