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High magnetic field study of the specific heat of CeB₆ and LaB₆

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Résumé. — La chaleur spécifique de CeB₆ et de LaB₆ a été mesurée sur une large gamme de température ainsi que sous champ magnétique jusqu'à 8 teslas. Les résultats confirment que la phase intermédiaire de CeB₆, dénommée phase II, est favorisée sous champ magnétique : la température de transition ainsi que l'anomalie de chaleur spécifique qui lui est associée sont en fait considérablement renforcées. Pour obtenir la contribution magnétique à la chaleur spécifique de CeB₆ avec plus de précision, nous avons mesuré la chaleur spécifique du composé non magnétique LaB₆. L'analyse de cette contribution magnétique confirme que l'état fondamental de l'ion Ce³⁺ est le quadruplet 03⁹₈₈. Nous estimons que la séparation avec le doublet 03⁹₈₇ est supérieure à 500 K.

Abstract. — The specific heats of CeB₆ and LaB₆ have been measured over a large range of temperatures and under magnetic fields up to 8 teslas. The data confirm that the intermediate phase of CeB₆, the so-called phase II, is favoured by an applied magnetic field. Actually both the transition temperature and the associated specific heat anomaly are strongly increased by a magnetic field. To get the magnetic contribution from the CeB₆ specific heat with more accuracy, we have measured the non-magnetic compound LaB₆. The analysis of this magnetic contribution confirms that the Ce³⁺ ground state is the 03⁹₈₈ quartet, and the splitting with the 03⁹₈₇ doublet is estimated to be larger than 500 K.

1. Introduction

Cerium hexaboride, which is one of the most typical Kondo lattices, has been intensively studied during the past last years [1-3]. Besides the Kondo behaviour, CeB₆ undergoes two successive phase transitions at $T_1 = 3.3$ K and $T_2 = 2.4$ K defining three different phases usually denoted phase I ($T > T_1$), phase II ($T_2 < T < T_1$) and phase III ($T < T_2$). Both transitions are intrinsic as shown by many experiments [1-10]. Phase III was established to be magnetically ordered with a complicated double $k$ magnetic structure of commensurate type [11-13], while the nature of phase II remained for a long time unclear. The discovery of an additional phase, III' [13] by applying a magnetic field along the $<111>$ direction, which implies the existence of two kinds of cerium ions, yields J. Rossat-Mignot to propose that some kind of antiferroquadrupolar ordering must build up in phase II. This has been observed by neutron experiments under high magnetic field [14] and some theoretical calculations have been done along this direction [15], so $T_1$ is identified as the quadrupolar transition temperature $T_Q$, and $T_2$ as the Néel temperature $T_N$.

In the trivalent cerium ion, the $^2F_{5/2}$ multiplet is split by the cubic crystalline electric field into a $Γ_7$ doublet and a $Γ_8$ quartet. Up to now, the $Γ_7$ was expected to be the ground state, and the $Γ_8$ lying about 60 K above, from magnetic [16] and specific heat experiments [6]. However, ESR measurements on dilute Er and Dy in LaB₆ have early reported the
possibility of a negative $A_4 \langle r^4 \rangle$ crystal field parameter, which should not change for different rare earth ion in the same hexaboride matrix, since it is mostly affected by the host ligands [17]. The negative sign of $A_4 \langle r^4 \rangle$ is then only consistent with a $I_8^-$ ground state for Ce$^{3+}$. Moreover, a comparative analysis of the large value of the paramagnetic Curie temperature of CeB$_6$ ($\theta_p = -60$ K) and the temperature dependence of the magnetic susceptibility was strongly suggesting the possibility of a $I_8^-$ ground state for Ce$^{3+}$ in CeB$_6$, as mentioned in reference [18].

In addition, some discrepancies between inelastic neutron scattering experiments on CeB$_6$ and magnetic measurements [19, 12, 20] have been reported since no inelastic crystal field peak up to 400 K have been observed, as expected for a CEF splitting of 60 K. This was a motivation for new investigations which have been recently performed to precise the CEF level scheme of Ce$^{3+}$ in CeB$_6$.

Results of neutron and Raman scattering on CeB$_6$ [21], and magnetic measurements on dilute Ce in LaB$_6$ [22] then revealed that the $I_8^-$ is the ground state, while the $I_γ$, is lying 540 K above. In the framework of this new CEF level scheme, a consistent interpretation of the elastic constants [23], susceptibility, and specific heat of dilute Ce in LaB$_6$ was given [24]. We have performed new and detailed specific heat measurements on CeB$_6$ over a wider range of temperatures and magnetic fields than available data [6, 7, 25] to confirm the CEF level scheme. Moreover, we measure the singular behaviour of the phase I-II transition with a particular emphasis. In order to determine the magnetic contribution, the specific heats of CeB$_6$ and LaB$_6$ were measured, using a differential experimental technique, well adapted to this purpose. A short report of this work was published in the proceedings of the Valence Fluctuations Conference held in Cologne [34].

2. Experimental.

Specific heat experiments were carried out using two devices which are both based on a dynamic, differential and adiabatic technique [26, 27]. The first one uses a helium-4 bath and gives access to the $T = 2$-300 K temperature range. A superconducting coil provides magnetic fields up to $H = 8$ teslas. The second one is working between $T = 0.3$ K and $T = 10$ K using a helium-3 refrigerator but without magnetic field.

The sample was put into an aluminium cell. An efficient thermal coupling of the sample is ensured by fixing and sticking it to the cell, and moreover this thermal coupling is improved by a residual pressure of helium inside the cell. As a reference a second cell is equipped like the first one with or without a sample. Both cells are enclosed inside a shield, the temperature of which is linearly increased. Two thermocouples are connected to the same point of the shield from each cell and can force them to follow the temperature of the shield. From the power supplied to each cell and the rate of temperature increase of the shield, the specific heat of the sample is deduced. This technique has however some practical problems:

\begin{itemize}
  \item i) the lack of perfect symmetry between the empty cells which need to be measured and to be taken into account;
  \item ii) the presence of small temperature gradients inside the sample, due to its finite thermal diffusivity, and to thermal radiation effects. Special care has been taken to minimize and to estimate the corresponding errors. Several experiments and tests have been performed.
\end{itemize}

One advantage of this technique is the possibility to measure directly the difference of heat capacities between two samples, placed both in each cell. It is then possible to compare such a measurement with the difference deduced from the two absolute measurements. Another advantage is that it is well adapted for the study of magnetic field effects, as the use of differential thermocouples eliminates any possible variation of the thermopower with field. The absolute temperature is obtained from calibrated carbon and platinum sensors; the magnetoresistance of the carbon resistance has been determined and used to correct the data with applied field [28]. The accuracy on the absolute temperature is better than 0.1 K below $T = 300$ K and about 0.05 K at $T = 4.2$ K. The estimated error on the specific heat is typically about 1-2 \% below $T = 20$ K and increases to 5 \% at the highest temperature.

Two single crystals of CeB$_6$ and one of LaB$_6$ grown by the floating zone method [4], were used for the present study. One CeB$_6$ single crystal has a spherical shape of 6 mm in diameter ($m = 0.537$ g) and was enriched with 99 \% boron 11 for neutron experiments [13]. The second CeB$_6$ and LaB$_6$ samples are cylinders of 8 mm in diameter and 8 mm in length with adjusted masses in order to provide the same molar fraction ($m_{\text{CeB}_6} = 1.4765$ g and $m_{\text{LaB}_6} = 1.3995$ g). The magnetic field was applied along the $\langle 111 \rangle$ axis for both CeB$_6$ samples.

3. Results.

3.1 ZERO MAGNETIC FIELD RESULTS. — The overall set of experimental results is displayed in figure 1. Above $T = 1.2$ K many runs have been made with different experimental conditions: various rates of increasing temperature, the helium bath at $T = 1.2$ K or $T = 4.2$ K. All data have been collected together, though only about one point out of ten are shown in figure 1 for the sake of clarity. The two CeB$_6$ samples give the same results within experimental accuracy.

The measurements down to $T = 0.3$ K have been performed only for one CeB$_6$ sample, using the helium-3 apparatus. The results, shown in figure 1, correspond to the smallest rate of increasing temperature and are in good agreement with the data above $T = 1.2$ K.
Fig. 1. — Specific heats of CeB₆ and LaB₆.

From \( T = 0.3 \) K to \( T = 1 \) K the results are independent of the rate within a few percent.

Above \( T = 20 \) K the specific heats of CeB₆ and LaB₆ display a very similar behaviour with comparable values: at \( T = 30 \) K \( C_p(\text{CeB}_6) = 6.9 \) J . mol\(^{-1}\) . K\(^{-1}\) and \( C_p(\text{LaB}_6) = 5.2 \) J . mol\(^{-1}\) . K\(^{-1}\). However below \( T = 20 \) K the two specific heats are considerably different due to the strong magnetic contribution for CeB₆ which exhibits the two expected peaks at \( T_Q = 3.4 \) K ± 0.1 K \( (C_p = 7 \) J . mol\(^{-1}\) . K\(^{-1}\)) and \( T_N = 2.5 \) K ± 0.1 K \( (C_p = 20 \) J . mol\(^{-1}\) . K\(^{-1}\)). Actually below \( T = 10 \) K, the heat capacity of LaB₆ is too small to be determined with some confidence.

The obtained results are in qualitative agreement with those reported previously [6, 7, 25] and in particular between \( T = 5 \) K and \( T = 35 \) K for CeB₆ and between \( T = 10 \) K and \( T = 60 \) K for LaB₆, our results are in quantitative agreement with specific heat data of Fujita et al. [6]. As far as the transition temperatures are concerned, our measurements give slightly higher temperature values, but the shift is estimated to be only one or two tenths of a degree. Actually about the same values of \( T_N \) and \( T_Q \) have been deduced with the same samples from other experiments: electrical resistivity, magnetic susceptibility, and neutron diffraction in the case of the enriched sample [13]. On the other hand, the apparent width of about 0.1 K of the specific heat jump at \( T_N \) is essentially due to the finite thermal diffusion in the sample, which is less important at \( T_Q \), where a peak is clearly seen. This is in contrast with the previous studies where only a bump has been noticed at the phase II transition in zero magnetic field [7]. The difference between the heat capacities of CeB₆ and LaB₆ has also been directly measured above \( T = 1.2 \) K, using the two samples of comparable molar fraction. The results are shown in figure 2 as well as the difference deduced from the absolute measurements. The agreement between both determinations is excellent below \( T = 160 \) K, and is particularly significant above \( T = 20 \) K where the two specific heats are of the same order of magnitude.

On the other hand, in the temperature range 0.5 K-1 K, there is a large difference between our results and those of Furuno et al. [7] which reaches about 30 % at \( T = 1 \) K. Below \( T = 1 \) K and down to \( T = 0.5 \) K, the specific heat varies as \( T^3 \) with temperature as expected from antiferromagnetic spin waves in this range of temperature. The \( \beta' = 950 \) mJ . mol\(^{-1}\) . K\(^{-4}\) value obtained from our measurements is lower than the corresponding value obtained by Furuno \( (\beta' = 1 200 \) mJ . mol\(^{-1}\) . K\(^{-4}\)) [7]. Below \( T = 0.5 \) K the \( T^3 \) variation vanishes, and the data can be simply analysed as \( C_p = \gamma T \), with \( \gamma = 300 \) mJ . mol\(^{-1}\) . K\(^{-2}\) in agreement with Furuno's data [7]. This change of temperature dependence below \( T = 0.5 \) K is probably connected with a similar change of the behaviour of the electrical resistivity [2]. This is ascribed to the vanishing of the antiferromagnetic excitation because of an anisotropy gap.

3.2 HIGH MAGNETIC FIELD RESULTS. — Below \( T = 20 \) K the thermal behaviour of CeB₆ is strongly modified by an applied magnetic field. This is clearly shown in figure 3 which displays the specific heat of CeB₆ measured for different magnetic fields \( H = 0, 2, 5, 8 \) teslas. As expected, the peak associated with the magnetic transition disappears for high fields. The large bump observed at \( H = 2 \) teslas is indicative that this field value is close to the threshold field between phases II and III, as expected from neutron experiments with \( H \) along the \( <111> \) direction [13]. In contrast with this decrease of \( T_N \) and of the related peak, the specific heat anomaly at \( T_Q \) is shifted by a large amount to higher values. These results confirm

Fig. 2. — Magnetic part of the specific heat of CeB₆. The solid curve is obtained by subtracting the measured specific heat of CeB₆ and LaB₆; the differential measurements are represented by (○).
and extend the previous experiments by Fujita et al. [6] which were limited to $H = 1.8$ teslas, and give a precise definition of the shape of the anomaly which becomes mean-field like in high magnetic field. The results are also displayed in a logarithmic plot in figure 4, which gives evidence of the increase of the negative slope of the tail above $T_\alpha$.

Above $T = 20$ K, no change for any field is observed for both experimental configurations: absolute measurements for CeB$_6$, LaB$_6$ or differential measurements.

The phase diagram of CeB$_6$ deduced from these measurements is given in figure 5 and compared with those previously published [1, 6, 14]. The qualitative behaviour of the transition line between phases I and II is confirmed, with an inflexion at $T = 4$ K and $H = 1$ tesla, but there is a general shift of the line to higher temperatures.

4. Analysis of the results.

As a first approximation, we assume that the electronic and lattice contributions to the specific heats of CeB$_6$ and LaB$_6$ are identical. Then by differential measurement or by numerical difference between the specific heats of CeB$_6$ and LaB$_6$, we determine the magnetic contribution (Fig. 2). Above $T = 20$ K the magnetic contribution is only a small part of the total specific heat of CeB$_6$, about 15 % at $T = 50$ K and only a few percent of magnitude above $T = 200$ K, i.e. of the same order as the experimental uncertainty. However two broad and flat anomalies may be present at about $T = 40$ K and $T = 150$ K.
As the cubic crystal field splits the \(^{2}\text{F}_{5/2}\) configuration of the trivalent Ce ion into a doublet \(I_7\) and a quadruplet \(I_8\), we analyse the magnetic specific heat in the paramagnetic phase in terms of a Schottky anomaly between \(I_7\) and \(I_8\) levels.

Whatever the CEF splitting, there is no agreement between experimental and calculated data with a doublet ground state. For two different splittings values \(\Delta = 60 \text{ K}\) or \(\Delta = 400 \text{ K}\), the calculated contribution is larger than the observed one by a factor of three that is well outside the experimental uncertainty (Fig. 6); even with larger splittings, the shape of the high temperature broad anomaly cannot be reproduced.

On the other hand, a configuration with a quadruplet ground state gives a better quantitative agreement with the experimental data (Fig. 6). From these first calculations it is not possible to determine a CEF splitting, because the first anomaly near \(T = 40 \text{ K}\) would be in agreement with a splitting of 70 K, but the other one near \(T = 150 \text{ K}\) corresponds to a large CEF splitting of 400 K. A splitting of the \(I_8\) ground state as a possible origin of the anomaly near \(T = 40 \text{ K}\) is also ruled out on grounds of the calculated specific heat intensity.

In order to test which splitting, determined from this high temperature analysis, is more consistent with the overall magnetic contribution, we calculate the magnetic entropy from the lowest temperature to room temperature for \(H = 0\) and \(H = 8 \text{ T}\). In view of the lack of experimental results below \(T = 0.5 \text{ K}\) for \(H = 0\) T, and \(T = 1.2 \text{ K}\) for \(H = 8 \text{ T}\), we extrapolate the magnetic specific heat to \(T = 0 \text{ K}\). For \(H = 0\), we use the \(\beta' T^3\) law \(\beta' = 950 \text{ mJ mol}^{-1} \text{ K}^{-4}\) obtained from the total specific heat of \(\text{CeB}_6\) between \(T = 0.5 \text{ K}\) and \(T = 1 \text{ K}\). This corresponds to the expected contribution from magnons in the commensurate structure. For \(H = 8 \text{ T}\) the magnetic specific heat below \(T = 1.2 \text{ K}\) is estimated by a simple graphical extrapolation as shown in figure 3. The entropy variations thus obtained are plotted in figure 7. In zero field the calculated entropy is close to \(R \ln 2\) at \(T = T_N\) and is larger than \(R \ln 4\) above \(T = 50 \text{ K}\). A small change of the low temperature extrapolation using the \(\beta' T^3\) law with \(\beta' = 1200 \text{ mJ mol}^{-1} \text{ K}^{-4}\) found by Furuno et al. [7] does not affect this result within the experimental accuracy. At room temperature the magnetic entropy reaches the expected value of \(R \ln 6\) corresponding to the \(J = 5/6\) ground state multiplet. But this value is certainly not reached at \(T = 150 \text{ K}\) within the estimated accuracy. As a consequence the energy splitting between the quartet ground state and the doublet excited state is much larger than 150 K. This result is consistent with the Schottky analysis of the broad specific heat anomaly near \(T = 150 \text{ K}\) discussed above, but rules out such an interpretation for the anomaly near \(T = 40 \text{ K}\). Moreover, this anomaly cannot again be due to a splitting of the \(I_8\) ground state (as it was recently suggested to explain the anomalous frequency shift upon cooling by Raman measurements [21]). Even a dynamical splitting is unlikely to account for the Raman measurement because the temperature tail of the specific heat extends only up to 15 K whatever the value of the applied magnetic field.

A magnetic field of 8 T reduces the magnetic entropy only at low temperatures but no field effect is observed above \(T = 40 \text{ K}\) (Fig. 7). The only effect of a magnetic field is to transfer the magnetic entropy from the lowest to the highest peak of the specific heat. Therefore there is no increase of the magnetic entropy below \(T = 40 \text{ K}\) due to the suppression of the Kondo effect by the magnetic field and this result is somewhat surprising.

The main conclusions of the first analysis of the magnetic specific heat are: i) from high temperature Schottky analysis, the CEF ground state is the quadruplet \(I_8\), ii) only a CEF splitting larger than 150 K is consistent with the Schottky analysis and the magnetic entropy results. However it is necessary to discuss
how these conclusions could be modified when the hypothesis of identical electronic and lattice contributions for CeB₆ and LaB₆ is released. Actually above T = 20 K only the lattice contribution must be taken into account.

In the temperature range where the electronic contribution of LaB₆ is small compared with the lattice contribution, a Debye specific heat calculation, using a Debye temperature determined from sound velocity measurements ($\theta_{\text{LaB}_6} = 770$ K) [31], gives a poor agreement with experimental data. However, a specific heat calculation which also involves an Einstein mode with a temperature of about 150 K, gives a better fit of the lattice contribution. Such a result is supported by recent inelastic neutron scattering experiments which show that the phonon dispersion curves are flat near over a large part of the Brillouin zone at an energy of about 140 K [32]. Therefore, in spite of the lack of a Debye model to describe the thermal behaviour of the hexaboride lattice accurately, we use such a calculation only to determine the residual lattice specific heat between CeB₆ and LaB₆, taking into account only the difference between the acoustical Debye temperatures of the two compounds ($\theta_{\text{LaB}_6}^{\text{ac}} = 396$ K) [31], ($\theta_{\text{CeB}_6}^{\text{ac}} = 371$ K) [10], and neglecting any difference between the optical modes. This residual contribution is weak and flat, and presents a maximum at about T = 100 K. After subtracting this lattice correction to the magnetic specific heat, two well defined broad anomalies still appear above T = 20 K near T = 40 K and T = 200 K (Fig. 8). The corrected magnetic entropy is strongly reduced, and well below R ln 6 at room temperature (Fig. 7).

A Schottky calculation with a quadruplet ground state and an energy splitting of 500 K is in agreement with both this corrected high temperature specific heat anomaly near T = 200 K and the corrected entropy. Nevertheless, it is not possible to determine an accurate CEF splitting value in view of the absolute uncertainty of the magnetic contribution above T = 200 K. From the Schottky analysis in the narrow temperature range 100 K – 200 K, of the magnetic specific heat, the CEF splitting cannot be less than 500 K. If we assume that all other differences between CeB₆ and LaB₆ are negligible, then from the experimental uncertainty the maximum CEF splitting value is about 600 K. Therefore, the main conclusions of the first analysis are confirmed, and the specific heat data are rather consistently analysed within the framework of the new CEF level scheme.

Because of the strong Kondo effect in CeB₆, it is difficult to calculate the difference between the electronic contribution of CeB₆ and that of LaB₆. It is not easy either to compare the electronic terms of the specific heat of CeB₆ and LaB₆, which are sample dependent [29, 30]. Such experimental differences seem to occur for other hexaboride metals and remain unclear [29]. Since both CeB₆ and LaB₆ have one conduction electron per unit cell and are good metals, we assume that the electronic difference has a negligible contribution to the specific heat at high temperatures. However at low temperatures the extra contribution could be attributed to the coupling between 4f and conduction electrons of Kondo-type which gives rise at low temperature to the high γ value.

The Ce³⁺ ground state being the $\Gamma_8$ quartet, well isolated from the excited doublet $\Gamma_7$, it is possible to fit the tail of the specific heat just above $T_Q$ for zero field by the impurity Kondo model with $J = 3/2$. A Kondo temperature, $T_K$, of 7 K gives a fairly good agreement. This value of $T_K$ is consistent with previous ones estimated from electrical resistivity measurements [1]. However, more recent and detailed studies of the magnetic susceptibility by Sato et al. [33] give a Kondo temperature $T_K$ of 1 K or 2 K, nearly independent on the Ce-concentration in $\text{Ce}_x\text{La}_{1-x}\text{B}_6$. A possible way to eliminate this contradiction is to consider some short range order effect above $T_Q$. On the other hand the magnetic field dependence of the specific heat tail is qualitatively consistent with a Zeeman effect but there is no quantitative agreement due to the strong Kondo effect and $\Gamma_8$ fluctuations in this range of temperature. The large increase of $T_Q$ with the applied field is quite unusual. For a normal antiferroquadrupolar structure, we can expect that the magnetic field competes with ordering. Actually the opposite situation is observed, which may be attributed to a strong decrease of $T_Q$ by Kondo fluctuations in low magnetic fields.

Finally, the origin of the broad peak around T = 40 K is not known. As some anomaly is reported even for the dilute Ce impurity in LaB₆, a more detailed study is needed.

![Fig. 8. — Magnetic contribution to the specific heat of CeB₆ taking into account a lattice correction. Dotted curve: Debye specific heat of LaB₆. Dotted dashed curve: Debye specific heat of CeB₆. Broken curve: difference between the Debye specific heats of CeB₆ and LaB₆. Solid curve: difference between the magnetic specific heat of CeB₆ and the residual lattice specific heat. (●) Experimental points.](image-url)
In conclusion, specific heat data on CeB$_6$ can be consistently analysed within the framework of the new CEF level scheme determined by various experiments. Since it is rather difficult to get a very accurate experimental determination of the magnetic contribution to the specific heat CeB$_6$ above $T = 50$ K, the CEF splitting between the $I_8$ quadruplet ground state and the $I_7$ doublet excited state can only be estimated to be larger than 500 K.

Another interesting result of the present work is the high enhancement by an applied magnetic field of the antiferroquadripolar ordering and the associated specific heat anomaly.

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