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# Thermodynamic properties and magnetism of $Ce_3Cu_3Sb_4$

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**Abstract**

The specific heat capacity $c_p(T)$ of $Ce_3Cu_3Sb_4$ was determined between 0.6 K and 100 K in magnetic fields up to $H_{ext} = 140$ kOe. The magnetic ordering transition at 10.8(1) K shows up as a tiny step-like anomaly in $c_p(T)$, while at lower temperatures a large anomaly centred at 4.8(1) K is observed. In small magnetic fields the transition shifts to higher temperature and disappears for $H_{ext} \approx 10$ kOe. The large anomaly broadens as well and shifts to higher temperature with the increase of $H_{ext}$ to 140 kOe. In Arrott plots of isothermal magnetization curves $M(H_{ext})$ the critical isotherm is found for $T_c \approx 4$ K. These thermodynamic data thus suggest that the evolution of magnetic order in $Ce_3Cu_3Sb_4$ and related compounds is more complicated than described previously.

## 1. Introduction

Intermetallic cerium compounds have attracted great interest due to their richness in low-temperature electronic groundstates. The physics of these materials is governed by a competition of the exchange by RKKY interaction and of the Kondo effect. Research has concentrated, for example, on intermediate valence materials, heavy fermion compounds, and magnetically ordered phases. One particular branch of this research is devoted to the search for semiconducting dense Kondo systems (Kondo insulators).

A few years ago $Ce_3Cu_3Sb_4$ was described as a ferromagnetic semiconductor [1, 2] with a Curie temperature $T_{trs}$ of $\approx$10 K. Recently, further investigations on this material concentrated on the estimation of the performance in thermoelectric applications [3, 4]. The ordered state of $Ce_3Cu_3Sb_4$ at low temperature, however, which in all previous investigations showed a spontaneous magnetic moment below $T_{trs}$, remained a matter of debate [5, 6]. Since the resistivity $\rho(T)$ showed a maximum at a certain temperature $T_{max}$, which varied in the different studies and which did not coincide with $T_{trs}$, and above which activated conduction was found, $Ce_3Cu_3Sb_4$ was classified as a degenerate p-type semiconductor [2, 3]. The values calculated for the activation energy $E_A$ at high temperature are very small ($E_A/k_B = 30$ K [3]; 38 K [4];

  

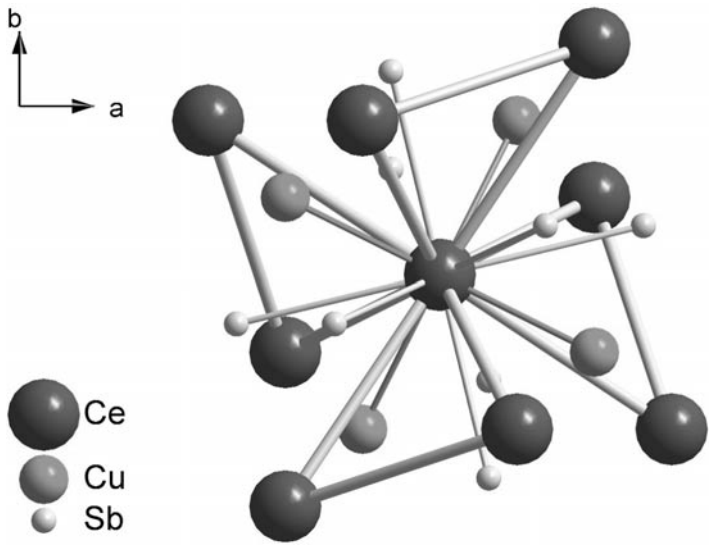


**Figure 1.** Co-ordination of a Ce-ion by Ce, Cu and Sb in $Ce_3Cu_3Sb_4$.

29 K [5, 6]), but are remarkably consistent among the various authors. Below $T_{max}$ the resistivity decreases, but until now no clear temperature dependence could be identified.

It was argued [5, 6] that it is unreasonable to discuss such small semiconductor gap values in an imperfect intermetallic compound. Also, a study of the substitution series $Ce_3Cu_xPt_{3-x}Sb_4$ demonstrated that the gap almost closes when approaching $x = 3$ [4]. Since the optical reflectivity of $Ce_3Cu_3Sb_4$ shows no indication of a gap (reflectivity approaches 100% for $\omega \rightarrow 0$) [5, 6], $Ce_3Cu_3Sb_4$ can rather be described as a semimetal. The temperature variation of $\rho$ was ascribed to the temperature dependence of the mobility as established from Hall-effect data [5, 6]. A description of $Ce_3Cu_3Sb_4$ as 'zero-gap semiconductor' [7] as given for the isostructural and isoelectronic $Ce_3Au_3Sb_4$ might also be adequate.

Crystal structure analyses [1, 3–6, 8] of $Ce_3Cu_3Sb_4$ find consistently a cubic structure ($Y_3Cu_3Sb_4$ type, space group $I\bar{4}3d$, $a = 9.721$ Å [1], $a = 9.765$ Å [3]; $a = 9.75$ Å [4]; $a = 9.7527(1)$ Å [5, 6]). Other $RE_3Cu_3Sb_4$ compounds (RE = Y, La, Pr, Nd, Sm, Gd–Er [1]; La, Gd, Er [3]; Nd, Sm, Tb, Dy, Ho [9]) crystallize in the same structure. The cerium sublattice (see figure 1) can be described as a three-dimensional network in which each Ce atom has eight neighbours at the distance 4.5614(1) Å (calculated from crystallographic data [5, 6]). Four Cu atoms and $2 \times 4$ Sb atoms (at two slightly different distances) complete the co-ordination of the Ce site (see figure 1).

The physics of the magnetically ordered phase of $Ce_3Cu_3Sb_4$ was investigated only recently. The magnetization does not saturate and the spontaneous moment was rather small [2, 5, 6]. Thus, a reduction of the ordered moment by Kondo effect or by crystal electric field (CEF) effects could be suspected. In [2] a quartet groundstate (cf the discussion of the CEF below) was made responsible for the reduced high-field magnetic moment. A recent neutron diffraction study [6, 8] clarified the situation. An antiferromagnetic order with canted magnetic moments was found. The spin arrangement derived from the data has Ce-spins with three different directions with ordered magnetic moments of $2.1(2)\mu_B$ at $T \approx 2$ K, i.e. no significant Kondo reduction of the ordered magnetic moments is found. The resulting ferromagnetic component is $1.6(2)\mu_B$/Ce-atom, consistent with the high-field magnetization data. Also, in

the neutron diffraction study [6, 8] no incompatibilities of the data at low temperatures with the cubic structure observed at room temperature were found.

Except for the magnetization measurements no other data of bulk properties and, especially, no thermodynamic data are known for $Ce_3Cu_3Sb_4$. In the following, we present the specific heat capacity of $Ce_3Cu_3Sb_4$ and of the isostructural La compound for 0.62 K $< T <$ 100 K and for magnetic fields up to 140 kOe. For an antiferromagnet, which orders with its nearly full free-ion moment, a sharp anomaly in $c_p(T)$ is expected at the Néel point. Surprisingly, we observe only a minor step-like anomaly at $T_{trs}$. Arrott plots of isothermal magnetization curves are used to determine the thermodynamic transition temperature, which can be markedly different from transition temperatures determined for example by transport measurements.

## 2. Samples and experimental methods

The samples were pieces cut from batches which were prepared by melting stoichiometric amounts of elements in sealed tantalum tubes and annealing for three weeks at 600°C in sealed quartz glass tubes [3]. Samples from the $Ce_3Cu_3Sb_4$ and from the $La_3Cu_3Sb_4$ batches contained no additional phases as judged by x-ray diffraction patterns. Details concerning the structure, further characterizing measurements and investigations of the Hall effect, thermopower and thermal conductivity of samples from this batch of $Ce_3Cu_3Sb_4$ are described in [3]. The pieces used for the heat capacity measurements were polycrystalline blocks of ≈120 mg mass.

The magnetic susceptibility was measured using a SQUID-magnetometer (MPMS, Quantum Design) between 2 K and 300 K in an external magnetic field of 100 Oe. Isothermal magnetization curves were recorded for external fields up to 70 kOe on a smaller piece taken from the sample block. For the heat capacity measurements the sample was mounted on the sapphire holder of the calorimeter with a minute amount of vacuum grease. The heat capacity of the sample holder and of the grease were measured separately and subtracted. We used the quasi-adiabatic step-heating method (Nernst's method). The inaccuracy of $c_p(T)$ is—due to the small sample mass—about 1.5%, between 2.2 K and 30 K and increases to about 3% at 100 K. The temperature calibration of the sample holder thermometer (Cernox 1050 type) was corrected for magnetoresistive effects. An additional zero-field measurement was performed with a similar calorimeter in a $^3$He cryostat for 0.62 K $< T <$ 2.2 K (inaccuracy about 2%).

## 3. Results

### *3.1. Magnetic susceptibility*

The magnetic susceptibility data $\chi_{mol}(T)$ of $Ce_3Cu_3Sb_4$ recorded for increasing temperatures after zero-field cooling are identical within experimental errors with the field-cooled data. A spontaneous magnetic moment is observed below $T_{trs} = 10.8(4)$ K, in agreement with [2–6]. Above ≈40 K the susceptibility is well described by a modified Curie–Weiss law $\chi_{mol} = \chi_0 + C/(T - \Theta_p)$. The fit to the data (range 50 to 300 K) results in $\Theta_p = -1.3$ K, and an average effective magnetic moment $\mu_{eff}$/Ce-atom $= 2.39\mu_B$ and $\chi_0 = +0.88 \times 10^{-3}$ emu mol$^{-1}$ (after core correction: $\chi_0' = +1.04 \times 10^{-3}$ emu mol$^{-1}$). The value of $\mu_{eff}$/Ce-atom is somewhat lower than the $2.54\mu_B$ for free $Ce^{3+}$-ions (groundstate $^2F_{5/2}$). The average magnetic moment indicates that Ce is in a stable 3+ oxidation state. The deviations from the law below ≈40 K are probably due to CEF effects. A simple Curie–Weiss fit $\chi_{mol} = C/(T - \Theta_P)$ for $T > 50$ K has at least two orders of magnitude larger least squares deviations and results in $\mu_{eff}$/Ce-atom ≈$2.5\mu_B$, closer to the free-ion value, in agreement with previous reports [2, 3].

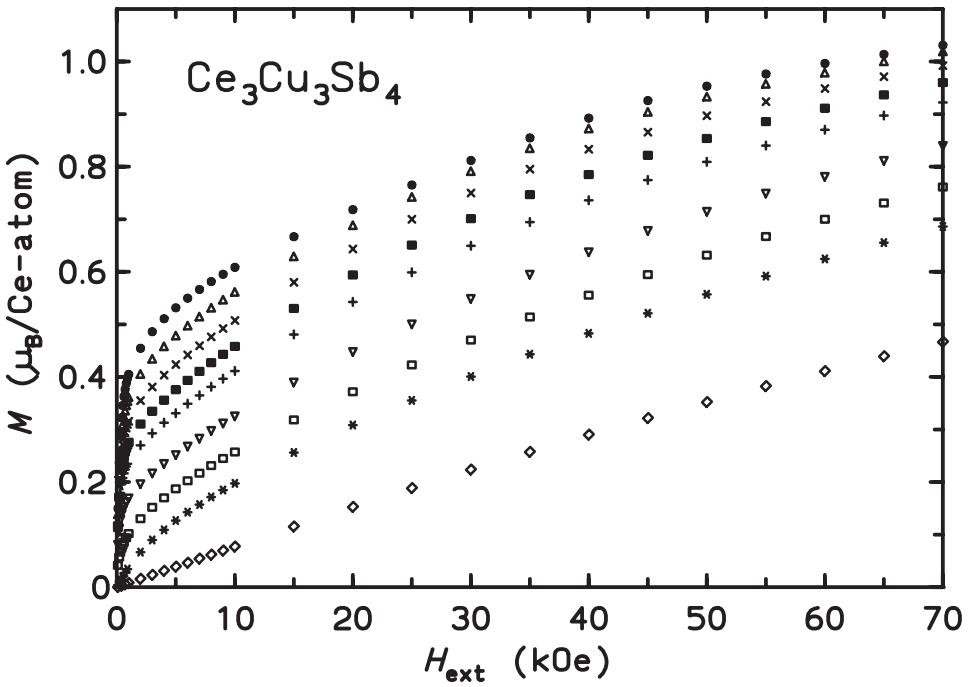


**Figure 2.** Isothermal magnetization curves $M(H_{\rm ext})$ for different temperatures (● 2.0 K, △ 3.0 K, × 4.0 K, ■ 5.0 K, + 6.0 K, ▽ 8.0 K, □ 10 K, ∗ 12 K, ◇ 20 K).

### *3.2. Isothermal magnetization*

The isothermal magnetic moment per Ce-atom of $Ce_3Cu_3Sb_4$ is plotted in figure 2 as a function of external field for temperatures below and above $T_{\rm trs}$. A spontaneous magnetization is observed on all isotherms with $T < T_{\rm trs}$, but also the isotherm at 12 K displays some curvature at low fields. The magnetic moment increases slowly and the Ce-ions reach only $1.03\mu_{\rm B}$/Ce-atom in 70 kOe, about half of the theoretical saturation moment $gJ$ ($2.143\mu_{\rm B}$). An extrapolation of $M(1/H)$ to $1/H = 0$ also yields only $1.24\mu_{\rm B}$, much less than $gJ$.

In order to check the nature of the ferromagnetic component and to locate the thermodynamic critical temperature $T_c$ exactly, the isothermal $M(H_{\rm ext})$ curves were corrected for demagnetization effect and re-plotted as $M^2$ against $H_{\rm int}/M$ (Arrott-plots; see figure 3). The isotherms form—for fields >8 kOe—straight lines with a similar slope as they should for mean-field critical exponents ($\beta = 1/2$; $\gamma = 1$). Modified Arrott plots $M^{1/\beta}$ against $(H_{\rm int}/M)^{1/\gamma}$ for reasonable ranges of the critical parameters $\beta$ and $\gamma$ did not result in considerably better results. Surprisingly, the critical isotherm (i.e. intersection at the origin; broken line in figure 3) is found for $(4 \pm 1)$ K and not for a temperature near $T_{\rm trs}$. The thermodynamic critical temperature $T_c$ is thus well below the temperature $T_{\rm trs}$ of the occurrence of the ferromagnetic moment, but coincides with the maximum of the dominant anomaly in specific heat capacity, as will be demonstrated in the next subsection.

### *3.3. Specific heat capacity*

The results of the heat capacity measurements in different external magnetic fields are shown in figure 4 for $T < 50$ K. In the zero-field data the phase transition is marked by a marginal

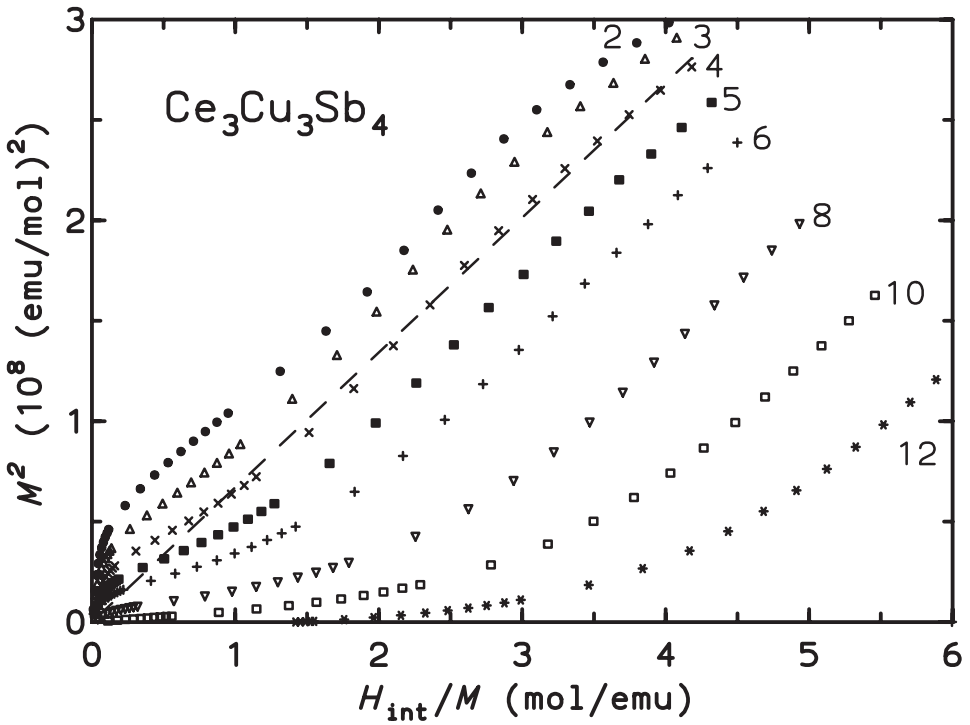


**Figure 3.** Arrott plot of isothermal magnetization curves of $Ce_3Cu_3Sb_4$. The (temperature/K) of the isotherms are indicated in the plot. The demagnetization correction $H_{\rm int} = H_{\rm ext} - 4\pi N M_{\rm vol}$ for the factor $N = 0.34$ has been applied where $N$ was determined from the inverse slope of $M(H_{\rm ext} \to 0)$ at 2 K.

second-order-type anomaly with $\Delta c_p \approx 0.8$ mJ mol$^{-1}$ K$^{-1}$ with midpoint at 10.8(2) K. Already in small fields the anomaly broadens and shifts to higher temperatures (see inset of figure 5), as could be expected for a ferromagnetically coupled spin system. In a field of 10 kOe the anomaly is smeared out and can not be detected any more. The low-temperature heat capacity is, however, governed by a broad anomaly centred at 4.8(1) K. In a $c_p/T$ representation (figure 4) the maximum at 2.35(5) K exceeds 2.5 J mol$^{-1}$ K$^{-2}$. In magnetic fields of some 10 kOe the anomaly also broadens and shifts to higher temperatures. In a field of 140 kOe the local maximum is smeared out completely and $c_p/T$ increases monotonically. The related entropy shifts to high temperatures. Even in the relatively small field of 30 kOe a clear difference is visible between the specific heat with and without field up to 30 K.

Since it has been claimed that $Ce_3Cu_3Sb_4$ is a semimetal [5, 6] the total heat capacity $c_p(T)$ may be considered to be composed of a lattice contribution $c_{\rm lat}(T)$ and a (hybridized) magnetic/electronic contribution $c_{\rm mag}(T)$. In order to estimate $c_{\rm lat}(T)$ of $Ce_3Cu_3Sb_4$ the heat capacity of the isostructural compound $La_3Cu_3Sb_4$ was measured for 4.25 K $< T <$ 100 K in zero field. Data at lower $T$ were not obtained. As a consequence, the $\gamma T + \beta T^3$ approximation was not sufficient and we had to add a $\delta T^5$ term to the fit of $c_p(T)$ at low $T$. The resulting parameters are $\gamma = 2.5(3)$ mJ mol$^{-1}$ K$^{-2}$, $\beta = 4.0(1) \times 10^{-4}$ J mol$^{-1}$ K$^{-4}$, corresponding to an initial Debye temperature $\Theta_{\rm D}(0) = 364$ K, and $\delta = 5.6(1) \times 10^{-6}$ J mol$^{-1}$ K$^{-7}$. $La_3Cu_3Sb_4$ displayed a nearly temperature-independent resistivity $\rho(T)$ and a small increase with decreasing $T$ below 220 K [3]. This and the presence of a linear term $\gamma T$ in $c_p(T)$

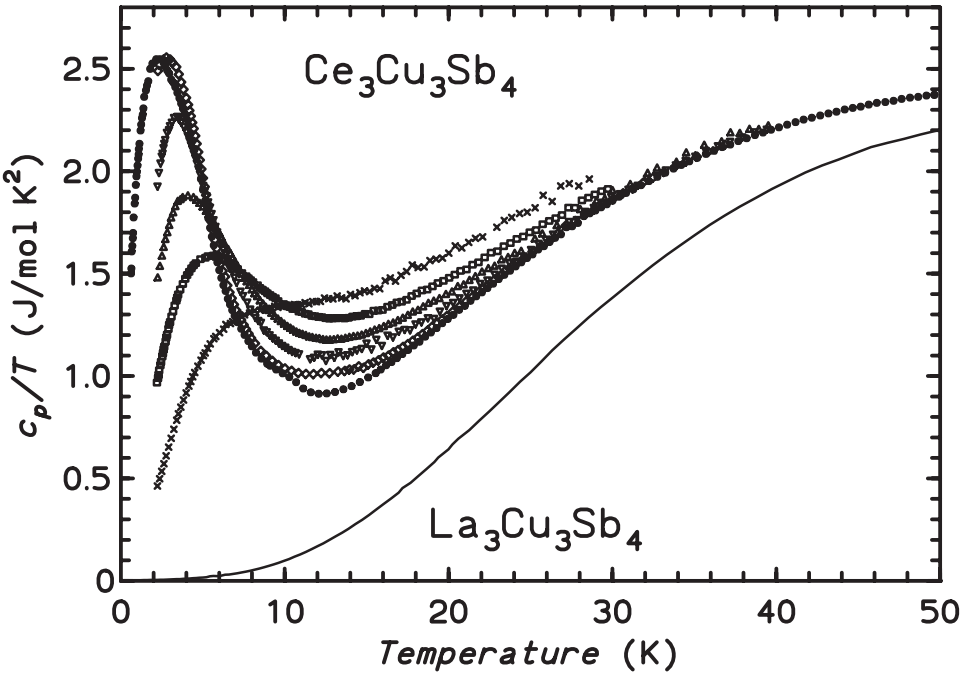


**Figure 4.** Specific heat capacity $c_p(T)/T$ of $Ce_3Cu_3Sb_4$ for $T$ between 0.62 K and 50 K in zero (●), 10 kOe (◇), 30 kOe (▽), 50 kOe (△), 80 kOe (□) and 140 kOe (×) external magnetic field and $c_p(T)/T$ of the $La_3Cu_3Sb_4$ sample in zero field (——).

suggest that also this non-f-electron compound can be considered a semimetal instead of a semiconductor with a small gap. The observed increase of $\rho(T)$ could as well be due to a magnetic impurity effect.

The magnetic contribution $c_{\mathrm{mag}}(T)$ of $Ce_3Cu_3Sb_4$ is given in figure 5 for the different fields. At low temperatures no simple temperature dependence of $c_{\mathrm{mag}}(T)$ is observed. Between 0.6 K and 1.5 K $c_{\mathrm{mag}}$ is approximately $\propto T^{1.5}$. With increasing magnetic field both anomalies smear out and the entropy is shifted to higher temperatures. Also for $c_p(T, H = 140\ \mathrm{kOe})$ no clear power law can be seen ($c_{\mathrm{mag}}(T) \propto T^{2.3}$ below 3.0 K).

The magnetic entropy $S_{\mathrm{mag}}(T) = \int_0^T (c_{\mathrm{mag}}/T')\,\mathrm{d}T'$ is shown in figure 6. For temperatures below the lowest measured data point (0.62 K) a $T^3$-extrapolation in $c_{\mathrm{mag}}(T)$ was utilized which yields, however, only $S = 0.019R$/Ce-atom ($R$ = gas constant). At $T_{\mathrm{trs}}$ a magnetic entropy of precisely $3R\ln 2$ is removed. This indicates that the groundstate involved in the magnetic ordering is a CEF-doublet. Because the point symmetry of the $Ce^{3+}$-ion in $Ce_3Cu_3Sb_4$ is tetragonal the $J = 5/2$ state is split into three doublets. It was suggested [5, 6] that the $\Gamma_7$ state is the lowest doublet. According to the evolution of the magnetic entropy $S_{\mathrm{mag}}(T)$ the first exited CEF-doublet is already populated at ≈40 K, irrespective of the magnetic field. The value at 100 K for $S_{\mathrm{mag}}(T)$ is $\approx 1.48R$/Ce-atom.

## 4. Discussion

The specific heat capacity of the semiconducting isostructural/isoelectronic and stable-valent $Ce^{3+}$ compound $Ce_3Au_3Sb_4$ [10] displays some remarkable similarities to our data.

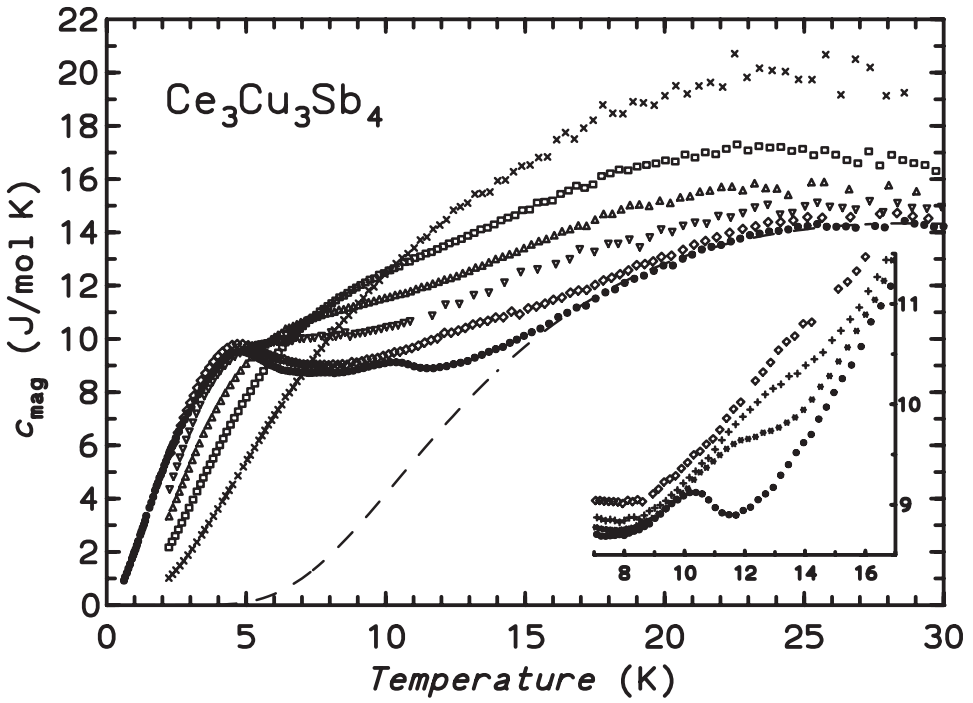


**Figure 5.** Magnetic contribution $c_{\rm mag}(T)$ to the specific heat capacity of $Ce_3Cu_3Sb_4$ in zero (●), 10 kOe (◇), 30 kOe (▽), 50 kOe (△), 80 kOe (□) and 140 kOe (×) external magnetic field. The broken curve is a Schottky anomaly calculated for CEF doublets at 0, 50 and 120 K. The insert shows $c_{\rm mag}(T)$ for low magnetic fields near the magnetic ordering at $T_{\rm trs}$ (● zero field, ∗ 3 kOe, + 6 kOe, ◇ 10 kOe).

For $Ce_3Au_3Sb_4$ $c_p(T)$ above 4 K could be fitted by a CEF Schottky anomaly with doublets at 0, 27 and 145 K. Our $c_{\rm mag}$ data above 15 K can be fitted with a similar CEF Schottky anomaly with doublets at 0, ≈50 and ≈120 K (see figure 5), but either the accuracy of our $c_p(T)$ data at high $T$ is not sufficient to get a good agreement with that model or this simple CEF scheme is not applicable for $Ce_3Cu_3Sb_4$. The first exited doublet thus is at about twice the energy splitting as in the $Ce_3Au_3Sb_4$.

A further similarity to $c_{\rm mag}(T)$ of $Ce_3Au_3Sb_4$ is the broad anomaly centred at 1.5 K [10], corresponding to our peak at 4.8 K, which also shifted to higher $T$ and broadened strongly with increasing magnetic field. This anomaly was assigned to a many-body resonance in the band gap [10]. The existence of both the broad anomaly around 1 K and the Schottky-like anomaly at ≈10 K in $c_p(T)$ of $Ce_3Au_3Sb_4$ was confirmed later on by another group (cited in [7]). Since also the magnetization of $Ce_3Au_3Sb_4$ against $H/T$ is nonlinear and far below the theoretical saturation moment even at 190 kOe $K^{-1}$, a magnetically ordered state can be expected. However, no corresponding anomaly was found in any measured property [10].

There are clear proofs for an antiferromagnetic ordering of the $Ce^{3+}$-ion moments with the full free-ion value at ≈2 K in $Ce_3Cu_3Sb_4$ [6, 8]. Since neutron diffraction experiments were only performed at 2.0 K and 18 K nothing is known about the evolution of the magnetic moment. The spontaneous magnetic moment below $T_{\rm trs}$ was observed in all previous studies, but from magnetization there is no indication of a continuous (or discontinuous) spin-reorientation below $T_{\rm trs}$. The anomaly in $c_p(T)$ at $T_{\rm trs}$ is extremely small for an ordering with the full

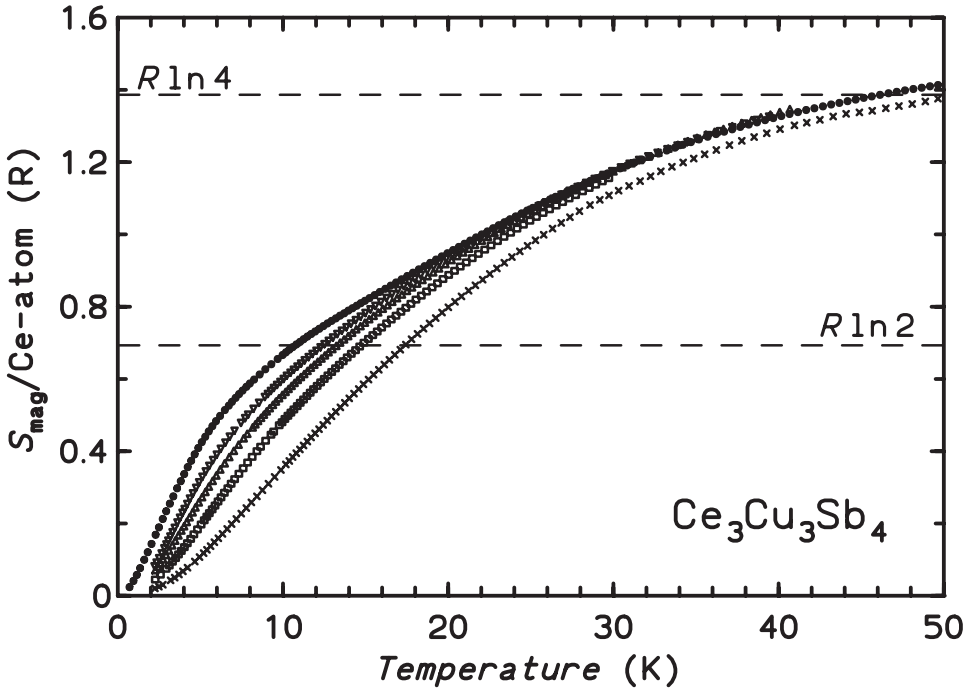


**Figure 6.** Development of the magnetic entropy $S_{mag}(T)$ with temperature for $Ce_3Cu_3Sb_4$ for different magnetic fields (see caption of figure 4 for the symbols).

(uncompensated) magnetic Ce-moment and the broad anomaly at 4.8 K could—not regarding the magnetization—be interpreted as a continuous spin-reorientation. On the other hand, our thermodynamic data indicate a critical temperature of 4(1) K (Arrott-plots) and of ≈4.8 K (magnetic specific heat).

The available neutron diffraction data for $Ce_3Cu_3Sb_4$ at low temperatures are compatible with the cubic room temperature structure [6, 8]. The geometry of the Ce-sublattice is built-up by corner-sharing equilateral triangles (see figure 1). Thus a partial geometrical frustration of long-range magnetic order can be suspected. In such a case a considerable amount of magnetic entropy is found already far above the long-range ordering temperature. Here, a magnetic entropy $3R \ln 2$ is found at $T_{trs}$, the value expected for a doublet groundstate. A partial geometrical frustration effect to the thermodynamic properties seems therefore unlikely.

In view of this partially contradicting behaviour, especially the unknown evolution of the microscopic magnetic Ce-moment with temperature, $Ce_3Cu_3Sb_4$ and similar compounds deserve further investigations.

## Acknowledgments

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## References

[1] Skolozdra R V, Salamakha P S, Ganzyuk A L and Bodak O I 1993 *Inorg. Mater.* **29** 26–9
[2] Patil S, Hossain Z, Paulose P L, Nagarajan R, Gupta L C and Godart C 1996 *Solid State Commun.* **99** 419–22
[3] Fess K, Kaefer W, Thurner C, Friemelt K, Kloc C and Bucher E 1998 *J. Appl. Phys.* **83** 2568–73
[4] Jones C D W, Regan K A and DiSalvo F J 1999 *Phys. Rev.* B **60** 5282–6
[5] Wachter P, Degiorgi L, Wetzel G and Schwer H 1999 *Phys. Rev.* B **60** 9518–24
[6] Wachter P, Degiorgi L, Wetzel G, Schwer H, Mattenberger K, Herrmannsdörfer T and Fischer P 2000 *Acta Phys. Polonica* A **97** 43–58
[7] Broderick S, Vescoli V, Buschinger B, Guth W, Trovarelli O, Weiden M, Degiorgi L, Geibel C and Steglich F 1998 *Solid State Commun.* **108** 463–7
[8] Herrmannsdörfer T, Fischer P, Wachter P, Wetzel G and Mattenberger K 1999 *Solid State Commun.* **112** 135–8
[9] Zhao J T, Song M H, Zhou S K, Huang Z L, Mi J X and Mao S Y 1999 *J. Rare Earth* **17** 228–30
[10] Kasaya M, Katoh K, Koghi M, Osakabe T and Sato N 1994 *Physica* B **199/200** 534–8