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Specific heat of CeB_6 under high pressure

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Abstract. The specific heat of the heavy fermion compound CeB_6 has been studied under quasi-hydrostatic pressure up to 1.35 GPa in the region 0.7–4.5 K. We find an increase of the antiferromagnetic transition temperature T_N of $0.1\,K\,GPa^{-1}$ and a constant antiferroquadrupolar transition temperature T_Q with increasing pressure. Additionally, a remarkable change in the shape of the antiferromagnetic λ anomaly is observed, whereas the antiferroquadrupolar transition is hardly affected by pressure. The electronic specific heat contribution γ shows a non-monotonic variation. We discuss possible mechanisms for this anomalous behaviour of γ and the deformation of the λ anomaly.

1. Introduction

During recent years close attention has been focused on heavy fermion systems. In particular, the variety of ground states of heavy fermion compounds is of interest in present-day research. These ground states can be non-magnetic ($CeCu_6$), superconducting (UBe_{13}), magnetic ($CeAl_2$) or even semiconducting (CeNiSn); for a review, see [1–4].

In general, heavy fermions can be described at high temperatures as metals with well localized f electrons, whereas at low temperatures hybridization effects take over generating a strongly correlated electron system of conduction and f electrons. Below a characteristic temperature T_K (the Kondo temperature) this leads to Kondo-like anomalies in the physical properties, including a strongly enhanced electronic specific heat. For the electronic contribution of the specific heat, the relation $\gamma \propto T_K^{-1}$ is a commonly used approximation, which is strictly valid, however, only for dilute Kondo alloys.

Due to the regular arrangement of localized f electrons, magnetic exchange competes with the Kondo effect. In the simplest picture the competition can be described by only one parameter, the exchange coupling J between conduction and f electrons. Now J itself is dependent on the interatomic distances between the localized electrons and increases with decreasing interatomic distance. Therefore, by applying high pressure an increase of the coupling J will be achieved.

In the case of a magnetically ordered heavy fermion system this increase of the exchange coupling J can be examined by means of a specific heat measurement under pressure. The *shift of the magnetic transition temperature* T_N *and of the Kondo temperature* T_K, *determined* by γ, give insight into their interplay and the role of J.

CeB_6 is a heavy fermion system that orders antiferromagnetically below $T_N = 2.3\,K$ in zero magnetic field [5]. It also undergoes a second-order phase transition at $T_Q = 3.3\,K$

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from a high-temperature paramagnetic to an antiferroquadrupolar (AFQ) ordered phase [6]. This phase is stabilized by a magnetic field; in fields above 2 T it forms the ground state instead of the antiferromagnetic (AFM) phase. For the electronic specific heat, γ values of 250–300 mJ mol^{-1} K^{-2} [7–10] have been reported.

Only one study on the pressure dependence of the low-temperature phase transitions of CeB_6 has been published up to now [11]. Brandt and co-workers measured the pressure dependence of the AC susceptibility and the magnetoresistance at low temperatures up to 1.2 GPa. They reported pressure derivatives of $\partial T_N/\partial p = -(0.39 \pm 0.02)$ K GPa^{-1} and $\partial T_Q/\partial p = (0.09 \pm 0.03)$ K GPa^{-1}.

Schefzyk and co-workers [12] measured the thermal expansion $\alpha(T)$ down to 1.5 K. They concluded that the AFM transition consists of two successive transitions at $T_{N_1} = (2.348 \pm 0.005)$ K and $T_{N_2} = (2.347 \pm 0.002)$ K. Using the Ehrenfest relation the pressure derivatives of both those transitions are expected to be $\partial T_{N_1}/\partial p = 0.4$ K GPa^{-1} and $\partial T_{N_2}/\partial p = -1.6$ K GPa^{-1}. Therefore, when applying pressure the specific heat anomaly at T_N should split into two peaks. Furthermore, the dilatometric data predict a small increase of 0.1 K GPa^{-1} for $\partial T_Q/\partial p$. For a closer examination of the phase transitions and the heavy fermion behaviour of CeB_6 we began a calorimetric study under pressure.

2. Experimental details

The details of the technique applied to study the specific heat under pressure have already been described elsewhere [13, 14]. The sample material, a heater and a thermometer are embedded in a cylinder of gallium, which serves as a pressure mediating and thermal contact medium. This cylinder is mounted in a conventional Cu–Be pressure clamp, thermally isolated from the clamp by a surrounding layer of diamond powder. A piece of indium placed in the sample space serves as a manometer.

The specific heat is measured by an AC technique. This technique requires the dimension of the sample, d, to be much smaller than the thermal penetration depth $\lambda_0 = \sqrt{2\kappa/\rho c_p \omega}$ (where κ is the thermal conductivity, ρ is the material density, c_p is the specific heat, and ω is the frequency of the AC heating current). For CeB_6 this provides the restriction $d \ll 1$ mm; a powder sample is therefore required.

The CeB_6 sample was taken from a single crystal, which was grown using an arc-floating zone technique in 6N pure argon under normal pressure. A part of the crystal was crushed into powder with an average grain size of about 10 μm; 4 mg of the powder was mixed with liquid gallium. The heater and thermometer were separately pressed in liquid Ga. After solidification of the gallium the three pieces were placed in a Teflon form with the thermometer at the bottom, the Ga–CeB_6 mixture in the middle and the heater at the top. By shortly remelting the gallium, the three pieces were attached to each other and after removing the Teflon form we gained a cylinder-shaped sample of 5 mm length and 2 mm diameter. This cylinder was placed in the pressure clamp.

Another piece of the same single crystal was checked with a boron-sensitive electron probe x-ray micro-analyser (EPMA). The EPMA study proved the sample to be homogeneous with the correct 1:6 composition, within experimental error.

The measurement itself was performed in a ^{3}He-cooled cryostat. In the evaluation of the data the addenda heat capacities had to be subtracted. These were small, not exceeding $\approx$ 20% of the heat capacity of CeB_6. After all corrections, the relative accuracy of c_p was $\approx$ 5%, and the absolute accuracy $\approx$ 10%.

When pressure was applied and changed, the clamp was kept at liquid nitrogen temperature in order to prevent the gallium from melting and, as a consequence, creeping into the diamond powder and/or transforming to the Ga II phase with its much larger specific heat [15]. The error of the pressure determination is affected by the inaccuracy of measuring $T_c(p)$ of the In manometer and the subsequent re-calculation into pressure, leading to errors δp between 0 and ± 0.04 GPa from lowest to highest pressure. However, due to the diamond powder used for thermal isolation, pressure differences between the manometer and Ga cylinder can occur. This effect has been studied in detail [16], and it was found that the pressure at the location of the In manometer can be up to 25% higher than the pressure in the Ga cylinder. Thus, the pressure determination error is given as $(+\delta p, -\delta p - 0.25p)$ (where p is the pressure as determined by T_c of In, and δp is the manometer inaccuracy). We remark that this pressure difference between the In manometer and the Ga cylinder is not the value of pressure inhomogeneity across the sample. The latter can be estimated from the broadening of the superconducting transition of the Ga itself and was found to be well below 10% of p.

3. Results and discussion

In figure 1(a) and 1(b) we show the data of the specific heat of CeB_6 for some of our measurements. Within experimental error the zero-pressure measurement is in good agreement with already reported data [5, 7–10, 17]. The essential results of the measurements under pressure are the broadening of the antiferromagnetic anomaly and an associated reduction of c_p at the Néel point, and in contrast the very small effect of pressure on the antiferroquadrupolar transition. Thereby, two pressure regimes can be distinguished: the regime of low pressure with $p \leqslant 0.34$ GPa (hereafter referred to as LPR and plotted in figure 1(a)) and the high-pressure regime of $p \geqslant 0.58$ GPa (figure 1(b); referred to as HPR). In the LPR there is a clear-cut anomaly at the AFM transition with a shape between mean-field-like and λ-like, which hardly changes under pressure. In the HPR, however, the λ anomaly is strongly broadened (at 1.22 GPa and 1.35 GPa a λ-like anomaly can no longer be seen), and there are additional contributions to c_p even above T_Q, increasing the absolute values of c_p at these temperatures.

This broadening of the AFM transition cannot be explained by a pressure inhomogeneity. In the LPR we observe a pressure derivative of $\partial T_N/\partial p \approx 0.1\,\mathrm{K\,GPa^{-1}}$. Assuming now that a pressure inhomogeneity is the driving force for the broadening of the transition, the pressure derivative would be $3\,\mathrm{K\,GPa^{-1}}$ at 1.35 GPa (in order to explain the increase of c_p above T_Q). Because at 1.35 GPa the antiferromagnetic peak rises from 2 K to 5 K, a pressure inhomogeneity as large as the pressure p present at the sample location had to be assumed to account for the broadening, in contradiction to the observed inhomogeneity of 10% of p.

The AFQ phase can also not contribute to the increase of c_p above T_Q in the HPR, because in that case the AFQ anomaly would smear out. This is not the case.

The physical reason for the broadening is not completely clear. We suppose that *the long-range-order correlations are gradually weakened under pressure at the benefit of* short-range-order correlations, which show up in an increasing spread of entropy (and a concomitant transfer to higher temperatures). It appears as if the AFM transition would end up in a kind of critical point at some finite temperature and pressure which, unfortunately, cannot unambiguously be determined from our data. This behaviour might be an outcome of a very sensitive dependence of the RKKY interaction on the atomic distances.

The determination of T_N and T_Q is quite difficult, due to the overlap of the two transitions as well as the broadening of the transition in the HPR. In order to use a reproducible criterion we choose the minima of $\partial^2 c_p/\partial T^2$ as transition temperatures. The pressure

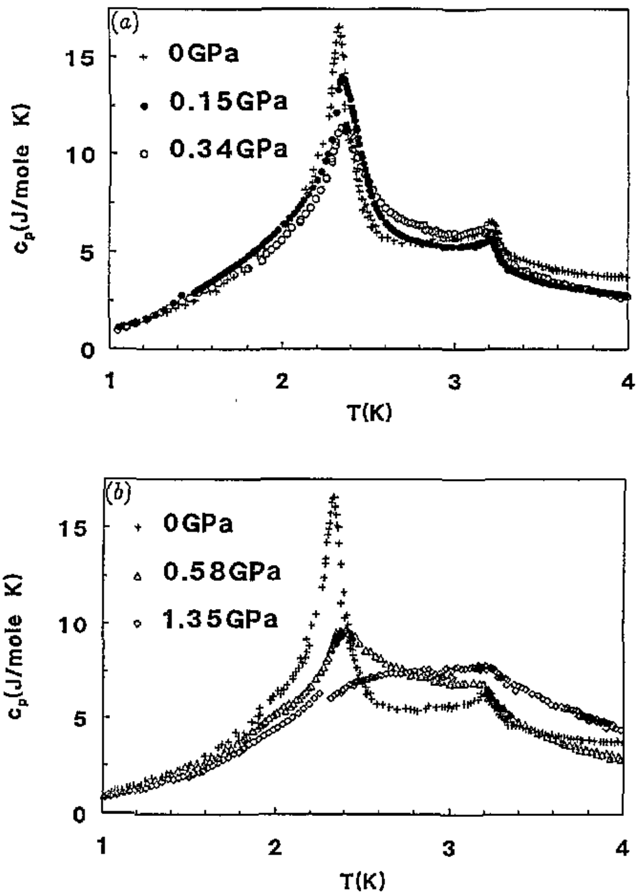

Figure 1. (*a*) The specific heat of CeB_6 in the low-pressure regime. The measurements are taken at 0 GPa (+), 0.15 GPa (•) and 0.34 GPa (○). (*b*) The specific heat of CeB_6 in the high-pressure regime. For comparison the zero-pressure measurement is included (+); further measurements are taken at 0.58 GPa (△) and 1.35 GPa (◇).

dependences of T_N and T_Q are plotted in figure 2(*a*) and 2(*b*). Within the error of the measurement, no pressure effect for T_Q can be observed. For T_N we observe a small increase with an average rate of about $0.1\,\mathrm{K\,GPa^{-1}}$. From this we obtain a Grüneisen parameter $\Gamma_N = -\mathrm{d}\ln(T_N)/\mathrm{d}\ln(V) \approx 5$, which is comparable in magnitude to other magnetic-ordering heavy fermion materials.

No clear-cut splitting of the antiferromagnetic anomaly with pressure is observed. Furthermore, there are no indications that the broadened peak at T_N could be generated by the superposition of two neighbouring peaks. Thus, we cannot verify the proposal of Schefzyk and co-workers [12] of a double transition at T_N. This situation is similar to $CeAl_2$, where thermal expansion measurements have also shown two transitions, but where in many high-pressure experiments of different types only one transition is found with one or other sign for $\partial T_N/\partial p$, respectively ([18] and references therein). The origin and nature of these closely neighbouring phase transitions remains an open question. Moreover, a systematic investigation on their dependence on sample quality is lacking. In any case, one has to be careful in simply extrapolating initial pressure dependences based on the Ehrenfest relation to higher pressures.

The pressure effects determined in our measurements are in disagreement with the values given by Brandt and co-workers [11]. For T_Q the disagreement is small and might be due to different ways of deriving the transition temperature. For T_N, however, we find an increase

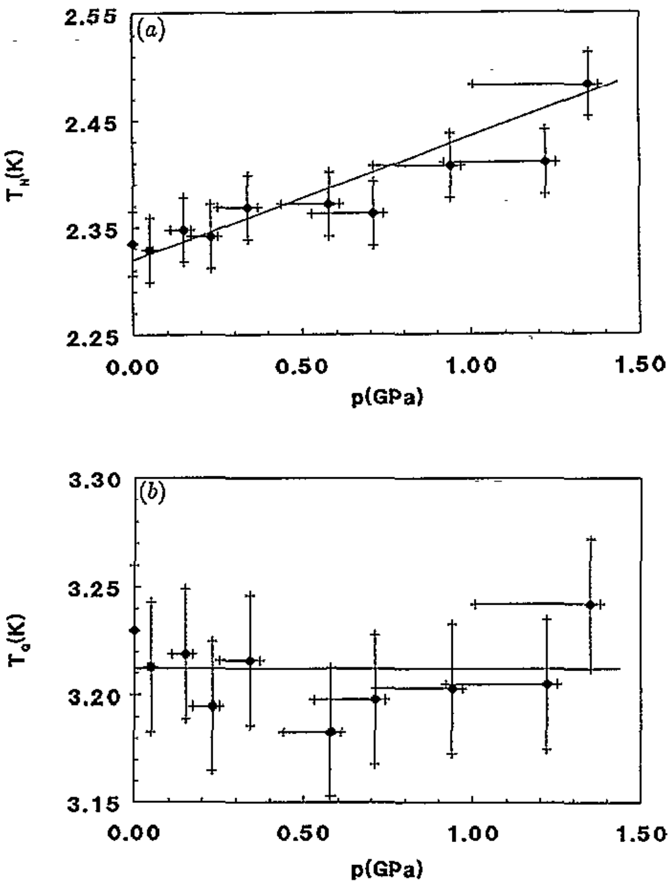

Figure 2. (*a*) The antiferromagnetic transition temperature T_N as a function of p. The line indicates an average pressure effect of $0.1\,\mathrm{K\,GPa^{-1}}$. (*b*) The antiferroquadrupolar transition temperature T_Q as a function of p.

contrary to the reported decrease of T_N. Here, too, we believe that a pressure inhomogeneity (due to our quasi-hydrostatic pressure conditions) cannot account for the different results, since the significant decrease of the absolute values of c_p in the HPR at temperatures below T_N is a further argument in favour of a shift of T_N to higher temperatures.

In this context another result of Schefzyk and co-workers [12] should be mentioned. They also reported results on a second single crystal, which they believed to be of inferior quality. The results for $\alpha(T)$ are the same for both crystals at temperatures above T_N. In both samples they observed a doubled jump of $\alpha(T)$ at T_N, but of opposite sign, respectively. This would lead to interchanged pressure effects. Schefzyk and co-workers argued that domain effects might be responsible for these differences. But of course it is well known that sample quality plays an important role in heavy fermion physics, and that pressure effects might be dependent upon sample quality. It appears from the results of Schefzyk and co-workers [12] that those proposed domain effects are sample dependent and are probably related to the exact sample quality. In effect, if the disagreement in $\partial T_N/\partial p$ between our measurement and that of Brandt and co-workers [11] is due to sample quality, we are not able to decide which of the used samples is the better one. In any case, in order to avoid ambiguity, we checked our sample, as reported, by EPMA, and this analysis as well as the sharp transitions in the specific heat at $p = 0\,\mathrm{GPa}$ rules out any possibility of macroscopic impurities or massive strain.

In the discussion of the mutual stability of the AFM and AFQ phases, however, these discrepancies in the observed $\partial T_N/\partial p$ are of minor importance, since the specific heat anomaly at T_N disappears faster than T_N goes either to zero (with the pressure effect found by Brandt and co-workers [11]) or merges with T_Q (with the pressure effect from the present work).

By fitting the low-temperature data between 0.7–1.5 K via a least-squares fits we evaluate the pressure dependence of the electronic specific heat contribution γ, as plotted in figure 3. The main peculiarity is the minimum of γ at about 0.2 GPa. Here again the distinction between the LPR, being roughly taken as the region of the minimum of γ, and the HPR, being the region of increasing γ, can be seen.

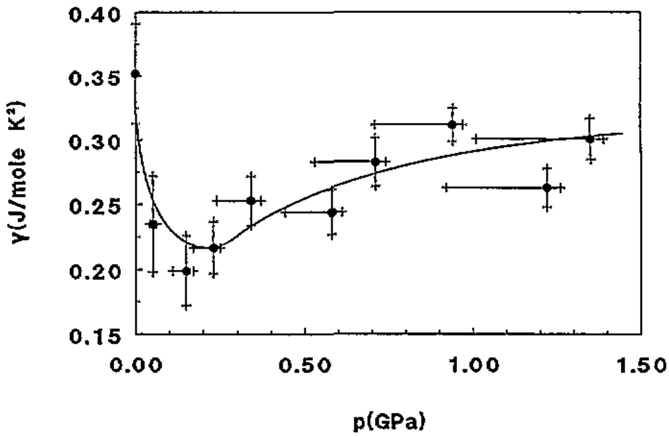

Figure 3. The electronic contribution γ to the specific heat as a function of p. The curve is a guide to the eye.

This minimum and the subsequent increase of γ is quite unusual in Kondo lattice systems. In the simplified model of Doniach, using the exchange coupling J as single parameter [19], a monotonic increase of T_K is expected, from which a corresponding monotonic decrease of γ would follow using the single-ion Kondo picture. Obviously CeB_6 is a system that cannot be described by the Doniach model.

However, in measurements of the specific heat in magnetic fields [8, 9] a similar anomaly of γ shows up. In these measurements a sharp maximum of γ is seen at 2 T, where the AFM phase goes over into the AFQ phase. The value of γ at the maximum is about 500 mJ mol^{-1} K^{-2}. Furthermore, the AFM peak smears out with increasing field [17]. At 1.8 T only a broad bump, quite similar to the broadening we observe in the HPR, indicates the antiferromagnetic transition.

We therefore argue that the increase of γ is a precursor effect of a pressure-induced transition from the antiferromagnetic to the antiferroquadrupolar phase. The minimum of γ would then be due to competing influences. While increasing pressure increases T_K, it also drives the system closer to the border of instability of the AFM phase. We remark that in the study of Brandt and co-workers [11] an increase of the AFQ phase area in the magnetic B–T phase diagram with increasing pressure was found, indicating a strengthening of the antiferroquadrupolar interactions. However, we are aware that here also sample dependences might influence the results, as in case of the disagreements for $\partial T_{N,Q}/\partial p$ between our work and that of Brandt and co-workers [11].

4. Conclusions

We have presented data on the pressure dependence of the specific heat of CeB_6. With our data we cannot confirm the proposal of a double transition at T_N put forth by Schefzyk and co-workers [12]. Furthermore, our measurements are in disagreement with earlier results on the pressure dependence of T_N and T_Q reported by Brandt and co-workers [11]. Sample dependences may account for these disagreements. Finally, we report the pressure dependence of the electronic specific heat contribution γ. We have found a minimum in $\gamma(p)$ and propose this to be a precursor effect of a pressure-induced transition from the antiferromagnetic to the antiferroquadrupolar phase at an even higher pressure. This idea is supported by the observation of a gradual disappearance of the specific heat anomaly at T_N with rising pressure. An extended calorimetric study to higher pressures and under a simultaneous magnetic field will be necessary to verify this conception. While we are quite aware of the experimental problems that will arise in such a work, we believe it would give more insight to the competition of different interactions in heavy fermion systems.

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