Anomalous negative thermal expansion of CeInCu$_2$

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The coefficients of linear thermal expansion, $\alpha(T)$, of the heavy-fermion compound CeInCu$_2$ and its non-heavy analog LaInCu$_2$ have been measured at low temperatures ($0.3 \text{K} < T < 12 \text{K}$). In the heavy-fermion regime $\alpha(T)$ of CeInCu$_2$ shows a large positive contribution (with an electronic Grüneisen parameter $\Gamma_\alpha \approx 40$), while below $\approx 4 \text{K}$ a crossover to a pronounced negative contribution takes place. The negative contribution is associated with (short-range) antiferromagnetic order ($\Gamma_\alpha = -32$). The temperature variation of $\alpha$ of CeInCu$_2$ bears a close resemblance to that of CeAl$_3$.

1. Introduction

The cubic Heusler alloy CeInCu$_2$ has attracted considerable attention because of its classification as a heavy-fermion compound on the verge of magnetic order. In a first series of experiments the low-temperature anomalies, observed in the magnetic, transport and thermal properties [1-4], were interpreted as arising from pronounced Kondo lattice effects with a Kondo temperature $T_K \approx 6 \text{K}$. In particular, the broad hump in the electronic specific heat centered at 2.3 K was explained as to originate from strong antiferromagnetic intersite correlations yielding an anomalously large value of the coefficient of the linear term: $\gamma = 1.2 \text{J/mol K}^2$. Subsequently, on the microscopic level, NMR measurements [5,6] evidenced an antiferromagnetic transition near $T = 2 \text{K}$. Elastic neutron-scattering experiments [7,8] confirmed antiferromagnetic order (the magnetic structure is the so-called type 1 structure of an FCC antiferromagnet) with a Néel temperature $T_N = 2.3 \text{K}$. The ordered moment is rather small (0.3–0.4$\mu_B$/Ce-atom), a general feature of heavy-fermion antiferromagnets. However, the interpretation of the low-temperature magnetic properties is substantially complicated, because the major part of the magnetic signal appears as diffuse magnetic scattering and only a small part appears as Bragg peaks [7,8]. The diffuse magnetic scattering can be interpreted as originating from either short-range antiferromagnetic correlations or imperfect magnetic order. Indeed, the residual resistance values of the CeInCu$_2$ samples produced so far are rather large ($\rho_0 \approx 70 \mu\Omega \text{cm}$) [1-4], which suggest imperfect crystalline and magnetic order. On the other hand, by substituting Ag for Cu, the residual resistance value decreases, while $T_N$ increases [1] as a result of the weakened hybridization, in accordance with Doniach’s phase diagram. This suggests that CeInCu$_2$ is indeed on the verge of magnetic order.

In the course of an investigation of the volume anomalies that accompany magnetic instabilities in heavy-fermion compounds (e.g., UPt$_3$, CeCu$_6$ and CeRu$_2$Si$_2$) [9,10], we here report on an accurate dilatometry study of polycrystalline CeInCu$_2$ and LaInCu$_2$ at low temperatures.

2. Experimental

Polycrystalline CeInCu$_2$ and LaInCu$_2$ samples were shaped by means of spark erosion into a cube (edge $5 \text{mm}$), with at least two surfaces parallel to within $5 \mu\text{m}$. The samples were mounted in a three-terminal parallel-plate capacitance cell machined of oxygen-free high-conductivity (OFHC) copper [11]. The sensitive dilatometer, with a detection limit of 0.01 Å, was attached via a heat impedance to the cold plate of a $^3$He cryostat operated with an adsorption pump. The coefficient of linear thermal expansion, $\alpha = L^{-1} \frac{dL}{dT}$, was measured by stepwise increasing the cell temperature ($\Delta T \geq 20 \text{mK}$), while recording the change in length ($\Delta L$). The measurements were performed in the temperature interval $0.3 \text{K} < T < 12 \text{K}$. The data have been corrected for the so-called cell effect, i.e., the signal of the cell with a dummy OFHC copper sample.
3. Results

The experimental results are shown in fig. 1. The temperature variation of $\alpha$ of CeInCu$_2$ is highly anomalous. It can be attributed almost completely to the anomalous behaviour of the f-electrons, since the $\alpha$ of the non-f-electron analog LaInCu$_2$ is at least one order of magnitude smaller in the whole temperature range. At high temperatures, $\alpha$ is large and positive with a maximum centered at $T_{\text{max}} = 4.5$ K. For $T < T_{\text{max}}$ a broad crossover to a pronounced negative contribution with a minimum centered at $T_{\text{min}} = 1$ K takes place. For comparison we have plotted in fig. 2 the specific heat data, $c(T)$ [1].

Recently, two other studies of $\alpha(T)$ of CeInCu$_2$ have been reported. Oomi et al. [12] employed a strain-gauge technique, focusing on a different temperature interval ($T > 4.2$ K) and, consequently, their data have little overlap with ours. A maximum in the magnetic contribution to $\alpha$, observed by Oomi et al. [12] around 25 K, was interpreted as arising from a Schottky anomaly caused by the population of the first excited doublet crystal field state at $\approx 60$ K. However, the data in fig. 1 suggest that the actual analysis is more complicated because of the broad large magnetic contribution at low temperature. Matsui et al. [13] have measured $\alpha(T)$ in the temperature interval 2 K $< T < 12$ K with a capacitance technique. Their results do agree qualitatively with our data in fig. 1, but show a large scatter.

4. Discussion

First it is of interest to compare the thermal expansion and specific heat data (figs. 1 and 2). The increase in $c(T)$ below $T = 4.2$ K leading to the broad hump centered at $T = 2.3$ K, concurrent with a decrease in $\alpha(T)$ below $T = 4.5$ K and a maximum in $d\alpha/dT$ close to 2 K. We attribute the broad low-temperature anomaly to the above-mentioned (short-range) antiferromagnetic order [5–8].

Next we investigate the (temperature-dependent) effective Grüneisen parameter, $\Gamma_{\text{e}}(T) = \alpha_e(T) V_m / \kappa c(T)$, where the coefficient of volume expansion is given by $\alpha_e = 3\alpha$ (cubic symmetry), $V_m = 4.728 \times 10^{-5}$ m$^3$/mol is the molar volume and $\kappa = V^{-1} dV/dP$ is the isothermal compressibility. Several values for $\kappa$ can be found in the literature: 1.35 Mbar$^{-1}$ (from the initial pressure dependence of the lattice parameter at room temperature as determined by strain gauges up to 15 kbar [3]), 1.8 Mbar$^{-1}$ (from low-temperature elastic constants [13]) and 1.0 Mbar$^{-1}$ (from the overall pressure dependence of the lattice parameter at room temperature as determined by X-ray measurements up to 140 kbar [14]). In fig. 3 we show the electronic Grüneisen parameter $\Gamma_{\text{e}}(T) = \alpha_{\text{e}}(T) V_m / \kappa c(T)$ (where we used a value for $\kappa$ of 1.35 Mbar$^{-1}$ [3]). The electronic contributions to $\alpha_e(T)$ and $c(T)$ have been deduced by subtracting the phonon parts, as determined by measurements on LaInCu$_2$, from the total signal. Note that in the temperature interval 0.3 K $< T < 1.3$ K, $c(T)$ has been obtained by an extrapolation conform the data in ref. [4]. Above 4 K, $\Gamma_{\text{e}}$ is only weakly temperature dependent and a large value, typical of heavy-fermion compounds [9], is observed. At $T = 4$ K, $\Gamma_{\text{e}} = 42$, in good agreement with previous estimates [3,13]. The electronic Grüneisen parameter for the low-temperature contribution equals $-32$. Associating $\Gamma_{\text{e}} = -32$ ($T \to 0$) with the (short-range) antiferromagnetic order we deduce a suppression of $T_N$ at
a rate of $dT_N/dp = -0.1 \text{K/kbar}$. This is in good agreement with the value for $\Gamma'_{el} = -35 \pm 5$ evaluated from the variation of $T_N$ at small negative chemical pressures in the series CeInAg$_{2-x}$Cu$_x$ for $1.7 < x < 1.9$ [1].

The thermal expansion of CeInCu$_2$ bears a close resemblance to $\alpha(T)$ of heavy-fermion CeAl$_3$, although in the latter compound the energy scale is reduced and $\Gamma'_{el}(T \rightarrow 0) = -200$ [15]. Also in CeAl$_3$ antiferromagnetic order with reduced moments develops below $T_N = 0.7 \text{K}$ [16]. Furthermore, negative thermal expansion contributions below $T_N$ have been observed in the heavy-fermion antiferromagnets CeRu$_3$Si$_2$ doped with La and UPt$_3$ doped with Pd [10]. The present data on CeInCu$_2$ confirm that the development of antiferromagnetic order in a strongly correlated electron system is accompanied by a strong reduction of the coefficient of volume expansion, in accordance with decreasing hybridization.

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References