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CePdSb: A possible ferromagnetic Kondo-lattice system

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Magnetic-susceptibility and electrical-resistivity measurements on CePdSb and GdPdSb have been carried out in the temperature range of 4.2–300 K. The measurements reveal that CePdSb orders ferromagnetically with an ordering temperature (T_M) of 17 K while GdPdSb orders antiferromagnetically with a Néel temperature (T_N) of 15.5 K. In the paramagnetic state, the susceptibility of CePdSb follows Curie-Weiss behavior between 50 and 300 K but deviates from it below 50 K. Its saturation magnetic moment per formula unit at 4.2 K is $1.2\mu_B$, which is reduced from the free-ion value of $2.14\mu_B$ for the Ce^{3+} ion. The resistivity of CePdSb shows a broad maximum at about 150 K and a $\ln(T)$ behavior at high temperatures, indicating the combined influence of crystalline electric fields and Kondo effect on the $4f$ moments. Thus CePdSb appears to be a Kondo-lattice system with ferromagnetic ordering of the cerium moments.

In the last few years, studies on cerium- and uranium-based intermetallic compounds and alloys have revealed that these systems exhibit a variety of unusual physical properties, such as magnetic ordering with anomalously high ordering temperatures, coexistence of heavy-fermion behavior and superconductivity, heavy-fermion behavior with an antiferromagnetic ground state or with a ferromagnetic instability, Kondo effect, valence-fluctuation phenomena, etc.[1–12] These unusual properties arise mainly due to the hybridization between the moment-carrying $4f$ and $5f$ electrons and the conduction electrons. Here we report on the structure, magnetic susceptibility and electrical resistivity of CePdSb and GdPdSb. These measurements indicate that CePdSb is ferromagnetically ordered with an ordering temperature (T_M) of 17 K, while GdPdSb is antiferromagnetically ordered with a Néel temperature (T_N) of 15.5 K. The T_M of CePdSb is anomalously high and suggests the presence of strong hybridization between the Ce $4f$ electrons and the conduction electrons. Its resistivity exhibits a broad peak at 150 K and a $\ln(T)$ behavior at high temperatures, which may be due to the combined influence of crystalline electric fields and Kondo-type interactions. These results suggest that CePdSb may represent a ferromagnetic Kondo-lattice system. Although ferromagnetism has also been observed in some other cerium-based intermetallic compounds,[13] theoretical models dealing with magnetically ordered Kondo lattices generally predict an antiferromagnetic ground state due to the antiferromagnetic nature of the coupling inherent in the single-ion Kondo problem.[14] A Kondo state has been found in ferromagnetic Ce-Si (Ref. 15) and in the pressure-induced ferromagnetic state of CeZn (Ref. 16) but this behavior is rather rare.

The *R*PdSb (*R* = Ce, Gd, and La) compounds were prepared by repeated arc melting of stoichiometric amounts of the high-purity constituent elements in a purified argon atmosphere and used as prepared for further studies. Magnetic susceptibility was measured between 4.2 and 300 K using either the Faraday method or a superconducting quantum interference device (SQUID) magnetometer. Magnetization-versus-field isotherms were obtained at various temperatures up to 8 kOe applied field. The resistivities were measured using the standard four-probe dc technique in the temperature range of 4.2–300 K. The data were acquired with a computer-controlled resistivity setup using a programmable current source, a nanovoltmeter, and a scanner unit. Current direction at each temperature is reversed and the average of the voltage readings taken to obtain the resistivity values. Low-field ac susceptibility measurements were made in the temperature range of 12–300 K using the mutual-induction principle.

The *R*PdSb (*R* = rare earth) compounds crystallize in various structure types[17–19] depending upon the *R* ion involved. Our x-ray-diffraction studies reveal that these compounds with *R* = La, Ce, and Gd were single-phase materials crystallizing in the hexagonal $CaIn_2$-type structure (space group $P6_3/mmc$) with two formula units per unit cell. In this type of structure the Ce atoms occupy crystallographic $2b$ sites and Pd and Sb atoms occupy crystallographic $4f$ sites. The lattice parameters obtained are $a = 4.596$ Å and $c = 8.094$ Å for LaPdSb, $a = 4.594$ Å and $c = 7.913$ Å for CePdSb, and $a = 4.565$ Å and $c = 7.443$ Å for GdPdSb. Figure 1 shows the plot of unit-cell volume of *R*PdSb compounds (normalized to one formula unit) as a function of the rare earth. The unit-cell volume of CePdSb deviates little from the lanthanide contraction observed in the *R*PdSb compounds with $CaIn_2$-type structure suggesting that Ce ions are essentially in a trivalent state in this compound.

A hump in the susceptibility of GdPdSb is observed at 15.5 K (inset in Fig. 2), which we take to be its Néel temperature T_N. (It is noted that the peak temperature does not exactly correspond to T_N,[20] but the difference be-

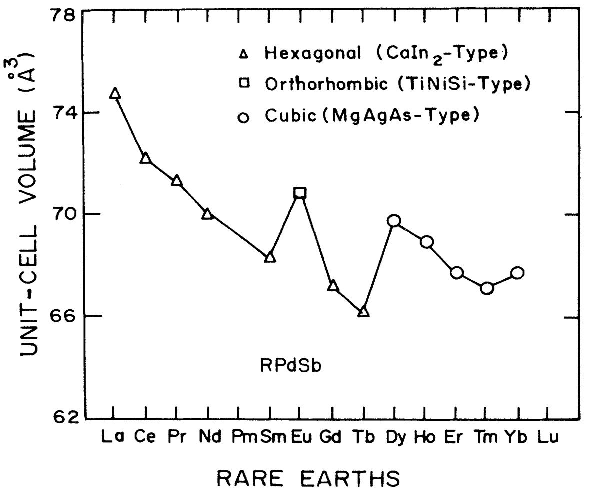

FIG. 1. Unit-cell volume of *R*PdSb compounds as a function of the rare earths.

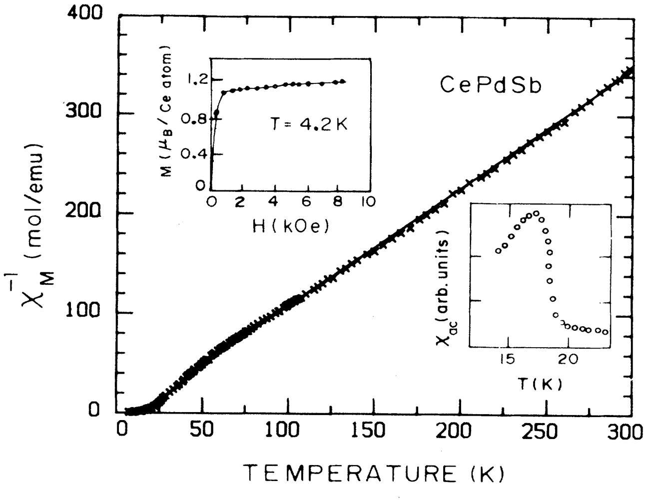

FIG. 3. Inverse magnetic susceptibility of CePdSb (in 5 kOe applied field) as a function of temperature (solid line shows fit using CEF model). Insets show magnetization-field isotherm at 4.2 K and ac susceptibility as a function of temperature.

tween the two is small and does not affect the discussions presented in this paper.) The susceptibility shows a rise below T_N even in an applied field of 200 Oe indicating the possibility of complex magnetic ordering. In fact, preliminary magnetic-susceptibility measurements, down to 2 K, on GdPdSb and some other *R*PdSb compounds, suggest the presence of at least one more transition, presumably of magnetic origin.[19] The susceptibility of CePdSb shows a rapid rise below 18 K due to the ferromagnetic ordering of the Ce moments. Low-field ac susceptibility of CePdSb also exhibits a peak at 17 K (inset in Fig. 3). Further, a sharp drop in the resistivity due to magnetic ordering of the rare-earth moments is also observed at about 17 K in both the compounds (inset Fig. 4), consistent with the magnetic ordering observed in the susceptibility measurements. The inset in Fig. 3 shows the field (H) dependence of the magnetization (M) of CePdSb at 4.2 K; M saturates in about 1.5 kOe field. The saturation magnetic moments, μ_s, obtained from the M-versus-$1/H$ plot, extrapolated to $1/H \rightarrow 0$, is $1.2\mu_B$ per formula unit at 4.2 K, which is smaller than the Ce^{3+} free-ion-moment value of $2.14\mu_B$. The M-H curve of GdPdSb at 4.2 K is nearly linear up to 8 kOe field but deviates from linear behavior in higher fields up to 55 kOe.

The inverse magnetic susceptibilities of CePdSb and

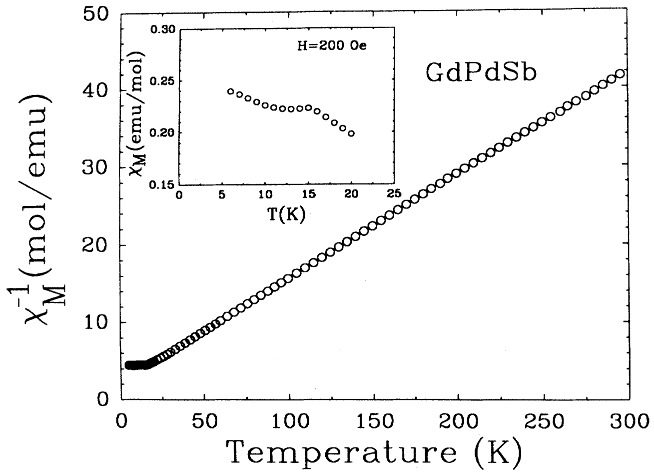

FIG. 2. Inverse magnetic susceptibility of GdPdSb (in 5 kOe applied field) as a function of temperature. Inset shows susceptibility vs temperature in 200 Oe applied field.

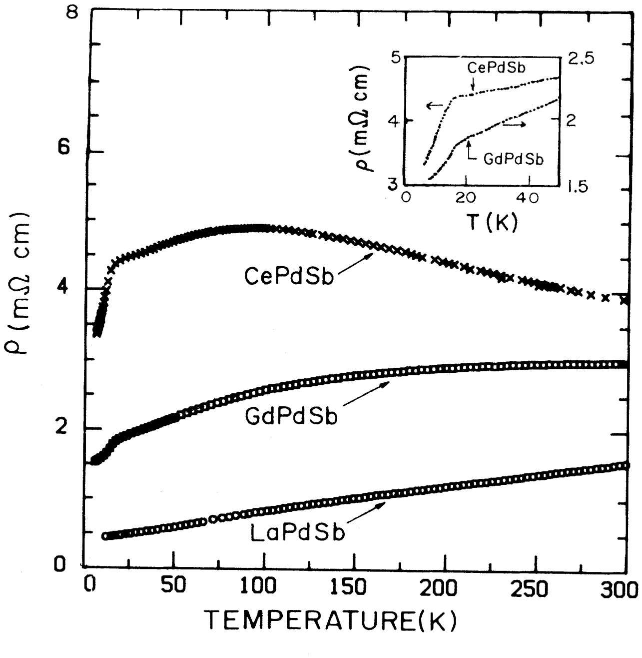

FIG. 4. Resistivity of LaPdSb, CePdSb, and GdPdSb as a function of temperature. Inset shows the behavior of resistivity at low temperatures near T_N.

GdPdSb (obtained in 5 kOe-applied field) are plotted as a function of temperature in Figs. 2 and 3. Between 20 and 300 K, the susceptibility of GdPdSb follows the Curie-Weiss behavior. The values of effective paramagnetic moment μ_{eff} and paramagnetic Curie temperature Θ_p obtained from a Curie-Weiss fit to the experimental data are $\mu_{\text{eff}}=7.73\mu_B$ and $\Theta_p=-16$ K. The susceptibility of CePdSb also follows Curie-Weiss behavior between 50 and 300 K with $\mu_{\text{eff}}=2.60\mu_B$ (close to $2.54\mu_B$ for the free Ce^{3+} ion), and $\Theta_p=10$ K. Below 50 K, the susceptibility shows deviation from the Curie-Weiss behavior. The non-$4f$ contributions to the susceptibility of CePdSb are taken to be the same as in isostructural LaPdSb in which La is nonmagnetic. These are found to be negligible. Thus the deviation in the susceptibility of CePdSb from Curie-Weiss behavior below 50 K is though to be due to the effect of crystalline electric fields (CEF) on the $4f$ moment of Ce^{3+} ion. Therefore, an analysis of the susceptibility of CePdSb has been carried out on the basis of such effects. The CEF Hamiltonian corresponding to $\bar{6}m2$ symmetry of the Ce ion is given by $\mathcal{H}_{\text{CEF}}=B_2^0O_2^0+B_4^0O_4^0$, where B_n^m are CEF parameters and O_n^m are Stevens' operators. The exchange interaction λ between cerium ions is taken into account by writing the susceptibility (χ) as $\chi(T)=\chi_{\text{CEF}}(T)/[1-\lambda\chi_{\text{CEF}}(T)]$, where χ_{CEF} is the susceptibility of Ce^{3+} ions in the presence of crystal fields alone and λ is such that $[1-\lambda\chi_{\text{CEF}}(T_c)]=0$ at T_c. The details of the analysis are given elsewhere.[21,22] The measured χ can be fitted with several combinations of CEF parameters and one such fit is shown as a solid line in Fig. 2 with $B_2^0=30.3$ K, $B_4^0=-0.18$ K, and $\lambda=37.1$ mol/emu. This set of CEF parameters gives an energy separation of 236 K between the ground-state doublet and the first-excited-state doublet and 557 K between the ground-state doublet and the second-excited-state doublet. The Θ_p or the ordering temperature calculated from the above value of λ is 18 K which agrees very well with the observed T_M of 17 K for this compound. The saturation moment at 0 K was calculated using the above CEF parameters and an appropriate molecular field which reproduces T_M. The powder average of the saturation moment obtained is $1.1\mu_B$, which is in good agreement with the experimentally observed value of $1.2\mu_B$. Some moment reduction due to the Kondo effect is also likely.

The temperature dependence of the electrical resistivity of CePdSb and GdPdSb is shown in Fig. 4. The phonon contribution to the resistivity is estimated from the resistivity of isostructural compound LaPdSb (Fig. 4). The resistivity of CePdSb is 3.8 mΩ cm at 300 K and about 3.3 mΩ cm at 4.2 K. These resistivity values are very high compared to those observed in several magnetic and nonmagnetic Ce-based compounds.[5] In fact, we observe very high resistivity in the whole series of RPdSb ($R=$Pr to Tm) compounds the origin of which is not understood at present. The magnetic scattering resistivity (ρ_m) of CePdSb, obtained by subtracting the resistivity of LaPdSb, initially increases as temperature is lowered from 300 K and passes through a broad maximum at about 150 K. It shows $\ln(T)$ dependence in the high-temperature regime, which is one of the characteristic features of the dense Kondo systems. According to the single-impurity Kondo theory proposed by Cornut and Coqblin,[23] the broad maximum in resistivity, such as that observed in CePdSb at 150 K, is associated with the combined effect of the crystalline electric fields on the localized $4f$ moments and Kondo-type interaction. This theory also predicts different $\ln(T)$ regions (or different Kondo temperatures) corresponding to different crystal-field levels. The absence of a low-temperature $\ln(T)$ behavior in the resistivity of CePdSb corresponding to Kondo temperature of the ground-state doublet may be due to the onset of ferromagnetic ordering of Ce moments in this system. The overall behavior of resistivity of CePdSb can be explained by considering the interplay between the Kondo and Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. At high temperatures, the Kondo interaction seems to dominate. As the temperature is lowered, the RKKY interaction overtakes the Kondo interaction. Hence, the system orders ferromagnetically at low temperatures.

The magnetic-ordering temperature T_M of CePdSb is higher than the T_N of GdPdSb as well as the $T_N=13$ K of orthorhombic EuPdSb (in which Eu is in the $+2$ and hence magnetic state[19]). Further, the type of magnetic ordering is also different in CePdSb (ferro) on one hand and GdPdSb and EuPdSb (antiferro) on the other hand. This implies that the exchange constant J_{sf} for the interaction between the conduction electron spins s and the $4f$ rare-earth spins S, is very different in CePdSb and GdPdSb (EuPdSb) compounds. The nearest-neighbor Ce-Ce distance in CePdSb is 3.96 Å along the c direction, which is greater than 3.25–3.4 Å, the Hill limit, beyond which the direct f-f overlap ceases.[24,25] Therefore, the direct f-f interaction can be ruled out as being responsible for the high T_M of CePdSb. In the presence of Kondo-type interactions (as inferred from resistivity measurements) the origin of unusually high magnetic ordering temperature in this compound may be understood by invoking strong hybridization between the $4f$ electrons with the conduction electrons as discussed below. In a Kondo-lattice model, the antiferromagnetic Kondo coupling J_{sf}, between the localized magnetic moments and the conduction electrons depends on the hybridization strength V_{sf}, the position of the localized $4f$ level with respect to the Fermi level E_F ($E_{\text{ex}}=|E_F-E_{4f}|$), and the intersite Coulomb repulsion U of two electrons with opposite spins in the same ion. In the case when $(V_{sf},E_F-E_{4f})\ll U$, then $J_{sf}=-|V_{sf}^2|/E_{\text{ex}}$.[26] Thus when $E_{\text{ex}}\rightarrow 0$, J_{sf} increases appreciably in magnitude; as a result, the magnetic ordering temperature, T_M ($\propto J_{sf}^2$), would be expected to show an anomalous increase until $|J_{sf}|$ becomes so large that the Ce moment is quenched.[14,27] As discussed by Brandt and Moschalkov,[3] in the presence of both Kondo and RKKY interactions, for a very large value of J_{sf}, $T_M=0$ or, in other words, $T_K>T_{\text{RKKY}}$, where T_K is the Kondo temperature and T_{RKKY} is a measure of the indirect RKKY exchange interaction. As J_{sf} decreases starting from a large value, the system shows magnetic ordering and exhibits a maximum in the T_M with further decrease in J_{sf}.

In conclusion, CePdSb orders ferromagnetically ($T_M=17$ K) and isostructural GdPdSb orders antiferromagnetically ($T_N=15.5$ K). The T_M of CePdSb is anomalously high relative to T_N of GdPdSb and de Gennes scaling. The resistivity of CePdSb indicates the presence of crystalline fields and Kondo effect. Therefore, it appears that CePdSb may represent a ferromagnetic Kondo-lattice system. It may be remarked that NdPdSb and SmPdSb also exhibit antiferromagnetic ordering with fairly high values of T_N (11 and 18 K, respectively).[19] However, their resistivities show normal metallic behavior and, therefore, it is possible that the mechanism giving rise to high T_N in these two compounds has a different origin.

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