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Gap suppression and development of antiferromagnetic order in CeRh\textsubscript{1\textminus x}Pd\textsubscript{x}Sb: Heat-capacity studies

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CeRhSb is a mixed-valent compound in which a gap opens up in the electronic density of states below a temperature of about 10 K. Earlier studies on Pd substitution at the Rh site in this compound showed that the gap is suppressed for around 10\% Pd and an antiferromagnetic ground state emerges with higher Pd substitution. Here, we report heat-capacity results on some of these samples, namely, CeRh\textsubscript{0.8}Pd\textsubscript{0.2}Sb and CeRh\textsubscript{0.7}Pd\textsubscript{0.3}Sb. We observe a sharp rise in $C_4/T$ of CeRh\textsubscript{0.8}Pd\textsubscript{0.2}Sb starting at around 5 K with a peak at about 2.5 K, which confirms the antiferromagnetic ordering in this compound. An entropy change of 2.5 J/mol K is obtained for the ordering. Above the Neél temperature, the value of the electronic specific heat coefficient $\gamma$ is found to be about 40 mJ/mol K$^2$. In CeRh\textsubscript{0.8}Pd\textsubscript{0.2}Sb, $C_4/T$ is found to rise below 10 K down to the lowest temperature of measurement, namely, 1.5 K with a $\gamma$ value of about 40 mJ/mol K$^2$. The rise may be due to non-Fermi-liquid behavior or could be due to impending magnetic order in the compound below 1.5 K.

Intermetallic compounds containing Ce are known to show interesting physical properties, such as mixed-valence, Kondo lattice, heavy fermion behavior, etc.\textsuperscript{1\textasciitilde12} A variety of ground states are exhibited by them, namely, magnetic, nonmagnetic, superconducting, etc. These phenomena are believed to arise due to hybridization between the Ce-4$f$ electrons and the conduction electrons. One such interesting compound is CeRhSb (Ref. 3) in which Ce ions are in a mixed-valence state as evidenced by a broad maximum in the susceptibility at around 100 K.\textsuperscript{3} Its resistivity is found to show a sharp rise at low temperatures. This is attributed to opening of a gap in the electronic density of states of CeRhSb, leading to the resistivity rise and an insulating-like ground state. A similar behavior is observed in CeNiSn (Ref. 4) and Ce$_2$Bi$_4$Pt$_3$.\textsuperscript{5} etc.\textsuperscript{6}

We have been carrying out systematic investigations of the gap formation in CeRhSb, by means of substitutional studies at the Ce and Rh sites, as revealed in electronic, transport, and magnetic measurements.\textsuperscript{7\textasciitilde9} We have observed that substitution at the Ce site by La leads to gap suppression with about 10\% La.\textsuperscript{7} Similarly, substitution at the Rh site by Ni also leads to gap suppression with around 10\% substitution.\textsuperscript{8} Pd substitution at the Rh site leads to very interesting results, namely, the development of antiferromagnetic ordering following gap-suppression\textsuperscript{9} as inferred from magnetic susceptibility and electrical resistivity measurements. These results are consistent with some of the theoretical models\textsuperscript{10\textasciitilde12} for doping effects in such gap-forming systems. In this paper, we report the heat-capacity results on two representative samples of the CeRh\textsubscript{1\textminus x}Pd\textsubscript{x}Sb series, namely, CeRh\textsubscript{0.8}Pd\textsubscript{0.2}Sb and CeRh\textsubscript{0.7}Pd\textsubscript{0.3}Sb. In the case of CeRh\textsubscript{0.7}Pd\textsubscript{0.3}Sb, a peak in $C_4/T$ is also seen at 2.5 K, thus confirming the antiferromagnetic ordering noted from resistivity and magnetic studies. No such peak is seen for nonmagnetic CeRh\textsubscript{0.8}Pd\textsubscript{0.2}Sb, where $C_4/T$ continues to rise down to 1.5 K. This may be due to non-Fermi-liquid behavior or due to impending magnetic order below 1.5 K.

The samples of CeRh\textsubscript{1\textminus x}Pd\textsubscript{x}Sb were prepared by the usual arc-melting technique, as discussed in Ref. 9 and are the same on which magnetic and resistivity measurements were reported earlier. At the Rh-rich end (0<x≤0.4), the samples are orthorhombic, isostructural to CeRhSb, crystallizing in the $\text{CsCl}$-type crystal structure (space group $Pnma$) while at the Pd rich end (0.7≤x<1) the samples are hexagonal, isostructural to CePdSb (space group $P6_3/mmc$). In the region 0.4<x<0.7, the samples are found to be multiphase. For the hexagonal phase samples, ferromagnetic ordering is observed with Curie temperature $T_C$ ranging from 8 K in CeRh\textsubscript{0.7}Pd\textsubscript{0.3}Sb to 17 K in CePdSb.\textsuperscript{13} For the orthorhombic phase samples (0<x≤0.4), with increasing Pd substitution, there is a small increase in unit-cell volume which may lead to corresponding decrease in hybridization strength between the conduction electrons and the 4$f$ electrons.

For the orthorhombic phase in the CeRh\textsubscript{1\textminus x}Pd\textsubscript{x}Sb series, for x=0.05 and 0.1, a rise in resistivity is observed similar to that seen in the CeRhSb, though the rise is slower compared to that in CeRhSb. For x>0.2, no rise in resistivity is observed. In fact, for samples with x=0.3 and 0.4, a drop in resistivity is seen at around 5 K. Moreover, the susceptibility of these two samples, shows a peak at around 3 K, attributed to antiferromagnetic ordering of the Ce moment. In light of this behavior seen for the orthorhombic samples, heat-
capacity measurements for some representative samples in the orthorhombic phase are carried out. Two samples have been chosen, one with the antiferromagnetic ground state, that is, the sample with $x = 0.3$, and the other nonmagnetic sample with $x = 0.2$, where the gap is just suppressed. The heat-capacity measurements have been carried out in the temperature range 1.5–40 K, using the semidiabatic heat pulse technique.

Before discussing the heat-capacity behavior of the Pd-substituted CeRhSb, we will first recapitulate the heat-capacity behavior of CeRhSb as discussed in Ref. 14. The heat capacity of CeRhSb gradually decreases with decrease in temperature down to 1.8 K. $C_{4f}/T$ (where $C_{4f}$ is the $4f$-related contribution to the heat capacity) rises with decrease in temperature down to 10 K, below which there is a drop down to 2 K (see Fig. 1). The increase down to 10 K suggests a tendency towards heavy-fermion-like behavior, but due to the development of the gap and a corresponding decrease in the density of states, $C_{4f}/T$ drops below 10 K.

Figure 2 shows a plot of heat capacity vs temperature for the two Pd-doped samples with $x = 0.2$ and $x = 0.3$. The heat capacity of LaRhSb (of the type $C = \gamma T + \beta T^3$ with a $\gamma$ value of about 7 mJ/mol K$^2$) is also shown for comparison. We first discuss the heat-capacity results on CeRh$_{0.7}$Pd$_{0.3}$Sb. Its heat capacity drops gradually on lowering the temperature and shows a peak at about 2.5 K. The temperature of the heat-capacity peak is the same as the temperature of the susceptibility peak and the drop in the resistivity. The bulk antiferromagnetic ordering reported earlier is confirmed by the present measurements taking into account the entropy associated with the peak (see below). This ordering is indeed intrinsic, as microprobe studies do not indicate the presence of any noticeable second phase. The plot of $C_{4f}/T$ (where $C_{4f}$ is the $4f$-related contribution to the heat capac-

**FIG. 1.** $C_{4f}/T$ (where $C_{4f}$ is the $4f$-related electron contribution to the heat capacity) $T$ for CeRhSb (taken from Ref. 14).

**FIG. 2.** Heat capacity $C$ vs temperature $T$ for the samples of CeRh$_{0.7}$Pd$_{0.3}$Sb, CeRh$_{0.3}$Pd$_{0.2}$Sb, and LaRhSb.

**FIG. 3.** $C_{4f}/T$ vs $T$ plot for the compound CeRh$_{0.7}$Pd$_{0.3}$Sb. The inset shows the plot of $C_{4f}/T$ vs $T^2$ for the same.

**FIG. 4.** $C_{4f}/T$ vs $T$ plot for the compound CeRh$_{0.8}$Pd$_{0.2}$Sb. The solid line shows the $\ln T$ fit at low temperatures. The inset shows the plot of $C_{4f}/T$ vs $T^2$ for the same.
The extra phase may be CeSb which is also seen in CeRh\textsubscript{0.8}Pd\textsubscript{0.2}Sb. The area under the peak, in the temperature range 0–6 K, gives the entropy change for the transition to be about 2.5 J/mol K. Assuming that the Ce ions in CeRh\textsubscript{0.8}Pd\textsubscript{0.2}Sb are in a doublet ground state, possibly due to crystal field effects, one expects a value of $R \ln 2$, that is about 5.75 J/mol K for the entropy change due to the magnetic ordering. The obtained value of 2.5 J/mol K for the entropy change suggests that the full moment of the crystal-field-split ground state doublet of Ce does not take part in the magnetic ordering. In order to get an estimate of electronic specific heat coefficient $\gamma$ we may plot $C_{4f}/T$ vs $T^2$ (see inset of Fig. 3). Above 10 K, $C_{4f}/T$ is almost constant, which when extrapolated to $T \rightarrow 0$, gives a value of $\gamma$ of about 40 mJ/mol K$^2$, which is the same as that obtained for CeRhSb.\textsuperscript{14}

The heat capacity of CeRh\textsubscript{0.8}Pd\textsubscript{0.2}Sb, drops gradually with decrease in temperature (Fig. 2). At a temperature of 6 K, a small hump is seen which is most probably due to the presence of some magnetic impurity phases. In fact, for this sample, microprobe studies indicate the presence of about 2% of extra phase.\textsuperscript{15} The extra phase may be CeSb which is also seen in CeRh\textsubscript{0.8}Pd\textsubscript{0.2}Sb. The area under the peak, in the temperature range 0–6 K, gives the entropy change for the transition to be about 2.5 J/mol K. Assuming that the Ce ions in CeRh\textsubscript{0.8}Pd\textsubscript{0.2}Sb are in a doublet ground state, possibly due to crystal field effects, one expects a value of $R \ln 2$, that is about 5.75 J/mol K for the entropy change due to the magnetic ordering. The obtained value of 2.5 J/mol K for the entropy change suggests that the full moment of the crystal-field-split ground state doublet of Ce does not take part in the magnetic ordering. In order to get an estimate of electronic specific heat coefficient $\gamma$ we may plot $C_{4f}/T$ vs $T^2$ (see inset of Fig. 3). Above 10 K, $C_{4f}/T$ is almost constant, which when extrapolated to $T \rightarrow 0$, gives a value of $\gamma$ of about 40 mJ/mol K$^2$, which is the same as that obtained for CeRhSb.\textsuperscript{14}

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As seen above, the system CeRh\textsubscript{1–x}Pd\textsubscript{x}Sb presents interesting results. While in CeRhSb there is a drop in $C_{4f}/T$ at around 10 K believed to be due to the gap formation in the electronic density of states, there is no such drop at around 10 K for CeRh\textsubscript{0.7}Pd\textsubscript{0.3}Sb and CeRh\textsubscript{0.8}Pd\textsubscript{0.2}Sb. Instead, there is a rise below 10 K in both these samples. In the case of CeRh\textsubscript{0.3}Pd\textsubscript{0.7}Sb, the rise is followed by a peak at around 2.5 K, consistent with the antiferromagnetic ordering. In the case of CeRh\textsubscript{0.3}Pd\textsubscript{0.7}Sb there does not seem to be any ordering down to 1.5 K. The rise in $C_{4f}/T$ is most probably due to impending magnetic order at around 0.75 K. A non-Fermi-liquid behavior is expected for Pd substitution smaller than but close to 20%.

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