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Low-temperature thermal properties in the $CePd_3B_x$ system§

J Sereni†, G Nieva†, J P Kappler‡, M J Besnus‡ and A Meyer‡

† Centro Atomico, Bariloche, Argentina
‡ LMSES, Université Strasbourg I, Institut de Physique, F-67084 Strasbourg, France

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Abstract. Low-temperature ($0.4 \leqslant T \leqslant 20$ K) heat capacity data for typical boron concentrations in the system $CePd_3B_x$ ($0.07 \leqslant x \leqslant 1$) are reported. Schottky-like anomalies occur in the range 0.7–2 K for all boron concentrations investigated ($x = 0.07$, 0.19, 0.35, 0.60 and 1). For $x = 1$ a 'single-impurity-like' behaviour is observed with a value of $C/T = 3.9$ J mol^{-1} K^{-2} as $T \to 0$; the entropy gain at 6 K is found to be $\sim 0.9\, R \ln 2$ and this is in agreement with a Γ_7 crystal-field ground state. The observed anomalies are tentatively ascribed to either an aleatory cooperative magnetic state or to a dense Kondo model state of a heavy Fermi liquid system with some magnetic correlation effects.

1. Introduction

The valence change of cerium is well known to be driven by environmental modifications, such as external and 'chemical' pressure or alloying (Lawrence *et al* 1981). There are many examples of pseudobinary compounds in which Ce varies its valence continuously from an intermediate value to the trivalent value, as has been found to occur in Ce(Rh, Pt)$_2$ (Barberis *et al* 1982), Ce(Pd, Ag)$_3$ (Mihalisin *et al* 1981) and Ce(Sn, In)$_3$ (Elenbaas *et al* 1980).

A characteristic feature in intermediate-valence (written IV for short) compounds is the large value of the linear specific heat coefficient, γ, which is usually found to be one order of magnitude larger than that of a normal metal, as, for example, in Ce-based Laves phases (Sereni 1982), in $CePd_3$ (Besnus *et al* 1983a, 1985b) or in $CeSn_3$ (Cooper *et al* 1971). Still larger values of γ are observed in the nearly-trivalent (or Kondo-like) Ce compounds Ce(Pd, Ag)$_3$ (Mihalisin *et al* 1981), $(Ce_xLa_{1-x})Be_{13}$ (Besnus *et al* 1983b), $CePb_3$ (Cooper *et al* 1971) and $CeInAu_2$ (Besnus *et al* 1985a). Finally the heavy-fermion systems like $CeAl_3$ or $CeCu_2Si_2$ (see, e.g., *Proceedings of the 17th International Conference on Low Temperature Physics*) show low-temperature specific heat terms of about 1 J mol^{-1} K^{-2}.

In order to get a better understanding of the mechanisms driving such different γ values, i.e. values spread over three orders of magnitude, we choose to investigate the $CePd_3B_x$ system. In the limit $x = 0$, it shows typical γ values of IV systems, but for $x = 1$ the low-temperature ($T < 1$ K) linear specific heat coefficient increases up to about 3.9 J (Ce atom K^2)$^{-1}$.

In the $CePd_3B_x$ system, the addition of boron (at constant Ce and Pd concentrations) induces for the neighbouring Ce atoms a transition from their IV state to an almost

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trivalent state, as concluded by Dhar *et al* (1981a, b) on the basis of lattice parameter and susceptibility measurements ($T > 100$ K). Furthermore, the results of our study of the low-temperature properties of this system, through the magnetisation, susceptibility, resistivity and specific heat (Kappler *et al* 1985), are clear evidence of this transition towards the trivalent state, which is almost achieved for $x \gtrsim 0.4$. The same conclusion is reached by Wuilloud *et al* (1984) on the basis of spectroscopic measurements (XPS, BIS and EELS) which lead to a 4f occupation number n_f increasing to $n_f \sim 1$ for $CePd_3B_{0.5}$. In addition, our detailed study of the compound $CePd_3B$ demonstrates the fact that the Ce atoms are present in a tripositive ionic state, with the Γ_7 doublet as the ground state and an overall Γ_7–Γ_8 splitting of about 60 K. These results together with the results of a NMR study (Beaurepaire 1983, Beaurepaire *et al* 1985) suggest this transition to be of mainly local character.

The purpose of this paper is to present the results of a low-temperature heat capacity study ($0.4 \leqslant T \leqslant 30$ K, $0 \leqslant H \leqslant 3$ T) of this system with particular emphasis on the fact that we are able to investigate here the magnetic moment formation of the Ce atoms within special combined conditions: (i) localised 4f magnetisation and (ii) possible cluster formation in a concentrated rare-earth system. Such a cluster formation is indeed expected in this structure because of the existence of neighbouring Ce atoms which may become simultaneously magnetic due to their local boron environment in the samples not saturated by boron.

2. Experimental procedure

The samples were obtained by arc melting the required proportion of components (Ce(99.99%), Pd(99.995%) and B(99.9%) pure) under an argon atmosphere without further annealing. The x-ray patterns show no traces of spurious phases. Specific heat measurements were performed in a quasi-adiabatic ^{3}He calorimeter, using the heat pulse method. A germanium resistor (previously calibrated at zero and up to 3 T) was used as the thermometer. The applied magnetic field was produced by a superconducting magnet.

Samples with five different boron concentrations ($x = 0.07$, 0.19, 0.35, 0.60 and 1) were measured together with the comparison compound $CePd_3Be_{0.45}$ and their respective La reference compounds; one diluted alloy $(Ce_{0.1}La_{0.9})Pd_3B$, was also measured.

3. Results and discussion

A general overview of the specific heat data is given in figure 1, where the measured specific heats (C_p) up to $T = 10$ K (at zero magnetic field) are plotted. The main result is the presence of a Schottky-like anomaly in the temperature range 0.8–2 K, which may be representative of a magnetic contribution C_m. The value, C_{max}, and the temperature, T_{max}, of its maximum increase with increasing boron content in the concentration range $0 < x < 0.5$, as does the measured specific heat C_p for $T \gtrsim 5$ K. For $x = 1$ ($CePd_3B$) the tendency is reversed in all the three features C_{max}, T_{max} and C_p ($T \gtrsim 5$ K). Also shown in figure 1 are the C_p against T measurements on the reference system, $LaPd_3B$, which behave according to the 'normal' expression $C_p = \gamma T + \beta T^3$. The electronic term is found to be $\gamma = 8.5$ mJ mol^{-1} K^{-2} and the phonon term $\beta = 0.86$ mJ mol^{-1} K^{-4} are to be compared with the values for $LaPd_3$: $\gamma = 0.28$ mJ mol^{-1} K^{-2} and $\beta = 1.4$ mJ mol^{-1} K^{-4} (Besnus *et al* 1983a). Figure 2(*a*) shows the $C_p(T)/T$ results in the classical C/T against T^2 representation. As can be seen, a near linear behaviour is observed for $T > 7$ K.

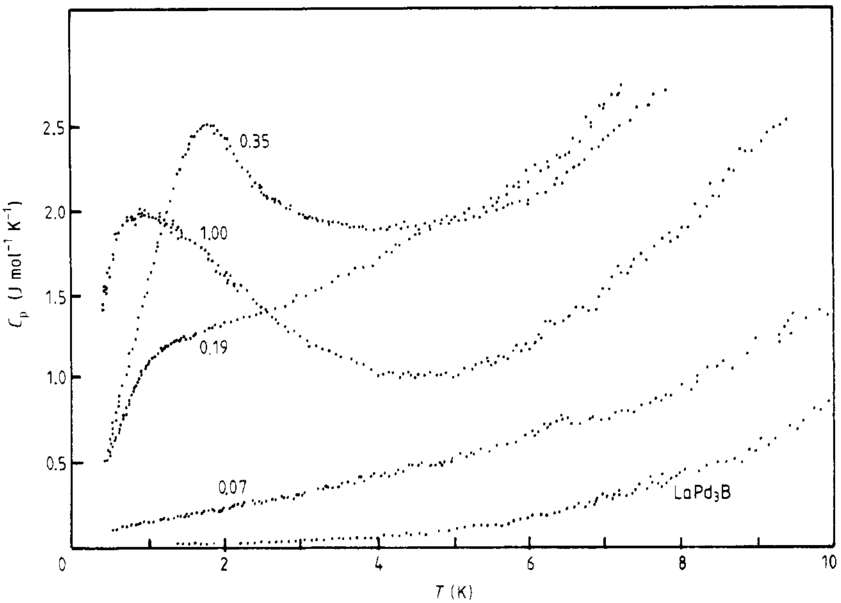

Figure 1. Measured specific heat, C_p, against temperature, $T \leqslant 10$ K, for typical boron concentrations ($x = 0.07$, 0.19, 0.35 and 1) for $CePd_3B_x$ and for the reference compound $LaPd_3B$ in zero magnetic field.

Thus, in this temperature range the C_p against T dependence may be again described, neglecting in a first approximation the small CEF and magnetic (C_m) contributions, by $C_p = \gamma_{HT} + \beta T^3$. For $x = 1$, the value of β is found to be close to that of the reference compound $LaPd_3B$. The low-temperature behaviour of $CePd_3B$ ($x = 1$) is shown in figure 2(*b*) where we have plotted the $C(T)/T$ variation after subtraction of the phonon contribution taken as that of $LaPd_3B$. The C_m term, defined as $C_m(T) = C_p(T) - \gamma_{HT}T - \beta T^3$, is shown in detail in figure 3 in a C_m against T plot.

As already mentioned, the maximum value of C_m (C_{max}) and the temperature at which it occurs (T_{max}) increase with increasing boron concentration up to $x = 0.35$ and then decrease for larger values of x. For $T < T_{max}$ one observes a linear C against T variation ($C_m \propto AT$), but $C_m(T)$ does not extrapolate to a zero value for $T \rightarrow 0$ for all boron contents x. The characteristic parameters deduced from the analysis of the zero-field heat capacity data are summarised in table 1 together with the entropy, S_m, involved in the C_m anomaly.

The specific heat results are shown as a function of applied fields (H) in figures 4(*a*) and (*b*) for the $x = 0.35$ and $x = 1$ samples, through the $C_m(T)$ variations. Within experimental accuracy, the high-temperature properties (γ_{HT}) seem to be independent of the field. The low-temperature properties are given in table 2, including for comparison data relative to the compound $CePd_3Be_{0.45}$. The most important features are (i) the shift in T_{max} towards higher temperatures and (ii) the quite different behaviour of $CePd_3B$ as compared with both $CePd_3B_{0.35}$ and $CePd_3Be_{0.45}$ with an increase in C_{max} with increasing applied field.

From magnetic susceptibility (χ) and lattice parameter (a) measurements (Kappler *et al* 1985), three different concentration regions can be distinguished. (i) A region of low boron concentration ($0 < x \leqslant 0.25$), where the susceptibility and lattice parameter data show a progressive change in the Ce valence state. (ii) An intermediate-concentration

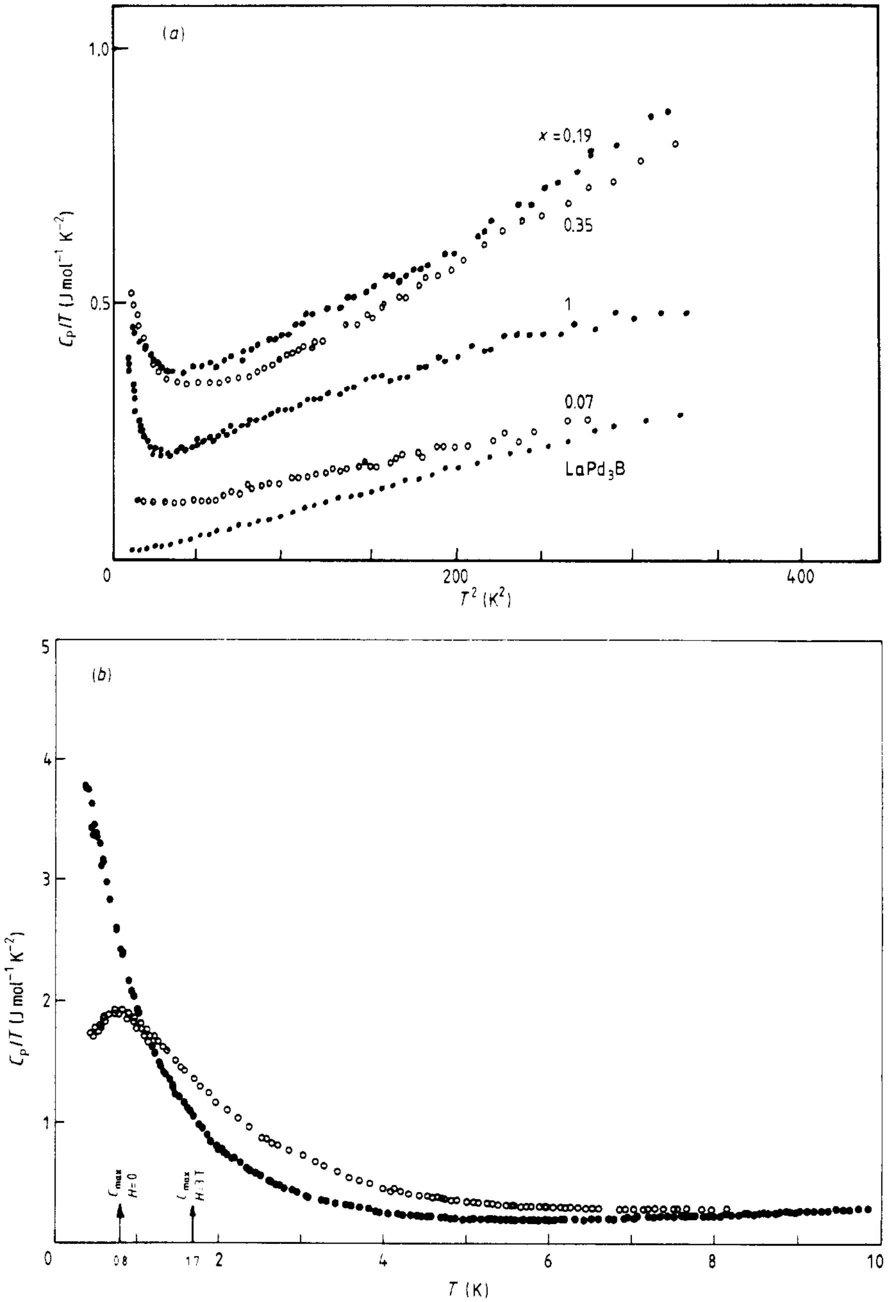

Figure 2. (*a*) High-temperature C_p/T against T^2 dependence for $CePd_3B_x$. (*b*) Low-temperature $C_p(T)/T$ against T dependence for $CePd_3B$ with subtracted lattice contribution taken from $LaPd_3B$: ●, $H=0$; ○, $H=3$ T. The temperature of the maximum of the $C_p(T)$ against T plots is indicated by arrows.

range ($0.25 \leqslant x \leqslant 0.5$), where the Ce atoms have enough boron neighbours to induce trivalency, despite the fact that there is a fractional boron concentration per unit cell. In this region the total Ce magnetisation (with a low-temperature Curie constant,

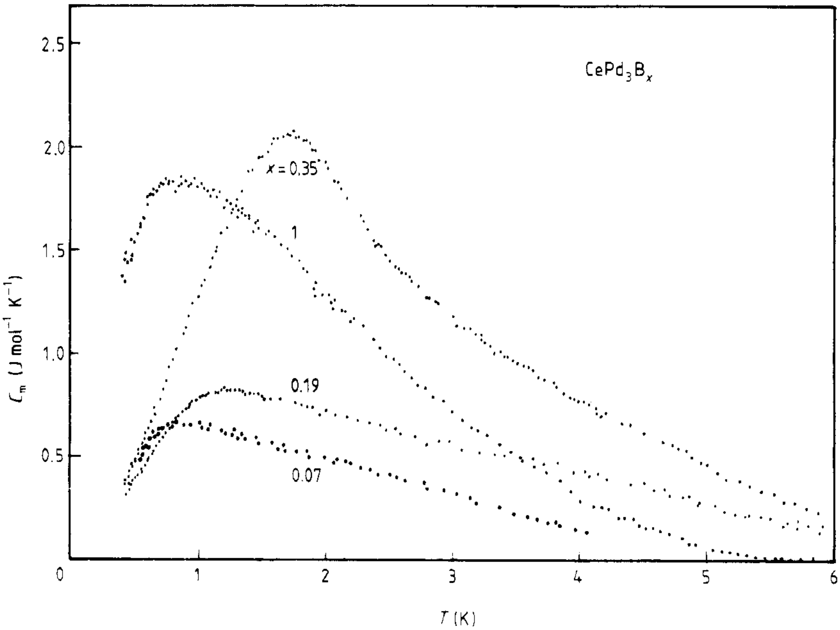

Figure 3. Schottky-like anomaly: $C_m = C_p - \gamma_{HT}T - \beta T^3$.

$C = 0.2$ EMU K per Ce atom, i.e. close to that of 0.19 for a Γ_7 ground state) and the maximum of $a = 4.20$ Å are reached. (iii) A region of high boron concentration ($0.5 \leqslant x < 1.5$), where neither magnetisation nor lattice parameter show any change. This feature is considered as indicative of no further modification in the Ce valence. These three regions are reflected in the $CePd_3B_x$ specific heat as follows.

3.1. Low boron concentration range ($0 < x \leqslant 0.25$)

From figure 1 and table 1 we observe the progressive enhancement in all the parameters which characterise the C_p against T dependence. In this region a non-homogeneous boron clustering could be expected, giving rise to different boron site occupations named $n = 0, 1, 2, 3, \ldots$, depending on the number of boron atoms grouped together. A detailed analysis of the thermal and magnetic properties allows us to recognise here for the Ce atoms three kinds of behaviour. (i) Unchanged IV or $CePd_3$-like behaviour in the space region where they have no boron atoms in the neighbourhood. Such a condition should rapidly disappear with increasing boron content. (ii) Concentration-dependent Ce IV atoms, which have some boron atoms in their neighbourhood, but not enough for reaching trivalency. This situation is responsible for the continuous change in some of the magnetic properties like the low-temperature susceptibility $\chi_0(T \to 0)$ and the temperature of the susceptibility maximum at high temperatures (Beaurepaire 1983). (iii) Finally, the case where a critical number of boron first neighbours should simultaneously drive the Ce atoms (involved in their cluster) into their trivalent state.

Figures 5(*a*) and (*b*) illustrate the concentration dependence of the thermal and magnetic parameters gathered in two groups: (*a*) those depending mainly on the IV behaviour: $\chi_0(T \to 0)$, the temperature $T(\chi_{max})$ of the high-T susceptibility maximum and γ_{HT}; (*b*) those describing mainly the magnetic (trivalent) properties: $\Delta\chi_{4.2\,K} = \chi_{4.2\,K} - \chi_{CePd_3}$, A and C_{max}.

Table 1. Specific heat data for the $CePd_3B_x$ system and the reference compound. The classical linear term (γ_{HT}) and the phonon contribution (β) are extracted from the linear C/T against T^2 range (5–15 K for $CePd_3B$); parameters characterising the low temperature anomaly: linear contribution A, value (C_{max}) and temperature (T_{max}) of the specific heat maximum, entropy gain S_m involved in the C_m anomaly.

x	γ_{HT} (mJ mol^{-1} K^{-2})	β (mJ mol^{-1} K^{-4})	A (J mol^{-1} K^{-2})	C_{max} (J mol^{-1} K^{-1})	T_{max} (K)	S_m (J mol^{-1} K^{-1})
0†	38	0.25	—	—	—	—
0.07	75	0.75	~0.1	0.07	0.9	0.20
0.19	280	1.6	1.1	0.84	1.2	1.8
0.35	230	1.7	1.7	2.10	1.75	3.0
0.60	210	1.3	3.3	2.00	0.95	4.8
1	160	1.2	3.7	1.85	0.80	5.0
$LaPd_3$ †	0.28	1.4	—	—	—	—
$LaPd_3B$	8.5	0.86	—	—	—	—
$(Ce_{0.1}La_{0.9})Pd_3B$	15.9	0.8	—	~0.14	<0.5	—

† Besnus *et al* (1983a).

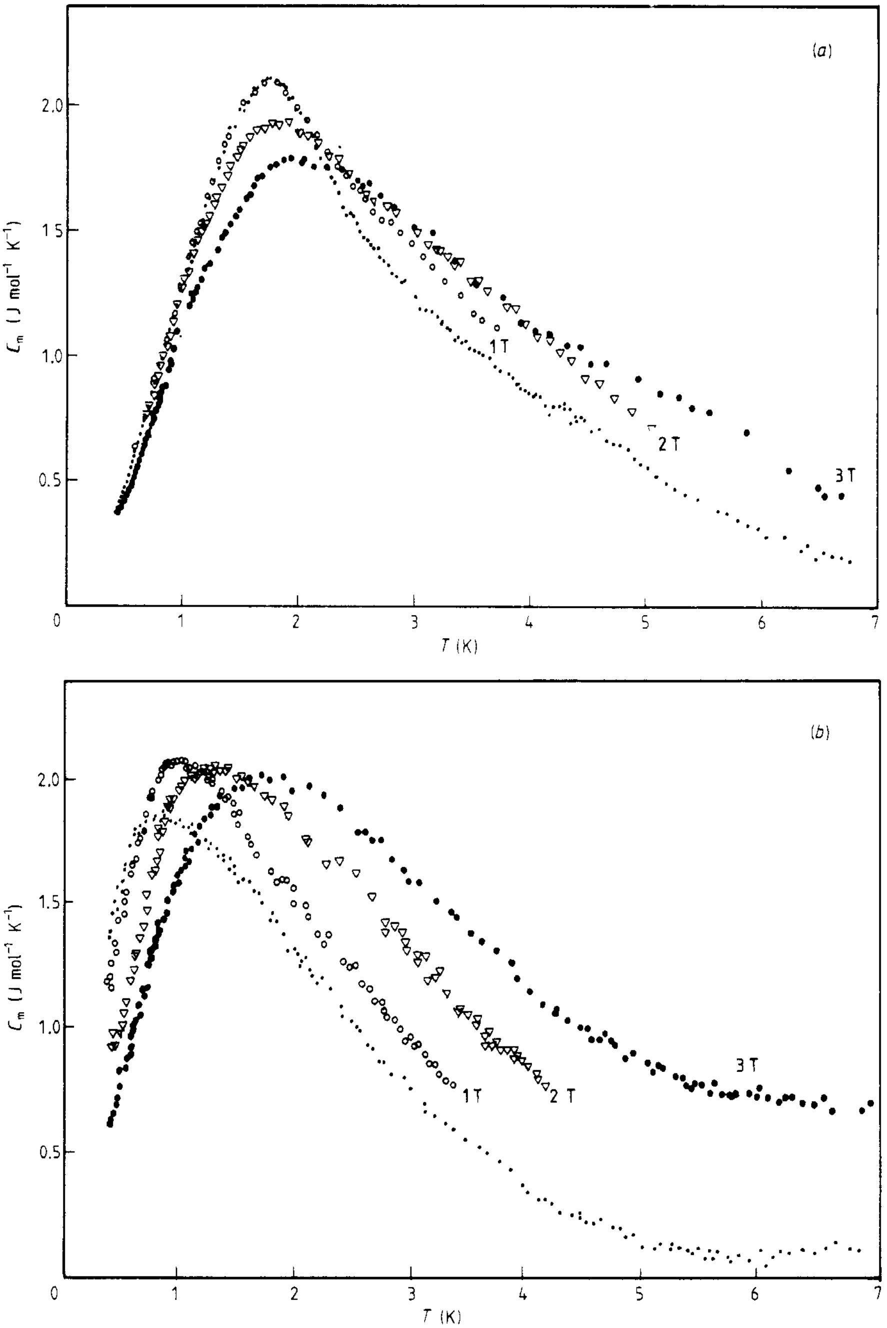

Figure 4. $C_m(H, T)$ against T at four different field values: $H=0$, 1, 2 and 3 T, for (*a*) CePd$_3$B$_{0.35}$ and (*b*) CePd$_3$B.

In figure 5(*a*) we see a small region ($x \leqslant 0.02$) where the type-(i) (CePd$_3$-like) behaviour predominates, but immediately followed by a linear concentration dependence of the characteristic parameters χ_0 and γ_{HT} (type-(ii) Ce atoms) indicating that one boron

Table 2. Low-temperature properties: linear specific heat term A, value (C_{max}) and temperature (T_{max}) of the specific heat maximum; effect of an external magnetic field H on the C_{m} anomaly.

Sample	H (T)	A (J mol^{-1} K^{-2})	C_{max} (J mol^{-1} K^{-1})	T_{max} (K)	$\delta T_{\mathrm{max}}/T_{\mathrm{max}}$
$CePd_3B_{0.35}$	0	1.7	2.10	1.75	
	1	1.7	2.08	1.75	0
	2	1.6	1.94	1.90	0.09
	3	1.3	1.78	2.00	0.14
$CePd_3B$	0	3.7	1.85	0.80	
	1	2.9	2.02	0.95	0.19
	2	2.3	2.05	1.20	0.50
	3	1.8	2.10	1.70	1.12
$CePd_3Be_{0.45}$	0	4.0	2.05	0.80	
	1	3.1	2.03	0.84	0.04
	2	2.5	1.98	0.93	0.16
	3	2.2	1.76	1.10	0.37

neighbour affects the IV behaviour of Ce but is not enough for inducing trivalency. In figure 5(*b*) the 'magnetic' parameters show a cubic concentration dependence, suggesting that almost three boron atoms are needed as first neighbours to induce the trivalent magnetic state in Ce, in accordance with NMR results (Beaurepaire *et al* 1985). It must be pointed out that in such a boron coordination two Ce atoms are located in identical positions, i.e. almost two Ce atoms become simultaneously magnetic.

3.2. Intermediate boron concentration range ($0.25 \leqslant x \leqslant 0.5$): saturation region

We will focus here mainly on the analysis of the low-temperature properties. Here both C_{max} and T_{max} reach their maximum values, together with a change in the shape of the C_{m} anomaly which becomes sharper than a Schottky anomaly. This may be an indication of an increased homogeneity among the boron clusters. This cluster formation is also inferred from the $\chi(T)$ behaviour of the $CePd_3B_{0.5}$ alloy. At decreasing temperature, as $T \to T_{\mathrm{max}}$, $\chi(T)$ deviates from the Curie–Weiss behaviour and is enhanced with respect to the value expected for a Γ_7 ground state; simultaneously one notes the appearance of thermomagnetic effects.

The main results of the heat capacity study may be summarised as follows.

For the $x = 0.35$ sample, $C(T)$ ($T \leqslant 1.8$ K) does not extrapolate to zero when $T \to 0$. Under applied fields one observes a small decrease of C_{max} and a slight increase of T_{max}. Similar variations are also found in the comparison compound $CePd_3Be_{0.45}$ (table 2 and figure 4(*a*)).

The shift of T_{max} under applied magnetic field H ($\delta T_{\mathrm{max}} = T_{\mathrm{max}}(H) - T_{\mathrm{max}}(0)$) is found to have a quadratic field dependence for the 'trivalent' Ce compounds (i.e. $x = 0.35$ and 1, and also for $CePd_3Be_{0.45}$) (figure 6(*a*)). This δT_{max} value is related to the effective magnetic field seen by the Ce atom. By defining $\delta T_{\mathrm{max}}/T_{\mathrm{max}}$ as $\delta T_{\mathrm{max}}/T_{\mathrm{max}} = D_0 H^2$ we obtain: $D_0 = 0.015$ T^{-2} for $x = 0.35$; $D_0 = 0.12$ T^{-2} for $x = 1$ and $D_0 = 0.04$ T^{-2} for $CePd_3Be_{0.45}$.

Up to this concentration ($x < 0.35$) a linear T_{max} against x dependence is observed (figure 6(*b*)), characteristic of short-range magnetic order; however, as $x \to 0$, $T_{\mathrm{max}} \neq 0$

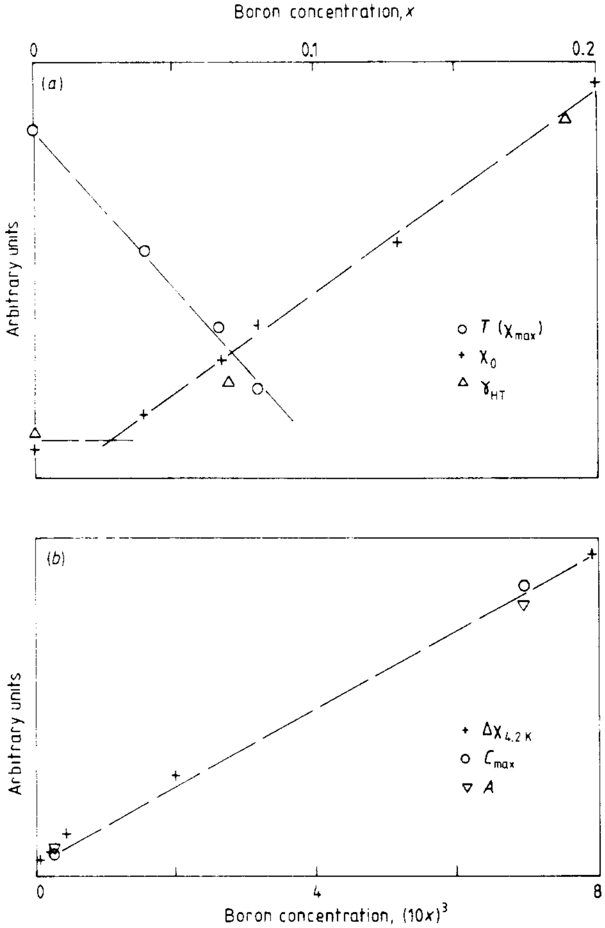

Figure 5. Boron concentration dependence of (*a*) $T(\chi_{max})$, $\chi(0)$ and γ_{HT}, related to Ce IV and (*b*) $\Delta\chi$ (4.2), C_{max} and A, related to trivalent Ce. For details see text. The lines are guides for the eye.

which may be an indication of a non-single-impurity limit for low boron content; such a linear T_{max} against x dependence has already been described (Aliev *et al* 1983) in terms of a paramagnetic phase transition. In this intermediate boron concentration range the $\gamma_{HT}(x)$ variation behaves proportional to the ratio $\partial\chi/\partial x$, reaching a maximum value of $\gamma_{HT} \sim 300$ mJ mol^{-1} K^{-2} (in agreement with previous results (Kuentzler *et al* 1984)) at $x \sim 0.2$, where the maximum change in $\chi(x)$ occurs (Kappler *et al* 1985). At first sight, the properties observed in this concentration range (enhanced γ_{HT} values, concentration dependence of T_{max}, δT_{max}, γ_{HT}) compare with those reported to occur in various spin-glass systems as, for example, **ThGd** (Sereni 1979) or **PdNi** (Chouteau *et al* 1968). They also show some analogy with the properties of the $CeSi_x$ system (Yashima *et al* 1982) which, however, orders ferromagnetically and is discussed there in terms of a dense Kondo system.

Finally, the entropy (S_m) involved in the Schottky-like anomaly for $x = 0.35$ does not reach the expected value of $S = R \ln 2 = 5.76$ J mol^{-1} K^{-1} (for the Γ_7 ground state) (table 1). The measured value $S = 3.04$ J mol^{-1} K^{-1} at 6 K is closer to the value expected

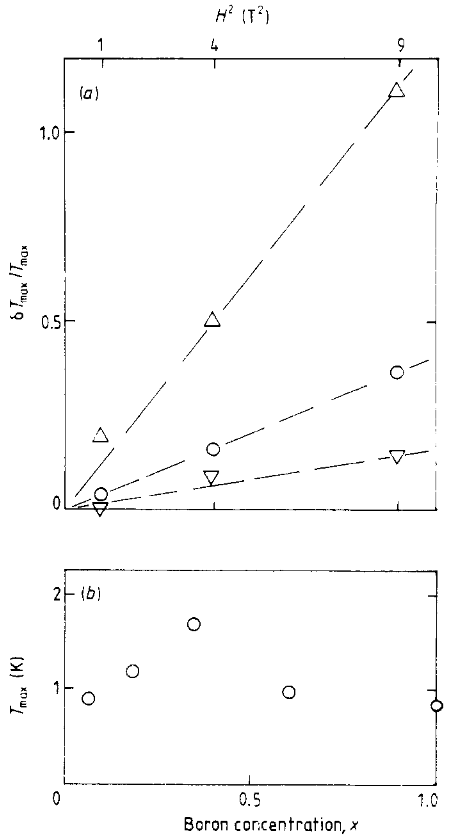

Figure 6. (*a*) External field dependence of $\delta T_{max}/T_{max}$ for $CePd_3B_{0.35}$ (▽), $CePd_3B$ (△) and $CePd_3Be_{0.45}$ (○). (*b*) Boron concentration dependence of T_{max} in the $CePd_3B_x$ system. The lines are guides for the eye.

for clusters formed by three boron atoms (involving two Ce atoms) which is $S = R(2 \ln 2 - \ln 3) = 2.4$ J mol^{-1} K^{-1}. These deviations may also be understood taking into account an inhomogeneous boron distribution.

3.3. Concentrated boron region

The $CePd_3B_x$ system is found to form up to $x \sim 1.5$, involving more than one boron atom per unit cell, while for bigger interstitial atoms (Be, Si, Ge) one never reaches such large x values (Kappler *et al* 1983). The electrical resistivity of $CePd_3B$ and that of the reference compound $LaPd_3B$ are found to be nearly temperature-independent with an extremely large residual value $\rho_0(T \rightarrow 0) \simeq 200\ \mu\Omega$ cm (Kappler *et al* 1985), while for the comparison compound, $CePd_3Be$, the measured value is only $\rho_0 \simeq 5\ \mu\Omega$ cm.

From these features, a spatially disordered pattern appears likely to apply to the concentrated boron compounds. Because of their small atomic volume, boron atoms are able to occupy interstitial sites other than the octahedral ones. Then, for large x values, i.e. when a large number of boron atoms lie in their body-centred symmetry sites (pressing the neighbouring cells), the probability of a non-body-centre site occupation increases, which may allow the large x values and also explain the increased ρ_0 values. This spatial inhomogeneity may also affect the already trivalent Ce sites avoiding the possibility of a long-range magnetic order. This situation, which may result in the quite different thermal behaviour of $CePd_3B$ compared with that of the $x = 0.35$ compound, is partly reflected by the change in the shape of the Schottky-like anomaly which becomes broader, while T_{max} decreases, as would be expected in an 'impurity regime'. Further, for $CePd_3B$, the low-temperature part of the specific heat extrapolates to zero as $T \to 0$, the linear coefficient A reaching one of the largest values observed even in Ce-based compounds, $A = 3.7\ J\ mol^{-1}\ K^{-2}$ (table 1); in addition $\delta T_{max}(H)$ is found to be three times larger than that of the $x = 0.35$ alloy, i.e. $\delta T_{max} = 0.9$ K for $H = 3$ T (figures 4(*b*) and 6(*a*)); correlatively, as already mentioned, one observes an increase in C_{max} with applied field contrary to the case of $CePd_3B_{0.35}$ (or $CePd_3Be_{0.45}$). This behaviour of both δT_{max} and C_{max} is similar to that reported for the (Ce, La)Al_2 system (Bredl *et al* 1978).

The γ_{HT} term is found to be $\gamma_{HT} = 160\ mJ\ mol^{-1}\ K^{-2}$ for $x = 1$, a typical magnitude for many Kondo-like systems (Cooper *et al* 1971, Besnus *et al* 1983b, 1985a, b). This reduction of γ_{HT} with respect to the maximum value reached for $x = 0.19$ may be considered as indicative of a regime change (from a cluster regime to an 'impurity-like' regime). In order to gain more insight of this 'impurity-like' behaviour for $x = 1$, we measured the dilute compound $(Ce_{0.1}La_{0.9})Pd_3B$. γ_{HT} is found to decrease proportionally to the Ce concentration (table 1) and T_{max} to shift down to lower temperatures ($T_{max} < 0.4$ K); this behaviour is similar to that encountered in $Ce_{0.1}Y_{0.9}InAu_2$ (Besnus *et al* 1985a) and $(Ce_xLa_{1-x})Al_2$ (Bredl *et al* 1978).

4. Discussion

The occurrence of a Schottky-like low-temperature specific heat anomaly in a cerium system raises the exciting question of the electronic state present. Here in the $CePd_3B_x$ system, the magnetic anomaly C_m and its entropy S_m grow with boron content, while the typical intermediate-valent behaviour of $CePd_3$ is lost. The most important indication of this is the change of the low-temperature ground-state degeneracy, $(2J+1) = 6$, of intermediate-valent $CePd_3$ (Besnus *et al* 1985b) going over to the twofold degeneracy of a doublet for the Ce atoms which have boron neighbours. Further, this doublet has a low-temperature magnetic behaviour characterising one 4f electron in a Γ_7 cubic crystal-field ground state; this is borne out by the low-temperature susceptibility and by the high-field magnetisation which saturates near the Γ_7 moment value of $0.71\mu_B$. Clearly the observed ground state cannot be the Γ_8 quartet, the magnetic moment of which would be depressed by a spin-coupling (Kondo) or a fluctuation (mixed-valence) process.

One must therefore speculate on the nature of the low-temperature anomaly seen in both the susceptibility and specific heat at low temperatures: χ becomes temperature-independent below 1 K and $C(T)$ shows a Schottky-like anomaly centred on this temperature, as clearly demonstrated for $CePd_3B$. These anomalies occur on the isotropic Γ_7 crystal-field ground state, the full moment of which is observed above the transition while it is lost below it: evidence of this is the entropy gain of $S_m \simeq 0.9\,R\ln 2$ for the transition.

Obviously, the Ce moments have not ordered in some regular antiferromagnetic structure, the loss of which at the Néel temperature would result in a λ-like specific heat anomaly instead in the observed Schottky-like one. But weak exchange between Ce moments could be non-isotropic due to non-regular lattice site occupancy of the boron atoms, or to the fact that all Ce atoms have not gone into a stable Γ_7 state. In this case anisotropic exchange could, by frustration, result in a spin–glass structure with resulting zero spontaneous magnetisation. The thermal destruction of such an inhomogeneous state will not result in a λ-like second-order transition. Instead, it can result in a Schottky-like anomaly following a model calculation of Schotte and Schotte (1975) and Bredl *et al* (1978). For an $S=\frac{1}{2}$ two-level system split by a temperature-independent short-range exchange energy ε with a lorentzian distribution of width δ and Zeeman energy E, this results for $\delta = 2$ K and $E=0$ in a maximum of the specific heat $C_{\max} = 1.5$ J mol^{-1} K^{-1} at $T_{\max} \simeq 0.5\delta/k \simeq 1$ K and a high initial $C(T)/T(T \rightarrow 0)$ value of the order of a few joules, as in this model $C(T)/T(T \rightarrow 0) = R\pi\delta/3(\delta^2+E^2) \simeq 4.4$ J mol^{-1} K^{-2}, where R is the gas constant, in qualitative agreement with the observed data (the $T_{\max}$ and A values of table 1).

The calculated Schottky-like anomaly has a total entropy change of $S = R \ln 2$, close to the observed value in the case of $CePd_3B$. Such a model would also account for the field dependence of both $C(T)$ and $M(T)$ and also for the weak magnetic irreversibilities observed below the transition temperature (Kappler *et al* 1985). It further allows the opportunity to attach separate significance to the high-temperature linear term of the specific heat which is not connected with a spin-glass transition as for this one $C/T(T \rightarrow \infty) = 0$. The simplest interpretation of γ_{HT} would be as of an electron specific heat, its value being ascribed to f–d hybridisation effects, as commonly observed in Ce compounds, whether magnetic or not. Obviously the γ_{HT} value may be dependent on the boron concentration in an unpredictable way (table 1). In summary, this model for $CePd_3B$ would represent boron-induced localised trivalent Ce atoms, in a crystal-field-split Γ_7 ground state, inhomogeneously exchange-coupled in some cluster-glass state.

However, such a model does not account for two other experimental results: the temperature dependence of the electrical resistivity and the ^{9}B nuclear relaxation rate. The electrical resistivity of $CePd_3B$ shows a continuous decrease with increasing temperature with no anomaly at and below 2 K. Thus the spin freezing does not result in a scattering drop in the conduction band, in contrast to what is expected. However, the same behaviour is observed in $GdPd_3B$ (Besnus *et al* 1985c), which also shows spin-glass behaviour, namely for the specific heat at its freezing temperature $T_F \simeq 4$ K. But here for $T > T_F$ the resistivity $\rho(T)$ normally increases with T due to the phonon contribution, while $CePd_3B$ shows the inverse anomalous behaviour.

Increasing resistivity with decreasing temperature is a common experimental feature in anomalous Ce compounds with thermomagnetic properties encountered in heavy Fermi liquid systems. Experimentally these compounds are considered as mixed-valent or Kondo lattices systems depending on whether $\langle n_f \rangle$, the mean 4f occupation number, is an integer or not. The Kondo effect has been found in dense systems, for example $CeAl_3$, and has also been found to coexist with localised magnetic ordering such as in $CeAl_2$ and in (Ce–La)Al_2 alloys (Onuki *et al* 1984). In these ternaries lattice coherence effects are unlikely and the systems have some analogy with the inhomogeneous $CePd_3B$ system. If we invoke a Kondo effect to occur in $CePd_3B$, we have a qualitative explanation for the resistivity behaviour. However, if the low-temperature specific heat anomaly accounts for an 'impurity' compensation process by the conduction electrons, we would be faced with the heaviest Fermi liquid ever found as for $S=\frac{1}{2}$ and no exchange between Ce atoms. The calculations (Rajan 1983) yield, for the $S=\frac{1}{2}$ case and $H=0$, $T_K \simeq 2T_{\max} \simeq 1.8$ K, a low-temperature electron specific heat for $CePd_3B$ of $C(T)/T(T \rightarrow 0) = R\pi/3T_K \simeq$ 4.9 J mol^{-1} K^{-2}, somewhat larger than the experimental value 3.9. We note further that the experimental value of the maximum of the specific heat anomaly of $CePd_3B$ reaches 2.0 J mol^{-1} K^{-1}, above the theoretical value 1.5 for the $S=\frac{1}{2}$ Kondo model. On the other hand, the shift of the anomaly of the specific heat with applied magnetic fields is satisfactorily accounted for by the Schotte and Schotte (1975) Kondo model for spin $\frac{1}{2}$ and further $M(H)$ near $T=0$ should grow toward saturation without threshold field, as indeed is observed (Hewson and Rasul 1983).

This hypothesis, interpreting $CePd_3B$ as a Kondo lattice system, gives rise to some difficulties. There is, for example, the fact that $\chi(T)$, which is constant below 1 K, shows a kink at 1 K, whereas theory for an $S=\frac{1}{2}$ Kondo model predicts a smooth variation of the susceptibility; a further point is that the experimental low-temperature Curie constant of $CePd_3B$ ($1 \leqslant T \leqslant 20$ K) is close to its theoretical value of $C=0.19$ for a Γ_7 ground state, whereas theory in the case of non-interacting impurities gives for a Γ_7 Ce pseudo-spin ($S=\frac{1}{2}$, $g=\frac{10}{7}$) and $0.3T_K \leqslant T \leqslant 3T_K$, i.e. here $0.5 \leqslant T \leqslant 5$ K, a reduced apparent Curie constant of $C \simeq 0.13$. Thus if a Kondo effect with $T_K \simeq 1.8$ K is nevertheless present in $CePd_3B$, then the susceptibility behaves quite differently from the model calculation: it is increased and stays constant in a temperature range where it should show Curie–Weiss behaviour; moreover, it decreases suddenly above 1 K, all of which most probably reflect magnetic correlations effects.

Another problem is encountered with the value of the so called 'Wilson ratio', $R=(\chi_0/\gamma)_{\mathrm{exp}}/(\chi_0/\gamma)_{\mathrm{theor}}=\pi^2k^2\chi_0/g^2\mu_B^2J(J+1)\gamma$, which is found to be $R=6.6$ for $CePd_3B$ ($\chi_0=0.18\ \mathrm{cm^3\ mol^{-1}}$, $\gamma=3.9\ \mathrm{J\ mol^{-1}\ K^{-2}}$) in its Γ_7 ground state ($J=\frac{1}{2}, g=\frac{10}{7}$) instead of the expected spin-$\frac{1}{2}$ Kondo problem value, $R=(1+1/2J)=2$. This may be suspected as resulting from the enhanced χ_0 susceptibility, as already considered before. Yet a difficulty arises in the hypothesis of a Kondo model behaviour of $CePd_3B_x$ from the existence of a high-temperature constant C/T term (γ_{HT} values of table 1), whereas the theoretical Kondo model term $C(T)/T$ tends slowly to zero with increasing temperature. However, high-temperature constant C/T terms are observed in heavy Fermi liquid Kondo systems such as $CeAl_3$, $CeCu_2Si_2$ or UBe_{13} (Stewart 1984) and can therefore not be invoked against the hypothesis of a Kondo system in the present case but on the contrary may argue for it. In this case γ_{HT} should be integrated in the A, C_m and S_m values which will then become somewhat larger than the values quoted in tables 1 and 2. This total magnetic contribution, shown in figure 2(*b*) in a $C(T)/T$ representation for $CePd_3B$, displays a close analogy with the quoted heavy-fermion systems. A last point in favour of a Kondo regime may be found in the ^9B relaxation rate measurements which show in $CePd_3B$, instead of a Korringa law, a $T^{1/2}$ dependence as observed in many other heavy Fermi liquid systems (Beaurepaire *et al* 1985).

In conclusion, the common starting point of the two schemes proposed above is the fact that boron addition to $CePd_3$ suppresses its intermediate-valence state, the moments of the Ce atoms in $CePd_3B$ being more localised and displaying a Γ_7 doublet crystal-field ground state. The huge low-temperature manifestations of $CePd_3B$ are then attributed to either an electronic stable disordered spin-glass system with a 'mean' exchange energy of the order of 2 K, or alternatively, to an atypical Kondo model behaviour, with a small Kondo temperature of $T_K \simeq 1.8$ K, occurring here in a dense inhomogeneous system, with very heavy-fermion properties and enhanced low-temperature susceptibility. It is, however, not possible to give a definite interpretation with the results available at present.

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