Kondo behavior of U in CaB₆

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Abstract. – Replacing U for Ca in semiconducting CaB₆ at the few at.% level induces metallic behaviour and Kondo-type phenomena at low temperatures, a rather unusual feature for U impurities in metallic hosts. For Ca₀.₉₉₂U₀.₀₀₈B₆, the resistance minimum occurs at T = 17 K. The subsequent characteristic logarithmic increase of the resistivity with decreasing temperature merges into the expected T²-dependence below 0.8 K. Data of the low-temperature specific heat and the magnetization are analyzed by employing a simple resonance-level model. Analogous measurements on LaB₆ with a small amount of U revealed no traces of Kondo behavior, above 0.4 K.

The Kondo phenomenon, a many-body effect affecting the conduction electrons via their interaction with localized magnetic moments, is notorious for d-transition metal impurities in simple metals [1]. Kondo behaviour is also often observed in metallic compounds, in which a small number of cation sites are occupied by rare-earth ions, usually trivalent Ce. A well-known case for this type of dilute Kondo systems is (La, Ce)B₆, with a Ce-content on the few percent level. At low temperatures, all the typical Kondo anomalies, as for example in the resistivity [2] or in the specific heat [3], were observed. Adding the light actinide element U instead of the lanthanide Ce into the same metallic matrix does not lead to any Kondo anomalies, however [4]. This reflects the notorious observation that magnetic moments due to 5f electrons do not induce a Kondo effect in a metallic host with a large number of itinerant charge carriers. It is assumed that this is caused by a broadening of the 5f-states via hybridization with the conduction band states, and hence the f-electrons lose their localized character. In this work we demonstrate that the situation changes if U occupies a few cation sites in the low-carrier density matrix CaB₆, with a background density of conduction electrons of the order of 10⁻⁴ per unit cell [5]. Our data on the low-temperature behaviour of the electrical resistivity, the magnetic susceptibility and magnetization as well as the specific heat clearly indicate that 5f-electron moments may, under special circumstances, induce the classical Kondo effect.

A single-crystalline sample of Ca₀.₉₉₂U₀.₀₀₈B₆ was grown in a flux of Al, using the necessary high-purity starting elements U, Ca and B. For measurements of the resistivity between 0.4
Fig. 1 – Temperature dependence of the electrical resistivity for Ca$_{0.992}$U$_{0.008}$B$_6$ in zero magnetic field. The solid line in the main frame represents the result of the calculation explained in the text. The left upper inset shows $\rho(T)$ for $T < 30$ K and the fit employing eq. (1). The right lower inset emphasizes the $T^2$-dependence of $\rho$ for $T < 0.8$ K.

and 300 K, the sample was contacted at four small spots by a silver-epoxy glue and a low-frequency ac-method was applied. The specific heat was measured between 0.4 and 12 K, using a relaxation-type method. Measurements of the susceptibility and the magnetization, up to 5.5 T, were performed using a commercial SQUID magnetometer. In order to avoid the influence of possible magnetic impurities at the surface, the sample was etched several times for a short duration in diluted nitric acid.

The main frame of fig. 1 shows the temperature dependence of the resistivity $\rho(T)$ for Ca$_{0.992}$U$_{0.008}$B$_6$ in zero applied magnetic field and for temperatures between 0.4 and 300 K. Below room temperature, $\rho$ decreases almost linearly with decreasing $T$, reaches a minimum at $T = T_{\text{min}} \approx 17$ K and subsequently increases again with decreasing temperature, tending to a finite value at $T = 0$ K.

At $T > 30$ K, $\rho(T)$ is best described by employing a model that was recently introduced for handling Eu-based hexaborides [6, 7]. The conduction electrons are assumed to be scattered by disordered magnetic moments, lattice vibrations and lattice defects. Considering the low concentration of magnetic U ions and temperatures exceeding 30 K, our analysis establishes a negligible and temperature-independent spin-disorder resistivity and a defect resistivity $\rho_{\text{d}} = 1.68 \cdot 10^{-4} \, \Omega \text{m}$. The phonon spectrum of the B$_6$-lattice is assumed to be that of a Debye solid with a Debye temperature $\Theta_D = 1160$ K [8]. The motion of the Ca and U ions is taken into account by two independent harmonic oscillators with Einstein temperatures of $\Theta_{\text{Ca}}^E = 373$ K [7] and $\Theta_{\text{U}}^E = 137$ K, respectively. The solid line in fig. 1 represents the fit to $\rho(T)$ according to this calculation. The temperature dependence of $\rho$ in this regime is entirely due to electron-phonon scattering.

Below $T \approx 17$ K, the resistivity increases again with decreasing $T$. Between 2.5 K and 10 K, this increase is very close to logarithmic. In non-magnetic host materials with magnetic impurities, such a $T$-dependence is usually attributed to the formation of virtual bound states of the conduction electrons at the magnetic sites. According to Hamann [9], the magnetic-
impurity scattering leads to a resistivity

$$\rho_{\text{imp}} = \frac{\rho_0}{2} \left\{ 1 - \frac{\ln(T/T_K)}{\left[ \ln(T/T_K) \right]^2 + \pi^2 S(S+1)^{1/2}} \right\},$$

where $T_K$ is the Kondo temperature and $S$ is the spin of the magnetic impurity. The upper inset in fig. 1 shows $\rho(T)$ for $T < 30$ K. The fit according to eq. (1), displayed as the solid line in the inset, yields $T_K = 2.0 \pm 0.1$ K and $S = 1/2$, indicating a doublet ground state of the crystal-field split $U$ 5f-electron multiplet.

In compounds, $U$ adopts a tri- or tetravalent configuration. Under the simplifying assumption that Hund’s rule and Russel-Saunders coupling are valid, free $U^{4+}$-ions carry a total angular momentum of $J = 4$. Lea, Leask and Wolf [10] established the ground states for various values of $J$ in a variety of different cubic crystal-field environments. For $J = 4$, the ground state is either a singlet or a triplet. Free $U^{3+}$-ions adopt an angular momentum $J = 9/2$. For a value of the crystal field parameter $x < 0.4$, the CEF split ground state is the doublet state $\Gamma_6$. A spin value of $S = 1/2$ obtained from fitting eq. (1) to our data suggests that $U$ most likely adopts the trivalent 5f$^3$ configuration and the ground state is the $\Gamma_6$-doublet.

It is expected that at $T \ll T_K$, the Kondo system exhibits a crossover to Fermi liquid behavior [11]. For the $n$-channel Kondo model with $n = 2S$, the relevant contribution to $\rho$ is [12]

$$\rho_{\text{imp}}(T) = \rho_{\text{imp}}(0) \left\{ 1 - \left( \frac{\pi^2}{12T_L} \right)^2 (4n+5)T^2 \right\}.$$

In our case, $n = 1$ and the corresponding fit, shown in the lower inset of fig. 1, results in $T_L \sim T_K \cdot \pi \approx 6.0$ K. This corresponds to $T_K \approx 1.9$ K, in very good agreement with the value mentioned above. Since $\rho_{\text{imp}}$ strongly depends on the magnitude of the residual resistivity, this analysis is less reliable, however.

Further evidence for the Kondo behavior of $U$ in $\text{CaB}_6$ is obtained from measurements of the specific heat at low temperatures. Figure 2 shows, on double-logarithmic scales, the measured specific heat $C_p(T)$ in zero magnetic field for the same specimen of $\text{Ca}_{0.992}U_{0.008}\text{B}_6$.
between 0.4 and 12 K. The broad bell-shaped anomaly, observed at low T with a maximum at \( T = 0.61 \) K, indicates the formation of a ground state with a strongly enhanced electronic specific heat. The background of the lattice specific heat was calculated by invoking the same model parameters that were used in our calculation of \( \rho(T) \) described above. The result is represented by the solid line in fig. 2. For \( T > 6 \) K, we attribute the excess specific heat \( C_{CEF} \) to excitations to higher-lying crystal-field levels of the 5f electrons. The corresponding fit, employing well-known calculation procedures [13], is indicated by the dotted line in fig. 2 and suggests that the next higher levels are separated from the doublet ground state by \( \Delta_{CEF}/k_B = 25 \) K. It may be seen that at low temperatures, \( C_p(T) \) is dominated by the electronic contribution. Subtracting the mentioned two background contributions from the experimental \( C_p(T) \) data results in \( C_K(T) \):

\[
C_K(T) = C_p(T) - C_{lattice}(T) - C_{CEF}(T),
\]

which is plotted as open circles in fig. 3. This contribution is interpreted as being due to the Kondo-induced enhanced density of states at the Fermi energy \( D(E_F) \). Also shown in fig. 3 are \( C_K(T) \) data in different external magnetic fields.

The maximum of the bell-shaped curve of \( C_K(T) \) is, as expected, shifted in magnitude and temperature upon application of external magnetic fields. Our analysis of these data is based on the resonance level (RL) model of Schotte and Schotte [14], which assumes a Lorentzian shape of the electronic density of states \( D(\epsilon) \) centered at the Fermi level and given by

\[
D(\epsilon) = \Delta/\pi(\epsilon^2 + \Delta^2).
\]

We obtain consistent fits to the experimental curves of \( C_K(T, H) \) by postulating \( S = 1/2 \), setting \( \Delta/k_B = 1.6 \) K and inserting a \( g \)-factor of 1.7. They are shown as solid lines in fig. 3. The reduction of the \( g \)-factor is equivalent to a reduced effective magnetic moment \( \mu_{eff} \) of the U ions, reflecting the magnetic screening of the local moments by the conduction electrons [14, 15].
Inserting the value for $\Delta$ into eq. (4) yields, for $\epsilon = 0$, the density of states $D(E_F)$. Considering that the electronic specific-heat parameter $\gamma$ is given by

$$\gamma = \frac{2}{3} \pi^2 k_B^2 D(E_F),$$

we obtain $\gamma = 92 \text{ mJ}/(\text{K}^2 \cdot \text{mole-U})$. For comparison, we calculate $\gamma'$ for the case of an ordinary conduction band with a quadratic dispersion relation and populated by one electron per U-ion. The effective mass is $m^* = 0.28 m_0$, the same as for itinerant charge carriers in CaB$_6$ [16]. With these assumptions, we obtain $\gamma' = 0.19 \text{ mJ}/(\text{K}^2 \cdot \text{mole-U})$, implying that the Kondo interaction leads to an enhancement of the specific-heat parameter by

$$\gamma_K/\gamma' \approx 480.$$
both magnetic and specific-heat data can be well reproduced even quantitatively with this simple model. Of course, all these considerations are only valid at low temperatures, where the Kondo-induced features dominate the electronic properties.

Most earlier experimental attempts to demonstrate the onset of the Kondo effect due to U impurities were either unsuccessful or did not provide conclusive results. Previous work on the influence of U replacing La in LaAl\(_2\), e.g., claimed the first observation of the Kondo effect in a dilute actinide alloy [18]. We believe that, in retrospect, the experimental evidence for that claim is not convincing. We argue that also in that case, the local moment character of the U ions was not well enough developed. Some indications for a Kondo-type behaviour of the resistivity [19] and the low-temperature specific heat [20] data were reported for compounds of the type Th\(_{1-x}\)U\(_x\)Se and Th\(_{1-x}\)U\(_x\)S in the range 0.06 < x < 0.26. The available data did not allow to unambiguously distinguish between Kondo behaviour [20] and a mixed-valence situation [19]. A logarithmic T-dependence with a negative slope of \(\rho(T)\) was also reported for Th\(_{0.86}\)U\(_{0.14}\)Sb [21]. Again, the situation seems ambiguous and a mixture of mixed valency and Kondo effect cannot be excluded [22]. Our data, however, indicate that the insertion of U at the low at.% level into a matrix with a very low conduction electron concentration, such as CaB\(_6\), favors the stability of the local moment on the U site, leading to a well-developed classical Kondo effect at low temperatures.

Our observation of Kondo anomalies in the temperature dependences of selected physical properties, induced by U impurities in CaB\(_6\), is significant in various respects. First, if we consider that the background concentration of conduction electrons in CaB\(_6\) is of the order of \(10^{-4}\) per unit cell and that each U ion provides a magnetic moment as well as of the order of one conduction electron per impurity, our result demonstrates that Kondo screening is possible also when the concentration of magnetic moments and of the itinerant electrons is the same. Next, the stability of the U 5\(f\)-electron moments to be screened is due to the low background density of electronic states in the host matrix. In spite of the extension of the 5\(f\)-electron wave function, the essential matrix element describing its hybridization with itinerant electron states is thus kept small. This is believed to be a prerequisite for local moment behaviour in such cases [23]. Finally, for the experimental verification of the Kondo effect, the low value of \(T_K\) is favorable but it also reflects a very delicate balance of the relevant electronic energy scales in this particular case. As expected, at very low temperatures, the electron system providing the Kondo screening turns into a Fermi liquid with strongly renormalized parameters, such as a strongly enhanced density of states \(D(E_F)\) at the Fermi level.

The absence of a Kondo effect by U impurities in LaB\(_6\), a metal with a much higher conduction electron concentration, confirms this interpretation. Our results provide convincing evidence that the often demonstrated influence of 4\(f\) electrons on anomalous low-temperature properties of metals may, under special circumstances, also be provoked by 5\(f\) electrons.

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