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Thermal and Magnetic Anomalous Crystal Field Effects in Ce-Heavy Fermion Compounds*

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Abstract

Specific heat anomalies due to the $\Gamma_7 \rightarrow \Gamma_8$ thermal promotion were measured for $CePd_3B_{0.6}$ and $CePd_3Si_{0.3}$. For the heavy-fermion compound $CePd_3B_{0.6}$ one observes a quasi-linear $C(T)$ dependence, instead of the expected exponential one. Moreover, the cubic crystal field splitting in the $J = 5/2$ ground state alone does not explain the thermal dependence of the susceptibility. These results are discussed in terms of the different hybridization of the conduction electron states with the ground (Γ_7) and excited (Γ_8) crystal field levels.

1. Introduction

The number of reported Ce and U heavy fermion (HF) compounds has increased very rapidly during the last years. They usually show a low temperature specific heat (C) anomaly, which in the case of Ce has a maximum in C vs. T at temperatures between 1 and 4 K with a characteristic high C/T ratio of $0.3 \lesssim C/T \lesssim 3.5\,\text{J/mole K}^2$ as $T \rightarrow 0\,\text{K}$ [1, 2]. At higher temperature (i.e., the usual limit for the C vs. T measurements: $T \cong 10\,\text{K}$), where the full expected entropy of $S = R \ln 2$ is recovered by the anomaly, a high value of the C/T ratio is systematically observed on a number of Ce–HF compounds (Table I). They show a small value dispersion ($120 < C/T < 250\,\text{mJ/mole K}^2$) compared with those of the $T \rightarrow 0\,\text{K}$ region. The most striking feature is that the C/T ratio behaves quasi-independent of temperature, within a certain temperature range in all cases, excepted for $CeCu_2Si_2$.

Facing the quasi-linear C vs. T dependence, in this temperature range, two questions arise: (1) is it due to a similar mechanism as the one of the $T \rightarrow 0\,\text{K}$ limit (Fermi liquid, with very high electron effective mass)?, or (2) is it connected with the expected Schottky anomaly of the $\Gamma_7 \rightarrow \Gamma_8$ thermal promotion? Obviously both questions have to be answered by higher temperatures ($T > 10\,\text{K}$) specific heat and magnetic susceptibility measurements.

The lack of information on the specific heat of HF–Ce compounds at $T > 10\,\text{K}$ is essentially due to the fact that most of them have been under study only recently, exception made for some Ce–Al systems. In the case of the cubic compound $CeAl_2$ an anomalous Schottky specific heat was already observed, which does fit neither a $\Gamma_7 \rightarrow \Gamma_8$ nor a $\Gamma_8 \rightarrow \Gamma_7$ thermal promotion [7].

We have measured the specific heat of $CePd_3B_{0.6}$, which (together with $CePd_3B$) shows the largest measured C/T ratio at $T \rightarrow 0\,\text{K}$ ($C/T \gtrsim 33\,\text{J/mole K}^2$). The system $CePd_3Si_{0.3}$ was also measured as a reference compound, because it orders magnetically at $T_N = 2.44\,\text{K}$ without any evidence of Kondo or HF behaviour and with an entropy gain of $\Delta S = 0.94\,R \ln 2$ within the transition.

2. Experimental and results

The samples were obtained by arc melting, under an argon atmosphere, the proper amount of components (Ce–99.99%, Pd–99.995%, B–99.9% and Si–99.99% pure). The structure, a filled-up Cu_3Au type, and single-phase states of alloys studied were checked by X-ray diffraction powder patterns.

Specific heat measurements were performed in a semi-adiabatic calorimeter, described elsewhere [8], using the heat pulse technique. As thermometer a carbon resistor (Allan-Bradley, Ω270-1/10 W), calibrated up to 100 K against a reference one, was used. Susceptibility measurements were taken with a vibrating sample magnetometer operating in field ranges 0–2 T and between 1.5 and 300 K.

In Fig. 1 we show the specific heat measurements for both $CePd_3B_{0.6}$ and $CePd_3Si_{0.3}$ up to 40 K in a C/T vs. T^2 plot. The lattice contribution was evaluated as the Debye function for $\theta_D = 241\,\text{K}$, which is the Debye temperature extracted from the $LaPd_3B$ measurements [2].

The high temperature C/T ratio (at $T \cong 10\,\text{K}$) was obtained from a linear extrapolation to $T \rightarrow 0\,\text{K}$, using the $C/T = \gamma + \beta T^2$ function, where β accounts for phonons but the γ term does not necessarily represent a density of states as in the case of free electrons. The extrapolation was made from just above the temperature where the low temperature anomaly disappers. The extrapolation for γ is: $170\,\text{mJ/mole K}^2$ for $CePd_3B_{0.6}$ and less than $30\,\text{mJ/mole K}^2$ for $CePd_3Si_{0.3}$. In the inset of Fig. 1, the low temperature C vs. T behavior is displayed for both compounds under study to show the characteristic HF behavior of $CePd_3B_{0.6}$ and the magnetic transition of $CePd_3Si_{0.3}$.

In Fig. 2, we show that the Schottky anomaly for the $\Gamma_7 \rightarrow \Gamma_8$ thermal promotion of these systems, after subtracting the lattice contribution. In the abscissa the reduced temperature T/δ was used ($\delta = \Gamma_7$–Γ_8 splitting) in order to

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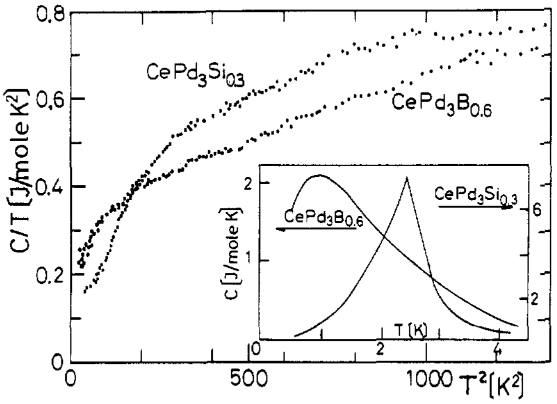

Fig. 1. High temperature C/T vs. T dependence of $CePd_3B_{0.6}$ and $CePd_3Si_{0.3}$. The inset shows the low temperature C vs. T anomaly of $CePd_3B_{0.6}$ and the magnetic order of $CePd_3Si_{0.3}$, after electronic and lattice subtraction.

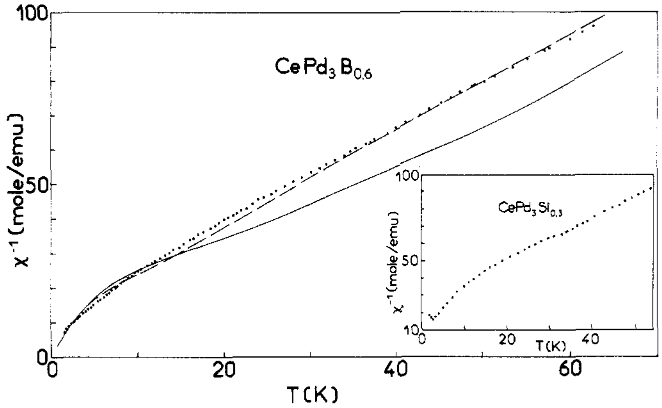

Fig. 3. Inverse magnetic susceptibility for $CePd_3B_{0.6}$ in the $T < 60$ K range. Continuous curve is the computed one for a $\delta(\Gamma_7\text{–}\Gamma_8) = 60$ K splitting and $\theta = 0$ K. Dashed curve was computed with $\lambda(\Gamma_7) = 0$ and $\lambda(\Gamma_8) = -48$ mole/emu. Inset: $\chi^{-1}(T)$ of trivalent $CePd_3Si_{0.3}$.

compare their behaviour with that of $CeAl_2$ [7], the archetype of Kondo systems. Only $CePd_3Si_{0.3}$ follows roughly the computed Schottky anomaly, with the expected maximum of $C_{max} = 6.4$ J/mole K. Both $CePd_3B_{0.6}$ and $CeAl_2$, show spread and reduced maximums with C_{max} of 4.8 adn 4.2 J/mole K, respectively. Such a reduction of C_{max} of about 25% from the normal "Schottky" one is out of the experimental error of 10% in this temperature range. The Γ_7–Γ_8 crystal field splitting is evaluated as $\delta = T_{max}0.377$, which gives $\delta \cong 60$ K for $CePd_3B_{0.6}$ (in good agreement with our magnetic measurements [10]) and $\delta \cong 120$ K for $CeAl_2$ [7, 9].

The entropy change observed is about 90% of the expected $\Delta S = R \ln 3$ for this transition, with $\cong 10\%$ of experimental dispersion.

The magnetic susceptibility within the $0 < T < \delta$ range is illustrated in Fig. 3 through a $\chi^{-1}(T)$ variation. Again we see there that $CePd_3B_{0.6}$ deviates strongly from the expected behaviour for a crystal field splitting of $\delta(\Gamma_7 \rightarrow \Gamma_8) = 60$ K. The magnetic contribution of the Γ_8 level does not follow the temperature dependence expected for the thermal promotion into a well energetically defined level. The Curie–Weiss temperature is $\theta = -2$ K at low temperature ($T < 6$ K) and $\theta = -12.$K at 60 K. The Curie constant value, also at 60 K, is close to the predicated for the full Ce momentum $J = 5/2$. On the other hand, the $\chi(T)$ behavior for $CePd_3Si_{0.3}$ is the expected one for a normal trivalent Ce ion (see inset in Fig. 3).

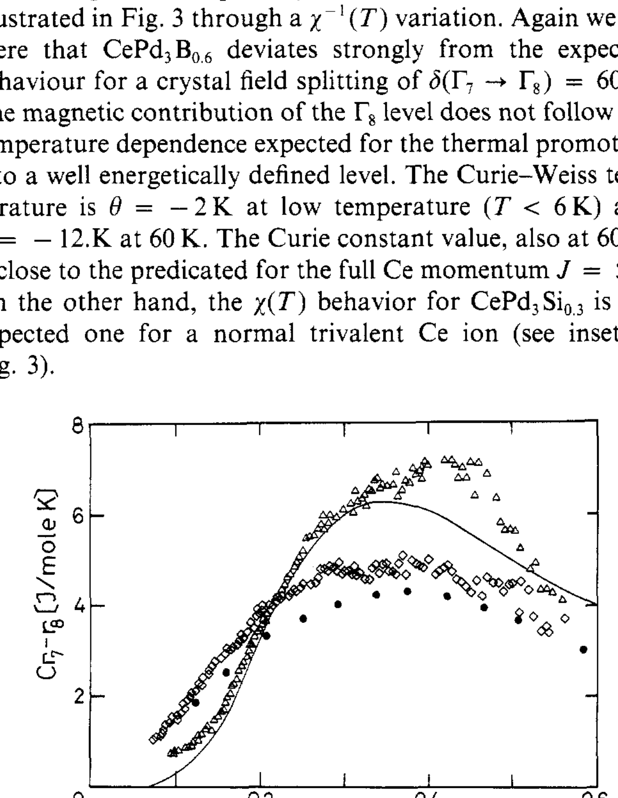

Fig. 2. Crystal field Schottky ($C_{\Gamma_7\text{-}\Gamma_8}$) anomaly vs. reduced temperature (T/δ) of $CePd_3B_{0.6}$ (◇) and $CePd_3Si_{0.3}$ (△) with $\delta = 60$ K and $CeAl_2$ (●) with $\delta = 120$ K. The continuous curve is the computed one for the Γ_7–Γ_8 thermal promotion.

3. Discussion

The measured C vs. T dependence, at $T > \delta/10$ was tried to be fitted by a normal Schottky curve, with a hypothetical $\delta = \delta(T)$ dependence and supposing a symmetry reduction (i.e., the Γ_8 quadruplet split into two doublets). The experimental results can be approached only with a drastic reduction of the baricenter (by a factor three), which seems unlikely because of the unphysical distortion requested to the crystal structure of these two different cubic systems ($CePd_3B_{0.6}$ has the Cu_3As structure and $CeAl_2$ is a Laves Phase).

Neither Kondo nor Fermi-liquid theories are able to explain this phenomenon under study, because of the low energy scale they involve: the characteristic temperature T_K is of a few degrees (see the low temperature C vs. T maximum in $CePd_3B_{0.6}$, for example).

Anyway the two questions asked in the introduction seem to have a common answer, i.e., the quasi-linear C vs. T dependence, the C_{max} reduction and the χ^{-1} vs. T dependence resemble an effect raising from a similar mechanism which involves the ground state, but with a different energy scale. We have to notice here that the pure trivalent $CePd_3Si_{0.3}$ (with a lattice parameter $a = 4.245$ Å and a magnetic transition temperature $T_N = 2.44$ K) does not show abnormal $C(T)$ or $\chi(T)$ behavior in the ground nor in the excited states.

Recently, the possibility of an independent Interconfigurational Mixing (IM) for each crystal field sub-level was proposed on the basis of the analysis of neutron scattering

Table I. *C/T ratio in mJ/mol K^2 of Ce-HF compoinds and the range of linearity for the C vs. T plot*

Compounds	C/T	Range (K)	Ref.
$CeAl_2$	130	10–15	[3]
$CeAl_3$	250	8–12	[3, 4]
Ce_3Al_{11}	120 × 3	12–14	[3]
$CeCu_6$	230	12–17	[1]
$CePb_3$	225	8–12	[5]
$CeIn_2$	140	11–13	[3]
$CeInAu_2$	130	7–12	[6]
$Ce_{0.1}Y_{0.9}InAu_2$	120/10	5–12	[6]
$CePd_3B$	160	7–12	[2]
$Ce_{0.1}La_{0.9}Pd_3B$	160/10	5–13	[2]
$CePd_3B_{0.6}$	170	6–10	[2]

measurements performed in Intermediate Valence systems [11]. Within this picture the linear C term (γ) is related to the entropy through a characteristic temperature T_f, i.e., $\gamma \cdot T_f = S(T_f)$, for each crystal field sub-level. For the $CePd_3B_{0.6}$ ground state we have $\Delta S(\Gamma_7) = 0.83\,R \ln 2$ and $\gamma \cong 3.3\,J/mole\,K^2$ [2], therefore $T_f(\Gamma_7) = 1.4\,K$, this value be related to the low temperature maximum $T_{max} \cong 1\,K$ [2] (see inset Fig. 1).

Now, for the excited level Γ_8 we expect $\Delta S(\Gamma_8) = R \ln 3$, because the total entropy of the Ce $= 5/2$ multiplet is $R \ln 6$, with the measured quasi-linear terms: $\gamma(CePd_3B_{0.6}) = 170\,mJ/mole\,K^2$ and $\gamma(CeAl_2) = 130\,mJ/mole\,K^2$ (see Table I), we obtain: $T_f(\Gamma_8) = 53$ and $70\,K$ respectively. We want to note that for both systems the electrical resistivity increases for decreasing T with a $\ln T$ dependence (after subtraction of the lattice contribution) at those T_f temperatures [12, 13]. Such an effect is usually attributed to a Kondo scattering which T_K temperature should be similar to the computed T_f.

For both systems, the high temperature magnetic susceptibility ($4 < T < 300\,K$) is not well fitted taking into account the sole crystalline field effect [12, 14]. In the case of $CeAl_2$, it was found to be higher than the expected value at $T < \delta$ and lower at $T > \delta$, in coincidence with the specific heat tendency. For $CePd_3B_{0.6}$, a good fitting of the experimental susceptibility data is obtained by assuming different exchanges s–f for the two states Γ_7 and Γ_8 as proposed by H. Lueken *et al.* [15]. Effectively, as shown Fig. 3, the data curve calculated with the exchange parameters $\lambda(\Gamma_7) = 0$ and $\lambda(\Gamma_8) = -48$ mole/emu and the splitting $\delta(\Gamma_7 \rightarrow \Gamma_8) = 60\,K$ is in good agreement with the experimental variation. In other words, this leads to suppose that the Curie–Weiss temperature θ depends on the excited Γ_8 level thermal population, as proposed for the characteristic temperature T_f in Ref. [11].

In terms of the specific heat contribution, the meaning of these large T_f values is that the thermal $\Gamma_7 \rightarrow \Gamma_8$ promotion has to be strongly perturbed because of the IM. Such a mixing leads to an enlargement of the Γ_8 level width, which should be responsible for the enhancement of the measured entropic contribution at the low temperature side of the Schottky anomaly.

We conclude that $CePd_3Si_{0.3}$ shows no evidence of Kondo or HF behavior and consequently the high temperature specific heat anomaly reflects the sole crystal field effects. In HF systems such as $CePd_3B_{0.6}$ and $CeAl_2$ the possible mixing effects of each field sub-level lead to a quasi-linear $C(T)$ variation and the flattening effect in the crystal field contribution to χ^{-1}. This effect should appear in most of the so-called HF cerium systems.

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