Antiferromagnetic ordering in the doped Kondo insulator CeRhSb

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CeRhSb, the so-called ''Kondo insulator,'' is a mixed-valent compound showing a gap formation in the electronic density of states. On the other hand, CePdSb is ferromagnetically ordered with a Curie temperature of ~17 K. We have carried out magnetic susceptibility and electrical resistivity measurements on $CeRh_{1-x}Pd_xSb$ ($0 \leqslant x \leqslant 1.0$), to study the ground-state properties of this system. For small Pd doping in CeRhSb, up to 20%, the gap continually diminishes and no magnetic ordering is observed down to 2 K. In the region $0.3 \leqslant x \leqslant 0.4$, as soon as the gap is suppressed, an antiferromagnetic ground state is observed. In the region $0.5 \leqslant x < 0.7$, the compounds are not single phase. At the CePdSb end, in the region $0.7 \leqslant x \leqslant 1$, the ground state is ferromagnetic. The observation of an antiferromagnetic phase in the phase diagram of $CeRh_{1-x}Pd_xSb$, where neither end is antiferromagnetic, is interesting and is discussed in the light of some recent theoretical models. [S0163-1829(97)00821-7]

I. INTRODUCTION

The compound CeRhSb shows insulating properties at low temperatures which have been attributed to the opening of a gap in the electronic density of states due to hybridization between the conduction electron states and the Ce-$4f$ electron states.[1] The susceptibility of this compound shows a broad maximum at around 100 K suggestive of mixed valence of the Ce ions. The electrical resistivity also shows a broad maximum at around the same temperature followed by a sharp rise below 10 K. The magnetic ($4f$) contribution to the heat capacity shows a sharp drop below 10 K indicative of a sharp decrease in the electronic density of states.[2] The thermoelectric power also shows a similar drop at the same temperature.[3] All these results are consistent with the opening of a gap in the electronic density of states in the compound CeRhSb. To date, it is one of the few Ce-based compounds to show this remarkable gap formation, the others being CeNiSn, $Ce_3Bi_4Pt_3$,[4,5] etc. Direct observation of the gap in CeNiSn and CeRhSb has recently been made by Ekino *et al.*[6] by means of tunneling experiments.

The unusual gap formation at low temperature in such systems—the so-called ''Kondo insulators''—has received much theoretical and experimental interest lately. Intensive theoretical studies on Kondo insulators have been made by Doniach and Fazekas,[7] Schlottmann,[8] Wang *et al.*,[9] etc. Doniach and Fazekas[7] have considered the effect of doping in Kondo insulators and have shown that on doping with a small amount of nonmagnetic metal, for example, La at the Ce site, the dilute gas of heavy holes which forms will have a tendency to be antiferromagnetically ordered due to the hole-hole exchange coupling. Wang *et al.*[9] have shown, via a variational Monte Carlo approach, that, in three dimensions, the phase diagram of a symmetric Kondo lattice, as a function of varying Kondo coupling, $\mathcal{J}$, would indeed consist of an antiferromagnetic phase even at finite temperatures. Schlottmann[8] also argues that with an increase in hole concentration, the hybridization gap is smeared and the susceptibility follows a Curie-Weiss behavior with an antiferromagnetic Curie-Weiss temperature. Our earlier studies on La-doped CeRhSb (Ref. 10) indeed showed the smearing of the gap with 10% La substitution at the Ce site.

In this paper, we report results on the measurements made on compounds with Pd substitutions at the Rh site of CeRhSb, i.e., the system $CeRh_{1-x}Pd_xSb$ ($0 \leqslant x \leqslant 1$). Our results show that there is a small region between $x = 0.3$ and 0.4 where the gap is not seen and the system is antiferromagnetically ordered. Since CePdSb is ferromagnetically ordered, one does not expect to see an antiferromagnetic phase in the phase diagram of $CeRh_{1-x}Pd_xSb$ due to simple dilution effects. In the regime $0 \leqslant x \leqslant 0.2$, the system is not magnetically ordered down to 2 K and the ground state is insulating with the gap continuously decreasing with increasing Pd substitution. Also, in the region $0.7 \leqslant x \leqslant 1$ the system is ferromagnetically ordered with Curie temperature (T_C) dropping from ~17 K for CePdSb to ~8 K for $CeRh_{0.7}Pd_{0.3}Sb$.

II. EXPERIMENTAL DETAILS

The polycrystalline samples of $CeRh_{1-x}Pd_xSb$ ($x = 0.02$, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 0.8, and 0.9) were prepared by first melting the master alloys of CeRhSb and CePdSb and then mixing them together in the right proportions and remelting them by the standard arc melting technique in a continuous flow of argon gas. The samples were checked for phase purity by the x-ray-diffraction technique. Magnetic susceptibility in the temperature range 2–400 K and magnetization vs field isotherms up to 50 kOe field at various temperatures were obtained using a superconducting quantum interference device (SQUID) magnetometer. Electrical resistivity measurements in the temperature range 2–300 K were carried out using the standard four-probe dc technique.

III. RESULTS AND DISCUSSIONS

The two end members, namely, CeRhSb and CePdSb, are structurally different. While CeRhSb is orthorhombic (space group $Pnma$), the compound CePdSb is hexagonal (space group $P6_3/mmc$).[11] An analysis of the observed x-ray d values showed that the samples with $0 \leqslant x \leqslant 0.4$ are single

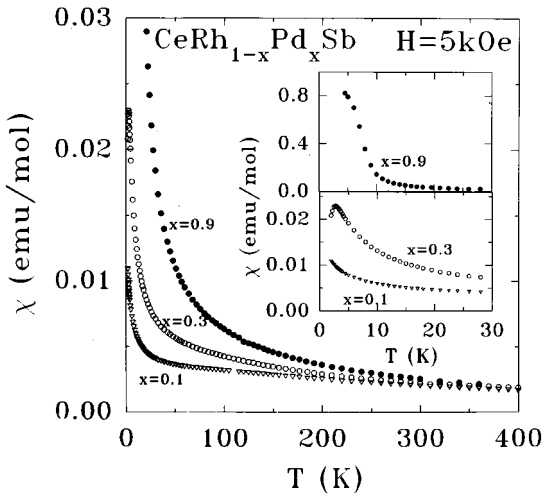

FIG. 1. Magnetic susceptibility χ vs temperature T for $CeRh_{1-x}Pd_xSb$ ($x=0.1$, 0.3, and 0.9) compounds. Inset shows the low-temperature behavior.

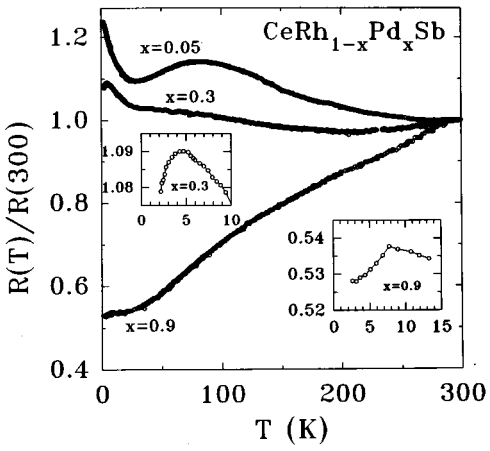

FIG. 3. Electrical resistivity ρ vs temperature T for $CeRh_{1-x}Pd_xSb$ ($x=0.05$, 0.3, and 0.9). Insets show the low-temperature drop in ρ for $x=0.3$ and 0.9.

phase, isostructural to CeRhSb and crystallize in the orthorhombic ϵ-TiNiSi-type structure. In the regime $0.4<x<0.7$, the samples are found to be multiphase. In the regime $0.7\leqslant x\leqslant 1$, the samples are again single phase, isostructural to CePdSb, and crystallize in the hexagonal structure.

The magnetic susceptibility vs temperature and magnetization vs field plots for some of the representative samples of the $CeRh_{1-x}Pd_xSb$ series, namely, with $x=0.1$, 0.3, and 0.9, are shown in Figs. 1 and 2, respectively. In this series, the susceptibility χ, of the samples with $0\leqslant x\leqslant 0.1$ shows a broad maximum at around 100 K, suggesting mixed-valent behavior of Ce ions in these compounds. The maximum becomes shallower as one goes from the $x=0$ to $x=0.1$ end. For samples with $x\geqslant 0.2$, the maximum in susceptibility is not seen. Instead, the susceptibility is nearly Curie-Weiss above 10 K suggesting that the Ce ions are largely in the 3+ state with no magnetic ordering down to 2 K. For compounds with $0\leqslant x\leqslant 0.2$, the magnetization varies linearly

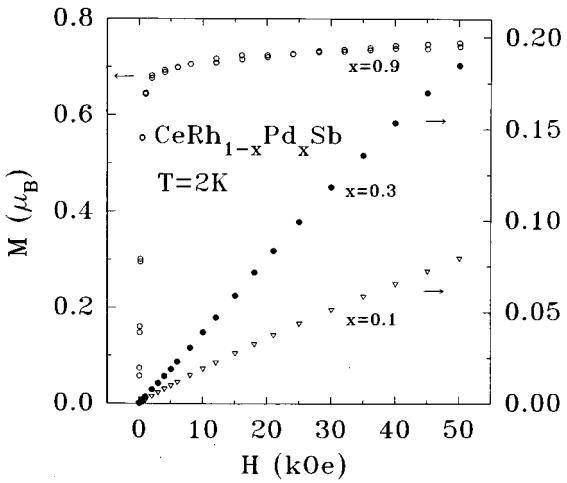

FIG. 2. Magnetization M vs field H for $CeRh_{1-x}Pd_xSb$ ($x=0.1$, 0.3, and 0.9). The left-hand side scale is for $x=0.9$ sample, and the right-hand side scale is for $x=0.1$ and 0.3 samples.

with applied magnetic field due to the nonmagnetic ground state of the system. However, quite remarkably, a peak is observed in the susceptibility at around 3 K in samples with $x=0.3$ and 0.4, attributed to the antiferromagnetic ordering of the Ce moments. The magnetic ordering is also borne out by resistivity measurements (see below).

At the Pd-rich end of the $CeRh_{1-x}Pd_xSb$ series, the magnetization (or susceptibility) of the compounds with $0.7\leqslant x\leqslant 1$ shows a saturation effect, suggesting ferromagnetic ordering in them. However, the Curie temperature (T_C) drops from 17 K for CePdSb to 8 K for $CeRh_{0.3}Pd_{0.7}Sb$. For the compounds with $0.7\leqslant x\leqslant 1$, the magnetization vs field isotherms at 2 K show saturation effects in conformity with the ferromagnetic ordering in these compounds. A representative M-H plot for $x=0.9$ is shown in Fig. 2. The magnetization varies linearly with applied field for $CeRh_{0.7}Pd_{0.3}Sb$ (Fig. 2) and $CeRh_{0.6}Pd_{0.4}Sb$ (not shown) which is not inconsistent with the antiferromagnetic ordering in these compounds.

Figure 3 shows a plot of resistivity vs temperature for some of the representative samples in the $CeRh_{1-x}Pd_xSb$ series, namely, with $x=0.05$, 0.3, and 0.9. For $x\leqslant 0.2$, the resistivity shows a rise below 8 K. From a fit to activation type of behavior, $\rho=\rho_0\exp(-\Delta/kT)$, the gap energy Δ can be calculated, which is found to drop from $\sim$4 K in CeRhSb to nearly zero in $CeRh_{0.8}Pd_{0.2}Sb$. In the case of compounds with $x=0.3$ and 0.4, which show a peak in the susceptibility, the resistivity also shows a drop at about the same temperature, confirming the presence of magnetic ordering in these compounds. Considering the peak in χ and the linear M vs H behavior, the ordering is perceived to be of antiferromagnetic type. For the compounds with $x=0.7$, 0.8, and 0.9, the resistivity is metallic above 10 K, below which it drops due to onset of ferromagnetic ordering.

The structural and magnetic phase diagram of the $CeRh_{1-x}Pd_xSb$ system is shown in Fig. 4. In the region $0\leqslant x\leqslant 0.2$ where the system is insulating, the gap energy is found to decrease with increasing Pd substitution. This is followed by the antiferromagnetic region ($0.3\leqslant x\leqslant 0.4$) with T_N's of the order of 3 K. There is a multi phase region for $0.4<x<0.7$ beyond which the system is again single phase and ferromagnetic with T_C increasing from 8 K in

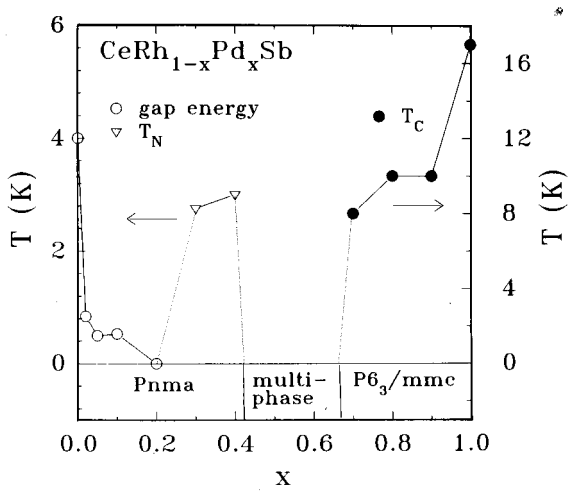

FIG. 4. Phase diagram of $CeRh_{1-x}Pd_xSb$ for $0 \leqslant x \leqslant 1$. In the figure, Δ refers to the gap energy, T_N to the Néel temperature, and T_C to the Curie temperature. The lines are drawn as a guide to the eye.

$CeRh_{0.3}Pd_{0.7}Sb$ to 17 K in CePdSb.

In order to understand the formation of the antiferromagnetic state, we will consider the phase diagram proposed by Wang *et al.*[9] for a symmetric Kondo lattice as a function of $\mathcal{J}/D$ where D is the conduction electron bandwidth. Their results are reported for a square Kondo lattice in two dimensions where, at zero temperature, a continuous transition occurs at a critical value $\mathcal{J}_c/D$ from the insulating state to the antiferromagnetic state. At higher temperatures, there is a paramagnetic regime sandwiched between the Kondo insulator regime and antiferromagnetic regime. These authors argue that in three dimensions, also, the antiferromagnetic order can persist to finite temperatures (refer to Fig. 2 in Ref. 9). Our phase diagram may be compared with their proposed phase diagram. The doping at the Rh site can indirectly, either by changing the conduction electron bandwidth or otherwise, lead to a small amount of holes at the Ce site. The substitution of Pd results in an increase in the unit-cell volume which rises from 267 $Å^3$ for $x=0$ followed by 269.8 $Å^3$ for $x=0.3$ to 270.5 $Å^3$ for $x=0.4$. This rise in unit-cell volume would lead to a reduction in the Kondo coupling $\mathcal{J}$, so that, according to the phase diagram of Wang *et al.*,[9] below a critical coupling the system should go into the antiferromagnetic state. Fazekas and Müller-Hartmann[12] have also argued that the ground state, whether magnetic or insulating, depends largely on the ratio $\mathcal{J}/D$, where $\mathcal{J}/D$ is above a critical value for the nonmagnetic case. Our experimental results are direct evidence in support of this argument.

The appearance of the antiferromagnetic phase depends critically on $\mathcal{J}/D$ as mentioned above. Thus, if $\mathcal{J}/D$ is increased, the antiferromagnetic state may not be observed. This is indeed seen in the $CeRh_{1-x}Ni_xSb$ system.[13] From an analysis of the x-ray data of the Ni-substituted samples, it is seen that the unit-cell volume decreases with increasing Ni substitution which would imply an increase in the Kondo coupling $\mathcal{J}$. Hence, according to theoretical predictions, no antiferromagnetic ordering is expected, and the system would rather remain in the nonmagnetic state. Preliminary studies on the Ni-substituted samples showed that the antiferromagnetic phase is not observed in any of them down to 2 K.[13]

IV. CONCLUSIONS

In conclusion, we have observed an antiferromagnetic phase in the ground state of a doped Kondo insulator CeRhSb. Our results on $CeRh_{1-x}Pd_xSb$ show the suppression of gap formation, followed by the development of an antiferromagnetic phase with increasing Pd substitution. The results are consistent with theoretical predictions. Ferromagnetic ground states with lowered T_C's continue to be observed at the CePdSb end.

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