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Heavy-fermion behaviour in a new phase antiferromagnetic CePb₂

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Abstract. The existence of a new phase CePb₂ has been confirmed by x-ray diffraction and SEM-EDX analysis. The magnetic properties, low-temperature specific heat and electrical resistivity of this compound have been investigated. The crystal structure has been identified to be a body-centred tetragonal structure with $a = 3.317 \text{ \AA}$ and $c = 16.187 \text{ \AA}$. Its magnetic state is antiferromagnetic with the Néel temperature $T_N = 3.6 \text{ K}$. A linear extrapolation above T_N of the C/T versus T^2 plot gives a high electronic specific heat coefficient of $210 \text{ mJ (mol Ce)}^{-1} \text{ K}^{-2}$. The magnetic entropy is reduced to 68% of the theoretical value, indicating itinerancy of some of the 4f electrons. Furthermore, the magnetic contribution to the resistivity shows a negative logarithmic temperature dependence in a wide temperature range in connection with the Kondo system. From these results it is concluded that the present new phase CePb₂ is an antiferromagnetic heavy-fermion system with the Néel temperature $T_N = 3.6 \text{ K}$.

1. Introduction

A great deal of interest has focused on the magnetic and electrical properties of several Ce and U heavy-fermion compounds (Steilich *et al* 1979, Stewart 1984, Kitazawa *et al* 1992, Kitagawa *et al* 1994, Kontani *et al* 1992). On account of the large effective mass, these heavy-fermion compounds exhibit an extremely large electronic specific heat coefficient and a large magnetic susceptibility at low temperatures. Various heavy-fermion systems have been developed during the last few decades and they can be classified into three groups in the ground state, namely paramagnetic, antiferromagnetic and superconducting states. CePb₃ is well known as a heavy-fermion system because it exhibits a large electronic specific heat coefficient of about $200 \text{ mJ (mol Ce)}^{-1} \text{ K}^{-2}$ (Cooper *et al* 1971, Lin *et al* 1985, Pillmayr *et al* 1990) and a logarithmic temperature dependence of resistivity (Lin *et al* 1985). Moreover, its neutron diffraction has revealed a modulated antiferromagnetic ground state below $T_N = 1.16 \text{ K}$ (Vettier *et al* 1986). The coexistence of the long-range magnetic order and the heavy-fermion behaviour in CePb₃ has been discussed extensively (Rahman *et al* 1990).

Detailed RE–Pb (RE \equiv rare-earth element) phase diagrams have not been established probably owing to oxidation of powder specimens which interferes with precise studies, and the existence of CePb₂ compounds has not been reported yet. Recently, however, we have confirmed the existence of this phase. Since the Ce content in this compound is high, the occurrence of long-range magnetic ordering is expected. Further, heavy-fermion behaviour would be observed in a similar manner to CePb₃. In the present paper, the crystal structure, low-temperature specific heat, electrical resistivity and magnetic properties of the

new phase CePb_2 have been investigated. X-ray diffraction analyses of LaPb_2 and PrPb_2 have also been made because La and Pr are adjacent to Ce in the periodic table and their crystal structures are not clear although the existence of these two phases has already been reported (McMasters *et al* 1968, McMasters and Gschneidner 1975). Measurement of the electrical resistivity of LaPb_2 which is isomorphic with CePb_2 has been carried out as a reference material because it is non-magnetic, with no heavy-fermion behaviour.

2. Experimental details

The starting materials were 99.9% pure Ce, La and Pr and 99.999% pure Pb. The specimens were prepared by arc melting in an argon gas atmosphere purified with a Ti getter. The ingot was turned over and remelted five times to ensure homogenization. The powder x-ray diffraction was carried out using $\text{Cu K}\alpha$ radiation. In order to prevent the powder samples from oxidizing, they were protected from the atmosphere by coating with Vaseline. The magnetization up to 55 kOe and the temperature dependence of the DC magnetic susceptibility from 2 to 300 K were measured with a SQUID magnetometer (Quantum Design). The low-temperature specific heat from 1.8 to 15 K was measured by a conventional heat pulse method with a mechanical heat switch in an adiabatic cell and a 1 K pot. The samples were fixed with nylon lines in a chamber evacuated to about 10^{-7} Torr to obtain thermal isolation. The temperature dependence of the electrical resistivity was measured by a conventional DC four-probe method.

3. Results and discussion

Figure 1 shows the powder x-ray diffraction patterns ($20^\circ \leq 2\theta \leq 80^\circ$) of CePb_2 , together with those of LaPb_2 and PrPb_2 . The existence of CePb_2 has not been confirmed yet, although the LaPb_2 and PrPb_2 phases have already been reported (McMasters *et al* 1968, McMasters and Gschneidner 1975). The existence of the CePb_2 phase is strongly expected because the chemical properties of the rare-earth elements are very similar and Ce is located between La and Pr in the periodic table. As seen from the figure, their diffraction patterns are very similar. Moreover, other phases were rarely confirmed in the microstructure observed by SEM and the compositional ratio of Ce to Pb by means of EDX analysis was very close to 1/2. Therefore, the formation of CePb_2 is confirmed and the x-ray diffraction pattern gives a tetragonal MoSi_2 -type structure (space group, $I4/mmm$) made up of three body-centred tetragonal formula units with $a = 3.317 \text{ \AA}$ and $c = 16.187 \text{ \AA}$. The indexed pattern data ($20^\circ < 2\theta < 95^\circ$) for CePb_2 are listed in table 1. The observed values of $\sin^2 \theta$ agree well with the calculated values for a tetragonal MoSi_2 -type structure. The crystal structures of LaPb_2 and PrPb_2 are the same as that of CePb_2 , and the lattice constants of RE Pb_2 ($\text{RE} \equiv \text{La, Ce or Pr}$) compounds exhibit a lanthanoid contraction, as seen from table 2. In the same table, the densities obtained by Archimedes' method are very close to the calculated values, indicating that the identification of the body-centred tetragonal MoSi_2 -type structure for these compounds is reasonable. The crystal structure of PrPb_2 has been determined to be a HfGa_2 -type structure from the powder x-ray diffraction (McMasters and Gschneidner 1975), but the reported structure is inconsistent with the present analysis. It should be kept in mind that the (019) peak of the HfGa_2 -type structure is very close to the (111) peak of

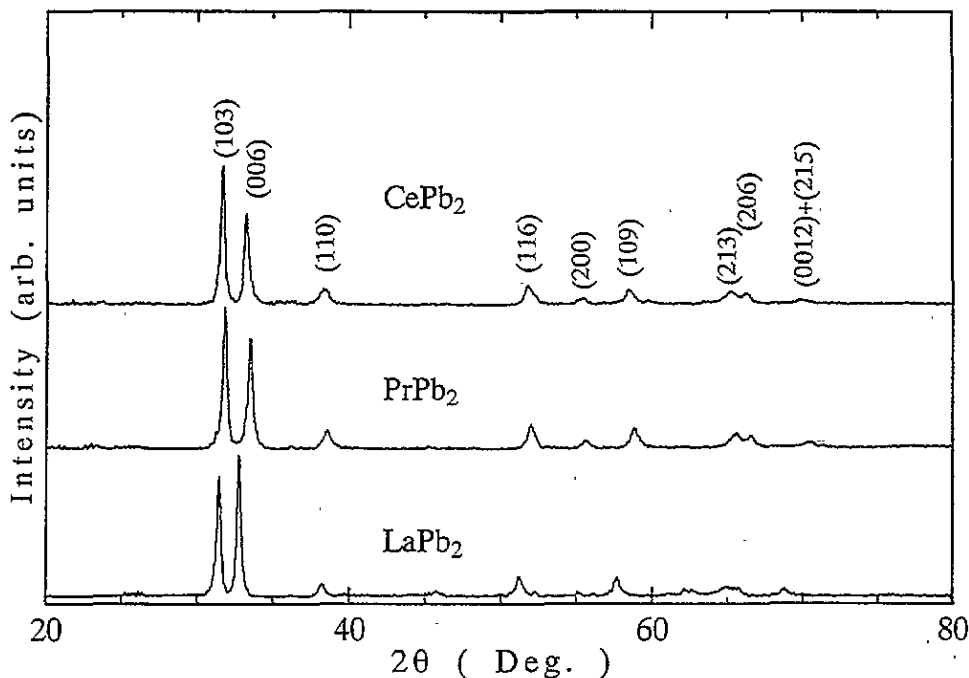


Figure 1. Powder x-ray diffraction patterns of three compounds $CePb_2$, $LaPb_2$ and $PrPb_2$.

Table 1. The observed values of $\sin^2\theta$ for $CePb_2$ and the calculated values for a $MoSi_2$ -type structure, together with the indexes.

hkl	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)
1 0 3	0.0743	0.0744
0 0 6	0.0815	0.0815
1 1 0	0.1083	0.1080
1 1 6	0.1900	0.1895
2 0 0	0.2159	0.2159
1 0 9	0.2382	0.2374
2 1 3	0.2911	0.2903
2 0 6	0.2981	0.2975
0 0 12	0.3262	0.3261
2 1 5	0.3262	0.3265
1 1 12	0.4346	0.4341
1 0 13	0.4370	0.4367
2 2 2	0.4403	0.4409
2 1 9	0.4536	0.4533
3 0 3	0.5056	0.5062
2 2 6	0.5129	0.5134
3 1 0	0.5401	0.5400

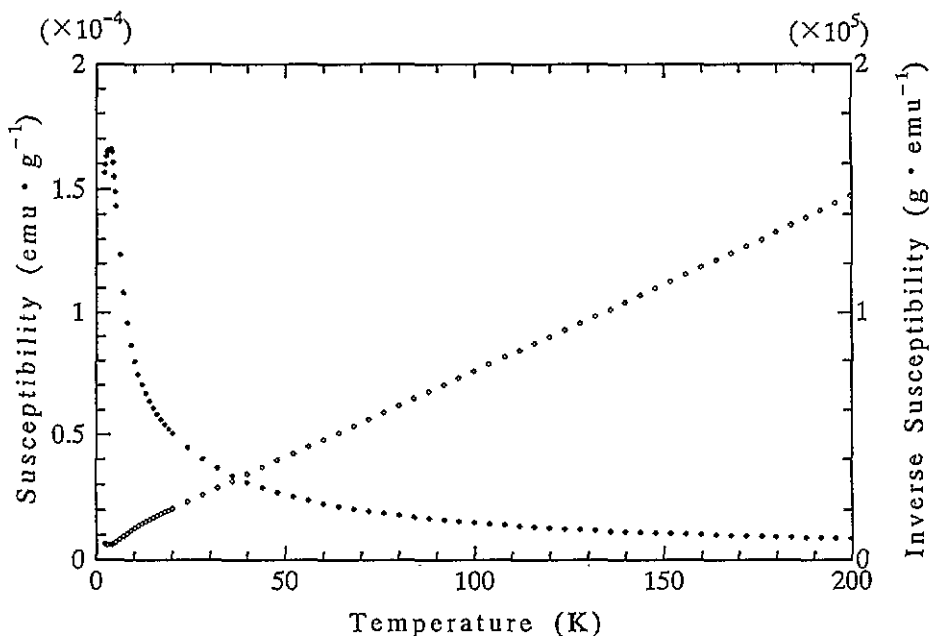
pure Pb which is often induced by selective oxidization of the rare-earth element in RE-Pb (RE \equiv rare-earth element) compounds.

Figure 2 shows the temperature dependence of the DC magnetic susceptibility χ_{DC} and its inverse magnetic susceptibility $1/\chi_{DC}$ in a field of 2 kOe in a wide temperature range.

Table 2. The lattice constants and experimental and calculated densities of CePb₂, LaPb₂ and PrPb₂.

Compound	Lattice constants (Å)		Density (g cm ⁻³)	
	<i>a</i>	<i>c</i>	Experimental	Calculated
LaPb ₂	3.331	16.918	9.9	10.09
CePb ₂	3.315	16.187	10.3	10.34
PrPb ₂	3.305	16.060	10.5	10.51

At high temperatures, χ_{DC} follows a Curie-Weiss law with the effective magnetic moment $\mu_{\text{eff}} = 2.54\mu_B$ which is very close to the value for the free Ce³⁺ ion. Consequently, the magnetic moment in CePb₂ is almost localized at high temperatures. Figure 3 displays the temperature dependence of χ_{DC} in the low-temperature range from 2 to 6 K in 2 kOe. The curve exhibits a broad maximum at 3.6 K. The magnetic susceptibility decreases rapidly around 2.8 K with decreasing temperature. Moreover, the temperature dependence of the low-temperature specific heat *C* shows two peaks at 3.6 and 2.8 K as seen from figure 4. Therefore, it is considered that the magnetic state of CePb₂ is antiferromagnetic with the Néel temperature $T_N = 3.6$ K. Another lower-temperature peak at 2.8 K may correspond to a magnetic order-order transition temperature T_0 . Such plural magnetic transitions have been confirmed in other compounds such as DyGa₂ (Gignoux *et al* 1991) and PrCo₂Si₂ (Shigeoka *et al* 1987). The Néel temperature T_N of CePb₃ has been reported to be 1.16 K from neutron diffraction (Vettier *et al* 1986) and specific heat (Lin *et al* 1985) experiments, and thus the present T_N of CePb₂ is higher than that of CePb₃.

Figure 2. Temperature dependence of the magnetic susceptibility χ_{DC} and the inverse susceptibility $1/\chi_{DC}$ for CePb₂ in a field of 2 kOe.

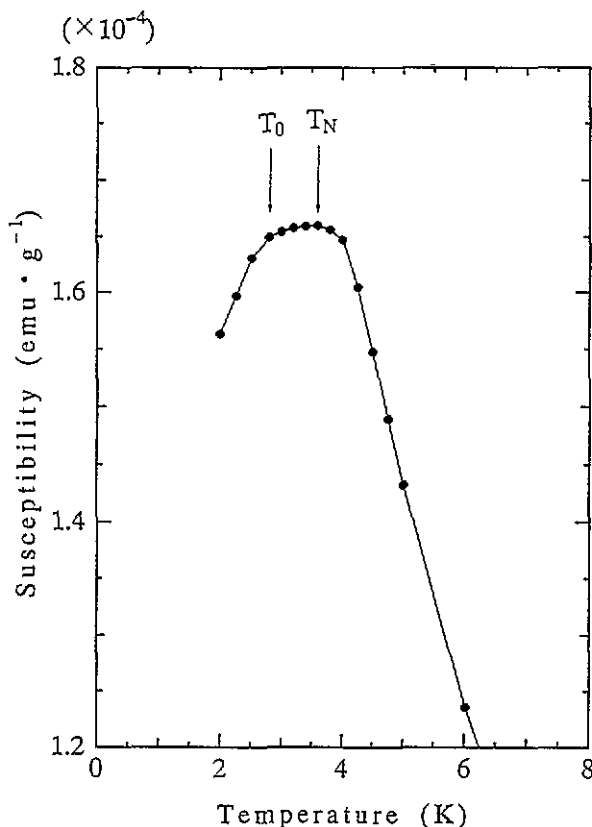


Figure 3. Temperature dependence of the magnetic susceptibility χ_{DC} in a field of 2 kOe for CePb₂ in the vicinity of the Néel temperature T_N . T_0 represents the magnetic order-order transition temperature.

One of the characteristic properties of heavy-fermion systems is a large electronic specific heat coefficient due to a high effective mass. Figure 5 shows the temperature dependence of specific heat in the form of C/T versus T^2 for CePb₂ and LaPb₂. The slopes of these two compounds are parallel. The electronic specific heat coefficient γ obtained by linear extrapolation above T_N ($50 \text{ K}^2 < T^2 < 100 \text{ K}^2$) is $210 \text{ mJ (mol Ce)}^{-1} \text{ K}^{-2}$. It should be noted that the C/T versus T^2 plots for CePb₂ and LaPb₂ are almost linear for $T^2 = 50$ – 100 K^2 and the Debye temperature Θ_D for CePb₂ of 127 K is very close to 125 K for the non-magnetic compound LaPb₂. Therefore, such a large γ -value would mainly come from the high effective mass and could scarcely be correlated with the Schottky anomaly and with the λ -type antiferromagnetic contribution. In fact, the antiferromagnetic contribution to the specific heat completely vanishes above 7 K as shown in figure 6.

The γ -value of CePb₃ with a AuCu₃-type structure has already been reported to be $225 \text{ mJ (mol Ce)}^{-1} \text{ K}^{-2}$ (Cooper *et al* 1971) and $200 \text{ mJ (mol Ce)}^{-1} \text{ K}^{-2}$ (Lin *et al* 1985). When the Schottky anomaly is taken into consideration, γ exhibits a larger value of $250 \text{ mJ (mol Ce)}^{-1} \text{ K}^{-2}$ (Pillmayr *et al* 1990). That is, subtraction of the Schottky anomaly reduces the slope of the specific heat curve and hence slightly enhances the γ -value. In any event, the γ -value of CePb₂ is very large. In the present study for CePb₃, the γ -value obtained by linear extrapolation in a similar manner as for CePb₂ is almost equivalent to the

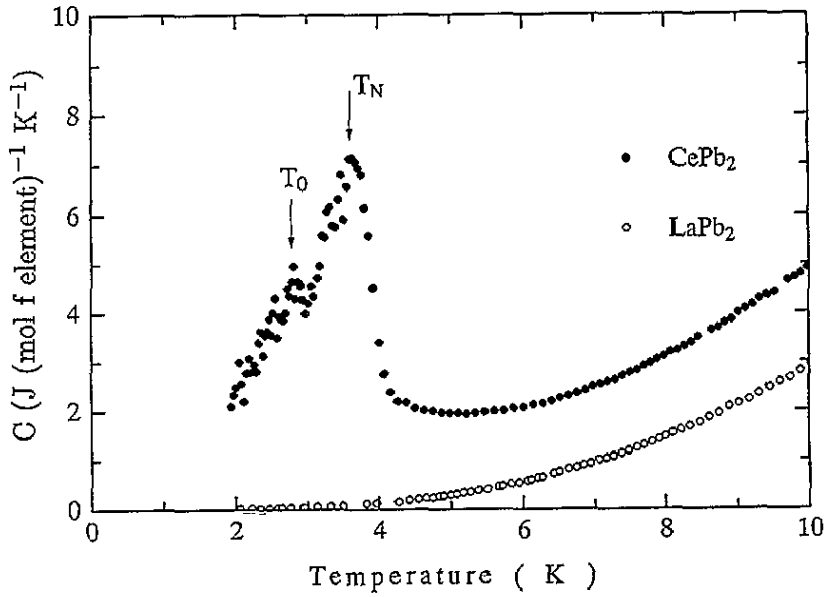


Figure 4. Temperature dependence of the specific heat C for CePb_2 , together with that for LaPb_2 as a reference material.

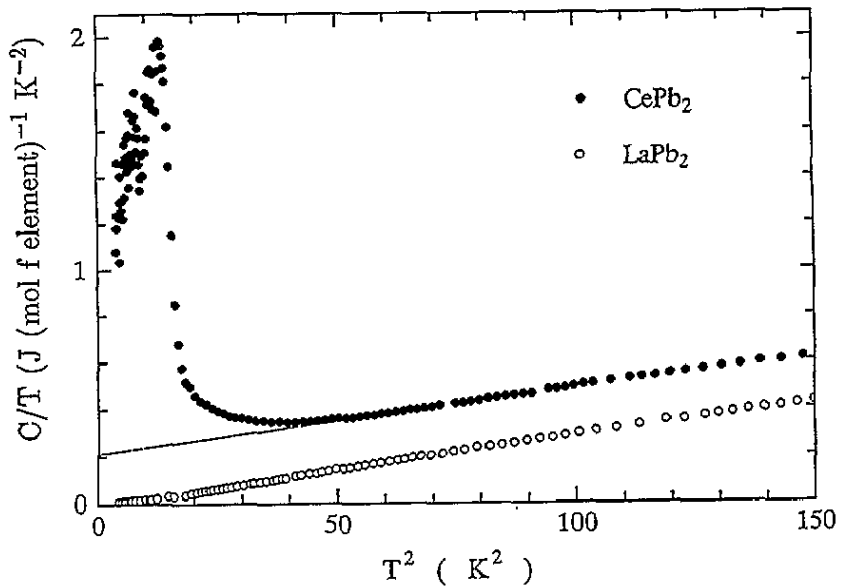


Figure 5. Low-temperature specific heats of CePb_2 and LaPb_2 in the form of C/T versus T^2 .

values mentioned above, and the Debye temperature Θ_D is estimated to be 125 K. These γ and Θ_D are comparable with those of CePb_2 in spite of the difference between their crystal structures.

Figure 6 shows the antiferromagnetic contribution to the specific heat C_{mag} divided by

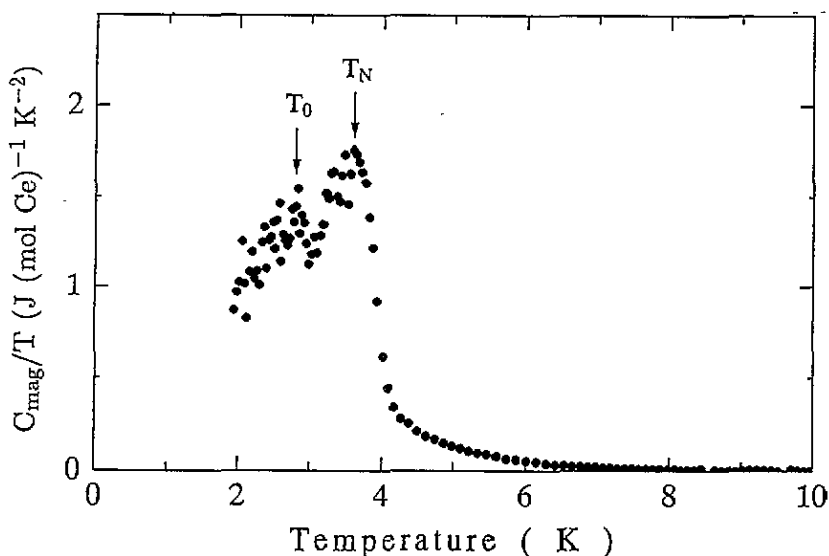


Figure 6. Temperature dependence of the magnetic specific heat divided by the temperature, i.e. C_{mag}/T , for CePb₂.

the temperature T for the new phase CePb₂. The value of C_{mag} is obtained by subtracting the electronic and the lattice parts from the total specific heat C_{total} , which is given by the following expression:

$$C_{\text{mag}} = C_{\text{total}} - \gamma T - \beta T^3 \quad (1)$$

where β is the lattice specific heat coefficient. The magnetic entropy change S_{mag} is obtained by integrating the C_{mag}/T versus T curve and estimated to be 3.9 J (mol Ce)⁻¹ K⁻¹. The value of S_{mag} associated with the long-range magnetic transition is also given by the following equation:

$$S_{\text{mag}} = k_{\text{B}} \ln(2J + 1) \quad (2)$$

where k_{B} is the Boltzmann constant and J the quantum number angular momentum. In general, the $J = \frac{5}{2}$ multiplet of the Ce³⁺ ion is considered to split partly under the influence of the crystalline electric field. The ground state of CePb₃ (Lethuillier and Chaussy 1976, Vettier *et al* 1986, Renker *et al* 1987) and CeAl₂ (Bredl *et al* 1978) is the Γ_7 Kramers doublet with an antiferromagnetic state; therefore, the theoretical value of S_{mag} expected from entropy decrease is $R \ln 2$. The magnetic entropy change of CePb₃ estimated from the specific heat is 64% of $R \ln 2$ (Fortune *et al* 1987). In the tetragonal CePb₂ compound, the ground state is considered also to be a Kramers doublet in a similar manner as other tetragonal Ce compounds such as CeCu₂Si₂, CeCu₂Ge₂ and CePt₂Si₂ (Horn *et al* 1981, Knopp *et al* 1987, Ayache *et al* 1987). The S_{mag} -value of 3.9 J (mol Ce)⁻¹ K⁻¹ is 68% of $R \ln 2$. Therefore, it is considered that 32% of 4f electrons in CePb₂ become non-magnetic because of itinerancy, and the magnetic entropy change is reduced in a similar manner as in CePb₃. Several physical properties of CePb₂ and CePb₃ are listed in table 3 for comparison. The γ -values and $S_{\text{mag}}/(R \ln 2)$, which are associated with the heavy-fermion behaviour,

Table 3. Comparison of the crystal structures, the Néel temperatures T_N , the electronic specific heat coefficients γ , the Debye temperatures Θ_D and the magnetic entropy changes divided by theoretical values, i.e. $S_{\text{mag}}/(R \ln 2)$, for CePb₂ and CePb₃.

	Structure	T_N (K)	γ (mJ mol ⁻¹ K ⁻²)	Θ_D (K)	$S_{\text{mag}}/(R \ln 2)$ (%)
CePb ₂	MoSi ₂	3.6	210	127	68
CePb ₃	AuCu ₃ †	1.16†	250	125	64§

† Zintl and Neumeyer (1933).

‡ Vettier *et al* (1986).

§ Fortune *et al* (1987).

and the Debye temperatures Θ_D for CePb₂ and CePb₃ are similar. However, it should be emphasized that the Néel temperatures are clearly different.

Shown in figure 7 is the temperature dependence of resistivity normalized by the value at 270 K, namely $\rho(T)/\rho(270)$ for CePb₂ and LaPb₂. The positive temperature coefficient of CePb₂ is smaller than that of LaPb₂. Since the Debye temperatures of these two compounds are very close to each other, the phonon contribution to the resistivity of CePb₂ is regarded as the same as that of LaPb₂. Therefore, the magnetic contribution ρ_{mag} to the resistivity of CePb₂ will be given by the difference $\rho_{\text{CePb}_2} - \rho_{\text{LaPb}_2}$ between the resistivities of the two compounds, as represented in the inset. The value of ρ_{mag} increases in proportion to $-\log T$ in the high-temperature range with regard to the Kondo system and deviates from the logarithmic temperature dependence with decreasing temperature. This behaviour is explained by the reduction in scattering due to the crystal-field splitting (Lin *et al* 1987) and/or the development of the coherence between the Kondo sites which behave independently at high temperatures (Sumiyama *et al* 1986). This type of temperature dependence is also observed in the antiferromagnetic heavy-fermion CePb₃ (Lin *et al* 1987). From the large γ -value, the reduction in magnetic entropy change and the logarithmic temperature dependence of the magnetic contribution to the resistivity, it is concluded that the present new phase CePb₂ is an antiferromagnetic heavy-fermion system.

4. Summary and conclusions

A structure analysis has been carried out in order to identify a new phase CePb₂. The electrical resistivity, low-temperature specific heat and magnetic susceptibility of CePb₂ have been investigated in connection with the heavy-fermion behaviour. The main results are summarized as follows.

(1) The existence of a phase CePb₂ has been confirmed by x-ray diffraction and SEM-EDX analysis. The crystal structure is identified to be a body-centred tetragonal MoSi₂-type structure with the lattice constants $a = 3.317 \text{ \AA}$ and $c = 16.187 \text{ \AA}$. The crystal structures of LaPb₂ and PrPb₂ have been confirmed to be the same as that of CePb₂.

(2) The magnetic state of the new compound CePb₂ is antiferromagnetic with the Néel temperature $T_N = 3.6 \text{ K}$. The effective magnetic moment at high temperatures is very close to the value of the free Ce³⁺ ion.

(3) The Debye temperature Θ_D of CePb₂ is 127 K and is almost the same as that of LaPb₂.

(4) The electronic specific heat coefficient of CePb₂ is very large, about 210 mJ (mol Ce)⁻¹ K⁻² which is comparable with that of the CePb₃ heavy-fermion compound.

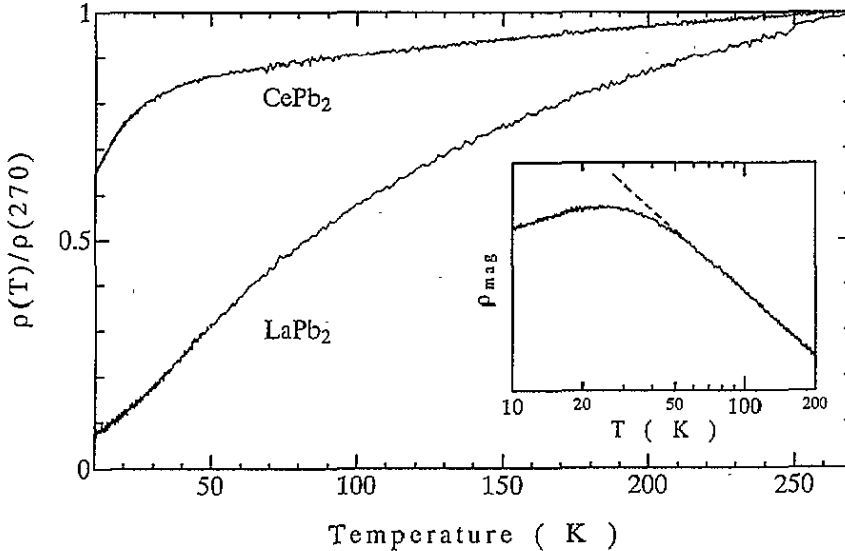


Figure 7. Temperature dependence of the resistivity for CePb₂ and LaPb₂ normalized by the resistivity at 270 K. The inset shows the logarithmic temperature dependence of the magnetic contribution $\rho_{\text{mag}} = \rho_{\text{CePb}_2} - \rho_{\text{LaPb}_2}$ to the resistivity.

(5) The magnitude of the magnetic entropy change due to the antiferromagnetic transition is 68% of $R \ln 2$ in connection with itinerancy of some 4f electrons at low temperatures.

(6) The magnetic contribution ρ_{mag} to resistivity exhibits a logarithmic temperature dependence in a wide temperature range, regarding the Kondo system.

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