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Abstract
Our measurements of the magnetic susceptibility, resistivity and specific heat of $CePd_2B_2C$, a quaternary borocarbide, show clearly that Ce is in a stable trivalent state in this compound and orders antiferromagnetically at $T_N \sim 4.5$ K. In contrast, our preliminary investigations of $CePt_2B_2C$ suggest that replacement of Pd by Pt led to the formation of a heavy-fermion state without magnetic ordering down to 2 K.

1. Introduction

Intermetallic compounds containing Ce, Yb or U often exhibit unusual physical properties arising due to the competition between Ruderman–Kittel–Kasuya–Yosida (RKKY) and Kondo interactions. $CePd_2B_2C$ and $CePt_2B_2C$ are members of the family of the quaternary borocarbides. The family of Ni-containing quaternary borocarbides RNi_2B_2C has aroused great interest because its various members provide an ideal and fertile playground for investigating various aspects of the interplay of superconductivity and magnetism occurring at relatively high temperatures [1]. The present work is motivated by the following considerations:

(i) Earlier studies of the alloys $Y_{1-x}R_xPd_5B_3C_{0.35}$ (R = rare earth) have shown that dilute substitution of Ce in place of Y in the superconducting phase YPd_2B_2C ($T_c \sim 23$ K) [2] lead to a larger depression of T_c [3] than expected on the basis of de Gennes scaling. This larger depression of T_c is indicative of the presence of the Kondo effect and suggests that $CePd_2B_2C$ might be close to the crossover from a magnetically ordered system to a heavy-fermion system.

(ii) Superconductivity is observed in $LaPt_2B_2C$ ($T_c = 10$ K) and $PrPt_2B_2C$ ($T_c = 6$ K) [4] but not in $CePt_2B_2C$ [5, 6]. The compound $CePt_{1.5}Au_{0.5}B_2C$ shows the heavy-fermion type of behaviour [5].

In an earlier report [5] it was suggested that in $CePd_2B_2C$, Ce ions are in nonmagnetic (implying nearly tetravalent) state. However, a later investigation [6] suggested that Ce ions in this material are in a nearly trivalent state. Here we present results of our resistivity, magnetization and specific heat measurements of essentially single-phase $CePd_2B_2C$ samples which not only confirm that Ce ions are indeed in the trivalent state, but also that the material orders antiferromagnetically below 4.5 K. In $CePt_2B_2C$, we find that at high temperatures Ce ions are trivalent, but the system does not order magnetically down to 2 K. Instead, it evolves into a nonsuperconducting nonmagnetic heavy-fermion state at low temperatures.

2. Experimental details

Polycrystalline samples of $CePd_2B_2C$ and $CePt_2B_2C$ were prepared by arc melting stoichiometric amounts of high-purity (cerium 99.9%, transition metal 99.9%, boron 99.8% and carbon 99.7%) elements, on a water-cooled copper hearth under an argon atmosphere. After each melting, the samples were flipped over to ensure homogeneity. The arc-melted buttons were annealed in an evacuated quartz tube at 1050 °C for six days. The occurrence and the fraction of the desired phase in the samples were checked using powder x-ray diffraction and a scanning electron microscope equipped for energy-dispersive x-ray analysis. Electrical resistivity measurements were carried out in the temperature range 1.8–300 K using the standard ac four-probe technique. Heat capacity measurements were performed in a commercial physical property measurement system (Quantum Design) using a relaxation method. A SQUID magnetometer (Quantum Design) was used for magnetization measurement.

3. Results and discussion

Powder x-ray diffraction revealed that $CePd_2B_2C$ forms essentially as single phase in the $LuNi_2B_2C$-type structure (space group $I4/mmm$). The lattice parameters we obtained, $a = 3.912$ Å and $c = 10.277$ Å, are in agreement with those published in the literature [6]. There are a few weak unidentified lines suggesting the presence of impurity phase(s) in the material which, we estimate, does (do) not exceed 5% of the main phase.

In contrast, the amount of foreign phase in our $CePt_2B_2C$ sample (nominal composition) was significant. However, at least 85% of the sample belongs to the $LuNi_2B_2C$-type tetragonal phase with the lattice constants $a = 3.839$ Å, $c = 10.712$ Å, in agreement with those reported in the literature [5, 6]. We could not identify the impurity phase(s).

3.1. CePd$_2$B$_2$C

Figure 1 shows the inverse magnetic susceptibility, χ^{-1}, of the sample between 2 and 350 K. The inset shows the magnetic susceptibility, χ, measured in a field of 1 T, of $CePd_2B_2C$ between 2 and 10 K. χ^{-1} follows a modified Curie–Weiss (CW) law: $\chi = \chi_0 + C/(T - \theta_p)$ between 100 and 350 K. From these data we found $\mu_{eff} = 2.6 \, \mu_B$ which is close to the value expected for the Ce^{3+} ion (2.54 μ_B). The paramagnetic Curie temperature, $\theta_p = -46$ K, is quite large, as is often found in Ce-based Kondo compounds. The deviation of χ^{-1} from the CW behaviour below ~100 K is a strong indication of the presence of crystal field effects. Around 4.5 K, an anomaly is visible in the temperature dependence of the magnetic susceptibility, suggesting the occurrence of antiferromagnetic order at this temperature. The behaviour of the susceptibility is quite similar to that observed in the structurally related compound $CePd_2Si_2$ [7].
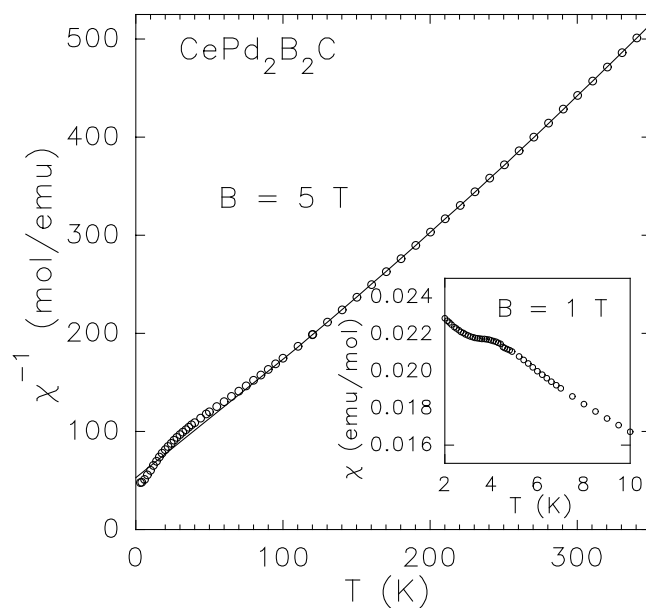
Figure 1. Inverse susceptibility (χ^{-1}) of CePd$_2$B$_2$C as a function of temperature. The inset shows the susceptibility at low temperature.
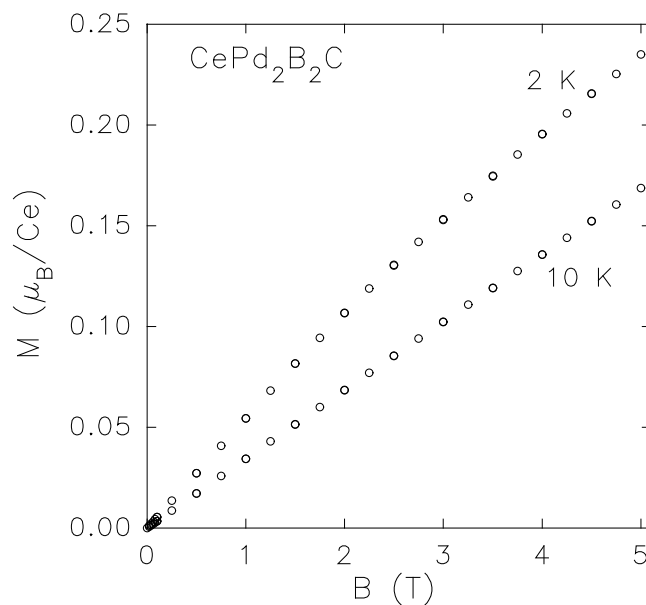
Figure 2. Magnetization of CePd$_2$B$_2$C as a function of field at 2 and 10 K.

Figure 2 shows the isothermal magnetization M measured at 2 K (below the ordering temperature) and 10 K (above the ordering temperature). In the magnetically ordered phase, M is linear in B up to $\sim$2 T and then shows a downward curvature. This observation is consistent with antiferromagnetic ordering of Ce moments.
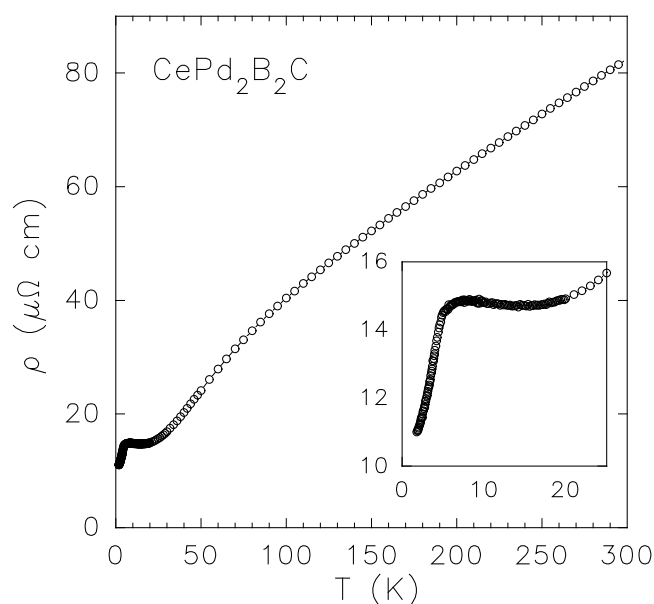
Figure 3. Resistivity of $CePd_2B_2C$ as a function of temperature. The inset shows an expanded view at low temperature.

The temperature variation of the electrical resistivity, $\rho(T)$, of $CePd_2B_2C$ is shown in figure 3. $\rho(T)$ decreases monotonically with temperature down to 20 K, below which it is essentially temperature independent down to 6 K. A small increase of $\rho(T)$ with decreasing temperature below $\sim$6 K (figure 3, inset) could be due to the presence of a weak Kondo effect or critical scattering above the region of long-range magnetic order. Such weak increases of $\rho(T)$ above T_N have often been associated with weak Kondo interaction [8, 9]. The sharp drop in $\rho(T)$ below 4 K (figure 3, inset), can be associated with the decrease of the spin disorder resistivity due to the antiferromagnetic order setting in at $\sim$4.5 K.
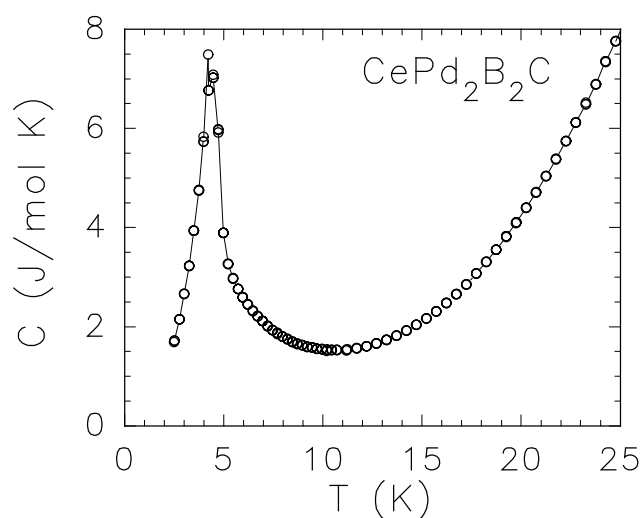
The specific heat, $C(T)$, of $CePd_2B_2C$ (figure 4) exhibits a large peak ($\sim$7 J mol^{-1} K^{-1}) at $\sim$4.5 K, the temperature at which the resistivity shows a sharp drop and the susceptibility shows an anomaly, clearly confirming the occurrence of bulk magnetic order in this material. The magnetic entropy at 8 K reaches a value of 0.87 $R\ln 2$. This suggests that the excited crystal field doublets are well separated from the ground state doublet. Thus all our results demonstrate that in $CePd_2B_2C$, Ce is in a stable trivalent state and orders antiferromagnetically at 4.5 K.

3.2. CePt$_2$B$_2$C

In contrast, our measurements of the magnetic susceptibility, the resistivity and the specific heat for our sample of $CePt_2B_2C$ suggest a much stronger hybridization of the Ce f electrons with conduction electrons, as indicated below.

The inverse magnetic susceptibility, χ^{-1}, of $CePt_2B_2C$ also follows a modified CW behaviour between 100 and 350 K (figure 5) with $\mu_{eff} = 2.52\ \mu_B$ and $\theta_p = -62$ K. The larger absolute value of θ_p is a first indication of a stronger hybridization.

Further evidence of strong hybridization stems from the temperature dependence of the resistivity (figure 6). $\rho(T)$ for the Pt-based compound decreases continuously with
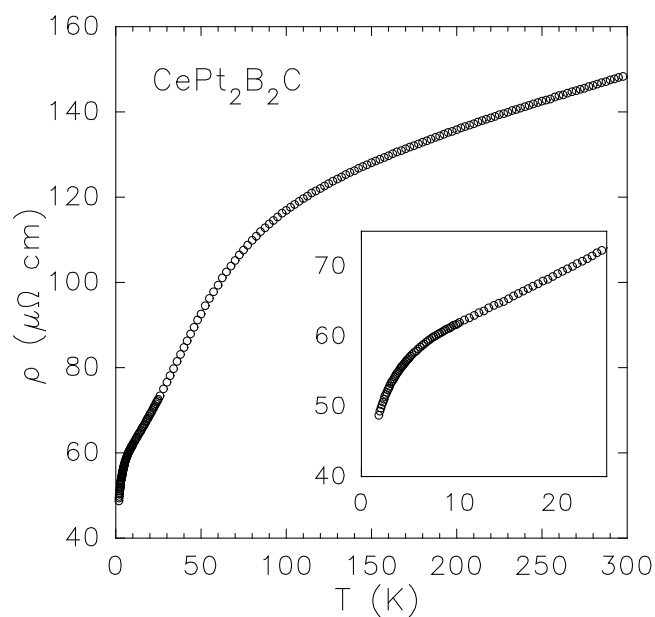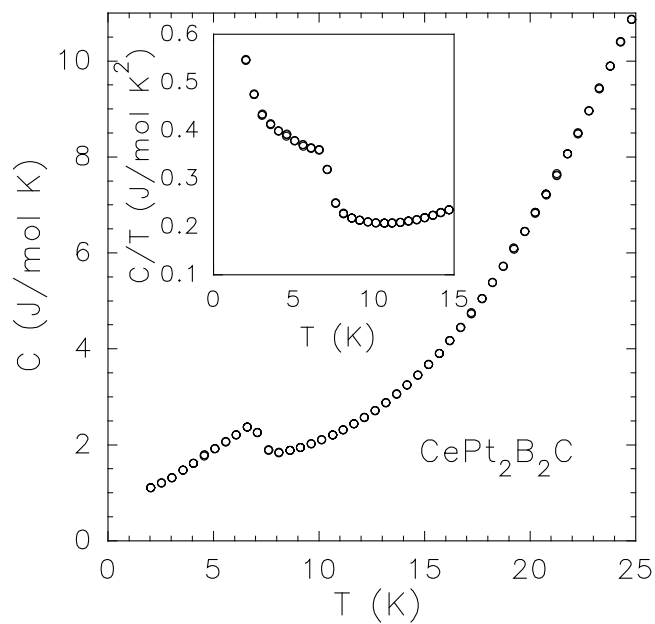
Figure 4. The specific heat of CePd$_2$B$_2$C.
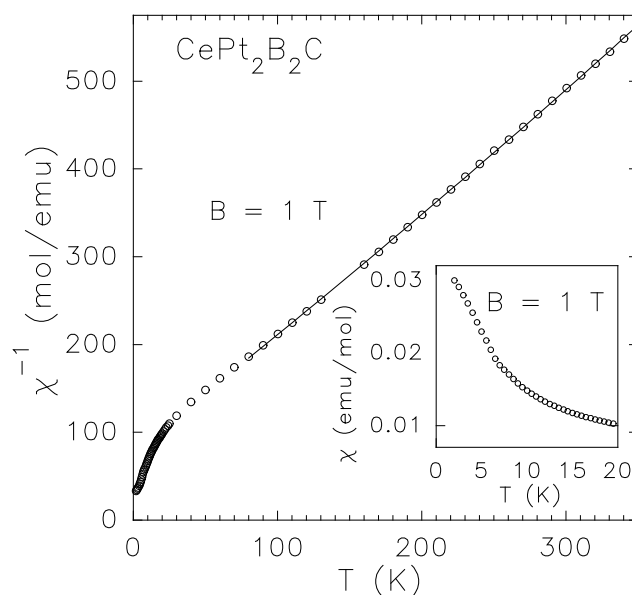
Figure 5. Inverse susceptibility (χ^{-1}) of CePt$_2$B$_2$C as a function of temperature. The inset shows the susceptibility at low temperature.

temperature, this decrease being rather weak between 300 and 100 K, but becoming very pronounced below 60 K. This behaviour is typical for nonmagnetic heavy-fermion compounds such as CeRu$_2$Si$_2$ [10]. A large part of the resistivity above 100 K is attributed to the Kondo scattering. Below 100 K, the onset of coherence amongst the Kondo scatterers led to a strong decrease of $\rho(T)$ with temperature. From the comparison with CeRu$_2$Si$_2$, one can get a first estimate for the Kondo temperature of CePt$_2$B$_2$C, $T_K \approx 30$ K. The drop in resistivity below 7 K in CePt$_2$B$_2$C is possibly associated with a magnetic transition of an impurity phase (see the specific heat results below).

Figure 6. Resistivity of $CePt_2B_2C$ as a function of temperature. The inset shows an expanded view at low temperature.

Figure 7. The specific heat of $CePt_2B_2C$. The inset shows the data plotted as C/T versus T.

Specific heat (C) measurements on the sample of $CePt_2B_2C$ have been carried out in the temperature interval 2–30 K. The results are shown in figure 7. $C(T)$ shows an anomaly at ~7 K. But the magnitude of the jump in $C(T)$ at the transition is quite small (0.7 J mol^{-1} K^{-1})

compared to that seen in CePd$_2$B$_2$C (figure 4) ($\sim$6 J mol^{-1} K^{-1}). Since 85% of our sample is main phase, we believe that the magnetic transition observed in the heat capacity data is associated with the impurity phase rather than due to CePt$_2$B$_2$C. We estimate the linear temperature coefficient of the specific heat $\gamma \sim 125$ mJ mol^{-1} K^{-2} from the C/T versus T^2 plot in the temperature range 10 K $< T <$ 15 K. Further, the shape of the C/T versus T curve (inset) shows a smooth increase with decreasing T below the transition temperature. This is incompatible with the transition being an intrinsic property of the main phase. Instead, this smooth increase is probably due to the combination of a decrease of the C/T contribution of the magnetically ordered foreign phase and an increase of the C/T contribution of the main phase to lower temperatures. This would indicate a C/T value close to 0.5 J mol^{-1} K^{-2} at 2 K for the main phase. A lower bound can be obtained from the C/T value just above the transition, 0.2 J mol^{-1} K^{-2}. This large value indicates that CePt$_2$B$_2$C is a moderate heavy-fermion system.

We conclude from these results that CePt$_2$B$_2$C is a moderate heavy-fermion system and does not exhibit any magnetic order down to 2 K. Of course, more precise information on this system should be obtained by working on samples of better quality and measurement at lower temperatures.

4. Conclusions

We have shown through electrical transport, magnetic susceptibility and specific heat measurements that in CePd$_2$B$_2$C, Ce is in a stable trivalent state and orders antiferromagnetically at 4.5 K, whereas in CePt$_2$B$_2$C, the hybridization of the 4f electrons with conduction electrons is stronger, leading to a heavy-fermion state without magnetic order down to 2 K. Considering that CePd$_2$B$_2$C is similar to CePd$_2$Si$_2$, we believe that pressure studies of this material should be quite exciting.

Acknowledgment

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