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Ferromagnetic Kondo lattice behavior in CeNiSb

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We report magnetic susceptibility, electrical resistivity, and magnetoresistance measurements on hexagonal CeNiSb. These measurements suggest that CeNiSb is ferromagnetically ordered with a transition temperature of about 4 K. Its electrical resistivity shows a weak shallow minimum (at about 15K), characteristic of Kondo lattice systems. Further, in contrast to the other closely related compounds, the orthorhombic CeRhSb and CeNiSn, this compound does not show a rapid rise in its electrical resistivity and hence no Kondo coherence gap formation in the electronic density of states at low temperatures.

I. INTRODUCTION

Equiatomic ternary intermetallic compounds of the form Ce*TX*, where *T* is a transition metal and *X* is an *sp* element, have recently been the subject of several studies. These compounds have been found to show interesting properties depending on the elements *T* and *X*. For example, CeRhIn and CeRhSb show mixed-valent behavior.[1,2] Others, like CePdIn (Ref. 3) and CePdSn (Ref. 4) show antiferromagnetic ordering while CePdSb (Ref. 5) shows ferromagnetic ordering and CePtIn (Ref. 6) is a typical heavy-fermion system. The compounds CeNiSn (Ref. 7) and CeRhSb (Ref. 2) are the only two in the equiatomic ternary series to show gap formation in the electronic density of states at low temperatures—a phenomenon observed in only very few Ce-based compounds. The compound CeRhSb crystallizes in the orthorhombic ϵ-TiNiSi-type structure, which is an ordered ternary variant of the $CeCu_2$-type structure. Its magnetic behavior is typical of mixed-valent cerium compounds characterized by a broad maximum in the susceptibility vs temperature plot. Its resistivity, which is metallic and decreases between 300 and 10 K, shows a sharp rise at low temperatures (below 10 K). The sharp rise in resistivity has been attributed to a gap formation (called hybridization or a Kondo coherence gap) in the electronic density of states. In contrast, the isostructural LaRhSb is superconducting below 2.5 K and metallic in the normal state.[8] Likewise, CeNiSn also exhibits a rise in resistivity at low temperatures attributed to the gap formation in the electronic density of states. On the other hand, CePdSb crystallizes in the hexagonal $CaIn_2$-type structure and is ferromagnetic below 17 K while LaPdSb is a normal metal and does not show superconductivity down to 0.6 K.[9]

In view of the very interesting properties exhibited by CeRhSb and CeNiSn, we have examined the magnetic and transport properties of the compositionally similar compound CeNiSb to see whether gap formation occurs in this compound. This compound may be thought to be derived either from CeRhSb by replacement of Rh by Ni or from CeNiSn by replacement of Sn by Sb. At the same time this compound is structurally similar to CePdSb. The present work suggests that CeNiSb is a hexagonal system with a ferromagnetically ordered ground state. The magnetic transition temperature is ~4 K. The resistivity of this compound shows a shallow minimum typical of Kondo lattice systems. However, no rise in the electrical resistivity is observed in this compound in the temperature range investigated (2–300 K), implying the absence of a Kondo coherence gap. The compounds LaNiSb and YNiSb are nonsuperconducting down to 2 K and are metallic in the normal state.

II. EXPERIMENTAL DETAILS

The samples of CeNiSb and its nonmagnetic analogs LaNiSb and YNiSb were prepared by arc melting of the constituent elements in the stoichiometric ratio in a continuous flow of argon gas. In order to see the effect of nonstoichiometry, the compound $CeNiSb_{0.9}$ was also prepared. The Ce used was of very high purity (99.99%), procured from the Materials Preparation Center, Ames Laboratory. Other elements were of stated purity better than 99.9% obtained commercially from Leico Industries. The alloys were prepared by first melting La, Ce, or Y with Ni and then melting the ingot so obtained with the appropriate amount of Sb. The loss during the first melt was negligible. Any further loss on Sb addition was attributed to the volatile nature of Sb and was compensated, if found necessary. The alloy ingots were turned over and melted several times to ensure homogeneity. X-ray patterns of the samples were obtained using the powder diffraction method in the 2θ range 20°–70° using Cu $K\alpha$ radiation. Susceptibility measurements were made using a superconducting quantum interference device (SQUID) magnetometer in the temperature range 2–300 K. Magnetization-field isotherms were measured at various temperatures up to 20 K. Resistivity measurements were made in the temperature range 2–300 K by the standard four-probe dc technique using a computer-controlled data acquisition system. Magnetoresistance measurements were made at a few selected temperatures with the magnetic field parallel to the direction of the current.

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III. RESULTS AND DISCUSSION

Powder x-ray patterns indicate that all the samples are single-phase materials within the detection limits of x rays. The observed x-ray lines of CeNiSb and $\mathrm{CeNiSb_{0.9}}$ could be indexed on the basis of a hexagonal (space group $P6_3/mmc$) structure containing two formula units per unit cell. The lattice parameters obtained from a least-squares analysis of the observed d or 2θ values are $a=4.394$ Å and $c=8.238$ Å for $\mathrm{CeNiSb_{0.9}}$ and $a=4.427$ Å and $c=8.302$ Å for CeNiSb. On the other hand, LaNiSb and YNiSb crystallize in the orthorhombic ϵ-TiNiSi-type structure containing four formula units per unit cell. The lattice parameters obtained are $a=7.946$ Å, $b=7.236$ Å, and $c=4.01$ Å for LaNiSb and $a=7.365$ Å, $b=6.072$ Å, and $c=4.793$ Å for YNiSb.

Figure 1 shows a plot of the magnetic susceptibility vs temperature for the compounds LaNiSb and YNiSb. They show nearly temperature-independent susceptibility above 50 K. Below 50 K there is a small increase in the susceptibility. The susceptibility of the two samples in the full temperature range of measurement, 2–300 K, can be fitted to the equation

$$\chi=\frac{C}{(T-\theta_p)}+\chi_0 , \tag{1}$$

where C is the Curie constant, θ_p is the paramagnetic Curie temperature, and χ_0 is the temperature-independent contribution to the susceptibility. For LaNiSb, from the fit we obtain the effective magnetic moment $\mu_{\mathrm{eff}}=0.09\mu_B$, $\chi_0=1.7\times10^{-4}$ emu/mol, and $\theta_p=-1.4$ K. For YNiSb, we obtain $\mu_{\mathrm{eff}}=0.04\mu_B$, $\chi_0=2.9\times10^{-5}$ emu/mol, and $\theta_p=-4.4$ K. This suggests that most of the contribution to the susceptibility comes from the temperature-independent part. Further, since μ_{eff} is negligible and La and Sb are nonmagnetic, it seems that the Ni ions have negligibly small or no moment in these compounds.

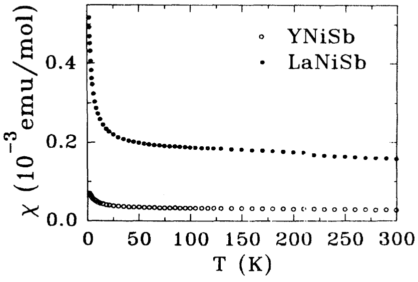

FIG. 1. Plot of susceptibility (χ) vs temperature for YNiSb and LaNiSb.

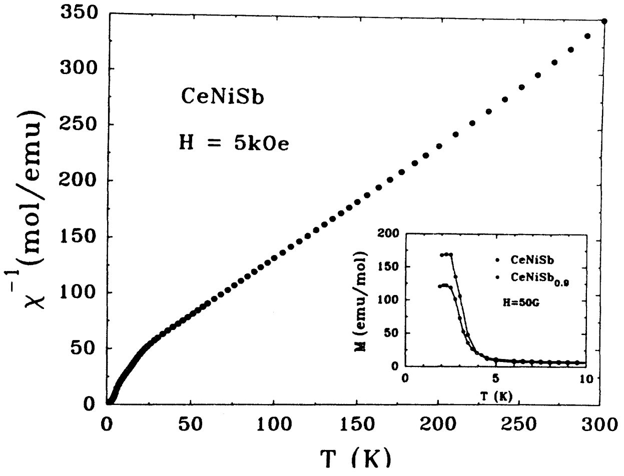

FIG. 2. Plot of the inverse of magnetic susceptibility (χ^{-1}) as a function of temperature for CeNiSb in the temperature range 2–300 K in an applied field of 5 kOe. Inset shows the magnetization M at low temperatures in a 50 Oe field for CeNiSb and $\mathrm{CeNiSb_{0.9}}$.

Figure 2 shows a plot of the inverse susceptibility χ^{-1} of CeNiSb as a function of temperature, in the temperature range 2–300 K. (The magnetic susceptibility of $\mathrm{CeNiSb_{0.9}}$ is very similar to that of CeNiSb and is not shown.) The susceptibility tends to saturate to a constant value below 2 K for both the compounds, indicative of magnetic ordering (see below). In the case of CeNiSb, a Curie-Weiss fit between 10 and 300 K gives $\mu_{\mathrm{eff}}=2.71\mu_B$ for the effective moment on the Ce ion, paramagnetic Curie temperature $\theta_p=-21$ K, and a temperature-independent susceptibility $\chi_0\sim5.6\times10^{-5}$ emu/mol. For $\mathrm{CeNiSb_{0.9}}$, the corresponding values are $\mu_{\mathrm{eff}}=2.61\mu_B$, $\theta_p=-21$ K, and $\chi_0\sim4\times10^{-4}$ emu/mol. The value of μ_{eff} for both the compounds is comparable to the value $2.54\mu_B$ for the free $\mathrm{Ce^{3+}}$ ion. A negative θ_p normally suggests the presence of antiferromagnetic or Kondo-type interactions. The value of χ_0 is comparable in magnitude to the temperature-independent contribution to susceptibility in LaNiSb.

A plot of magnetization (M) vs temperature (T) for CeNiSb and $\mathrm{CeNiSb_{0.9}}$ in a field of 50 G in the temperature range 2–10 K is shown in Fig. 2 (inset). There is a steep rise in the magnetization at around 5 K. From a plot of M^2 vs $(T-T_C)$, the Curie temperature T_C is obtained to be 4 K for both the compounds. The T_C value

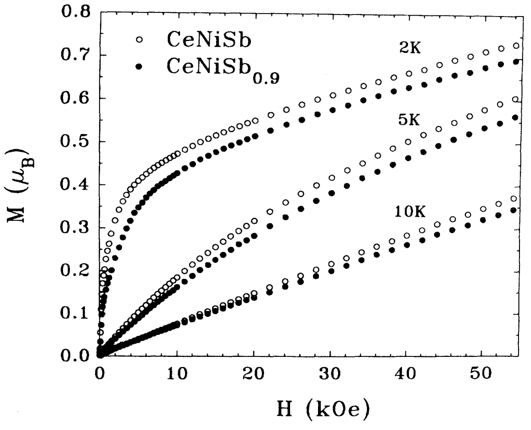

FIG. 3. Plot of magnetization (M) vs field (H) for CeNiSb and $\mathrm{CeNiSb_{0.9}}$ at various temperatures.

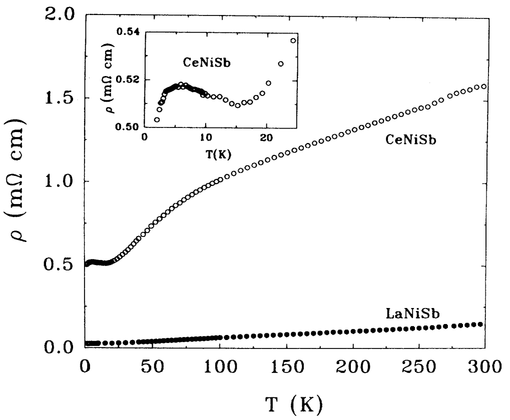

FIG. 4. Plot of electrical resistivity (ρ) vs temperature (T) for CeNiSb and LaNiSb. Inset gives the behavior at low temperature for CeNiSb, showing the drop at about 3 K and the shallow minimum at 15 K.

of the present sample is slightly lower than the T_C of 7 K obtained for the same compound in Ref. 10 and may be due to the high-purity Ce used in the present studies. Figure 3 shows a plot of magnetization-field isotherms of CeNiSb and $\mathrm{CeNiSb}_{0.9}$ at various temperatures. At 2 K, the magnetization shows considerable deviation from linear behavior consistent with the ferromagnetic ordering in the compound. However, saturation is not achieved in the highest available field of 5.5 T. Extrapolating the linear part of the M vs $1/H$ plot to $H \rightarrow \infty$, the saturation moment at 2 K is estimated to be about $0.8\mu_B$, which is small compared to the free-ion Ce^{3+} moment of $2.14\mu_B$. This may be due to a crystal-field or Kondo effect or a combination of both. At 10 K, the magnetization varies linearly with applied field, consistent with the paramagnetic nature of the compound at this temperature.

The temperature dependence of the electrical resistivity of the compounds LaNiSb and CeNiSb is shown in Fig. 4. The resistivity behavior of $\mathrm{CeNiSb}_{0.9}$ is nearly the same as that of CeNiSb and is not shown. Both LaNiSb and YNiSb do not show any superconducting transition down to 2 K. The resistivity of CeNiSb shows a drop at about 3 K. This is most likely due to the reduction in spin-disorder resistivity due to magnetic ordering. A weak and shallow minimum in the resistivity is observed at 15 K in CeNiSb, suggesting a Kondo-like behavior of the compound. However, this minimum is not clearly visible in the off-stoichiometric $\mathrm{CeNiSb}_{0.9}$. Above 75 K, the resistivity rises continuously and shows metallic behavior. There is however, a change in slope which suggests the influence of crystal fields. The magnetic contribution to the resistivity shows a $\ln(T)$ behavior in the range 5–15 K as expected for Kondo systems. The magnetoresistance of these compounds is somewhat sample dependent. For CeNiSb at 2 K, it is positive in the fields investigated. However, at 10 K it is positive in low fields but changes sign at high fields as expected in Kondo systems. The magnetoresistance of $\mathrm{CeNiSb}_{0.9}$ is more consistent with the ferromagnetic ordering in this compound.

The nearest-neighbor Ce-Ce distance in CeNiSb is 4.119 Å along the c axis. This is greater than the Hill limit of 3.25–3.4 Å—the minimum distance for Ce-Ce overlap to occur, which suggests that indirect exchange via conduction electrons [Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction] rather than direct f-f orbital overlap is responsible for the magnetic ordering in this compound. The compound CeNiSb is similar to CePdSb, both structurally and magnetically. However, the substitution of Pd by Ni has caused a sharp fall in the transition temperature from about 17 K in CePdSb to 4 K in this compound. The Kondo temperature in the two systems is nearly the same, about 15 K. The fall in T_C can be understood on considering the unit-cell volume of the two compounds. Since the unit-cell volume is smaller for CeNiSb, a larger value of the Kondo coupling constant J_{sf} is expected. While the RKKY interaction temperature $T_{\mathrm{RKKY}} \sim J_{sf}^2/W$, ($W$ is the width of the conduction band), the Kondo temperature is exponentially dependent on J_{sf} and is given by $k_B T_K \sim (gJ_{sf})^{1/2}\exp(-1/gJ_{sf})$, where g is the conduction-electron density of states. Hence the Kondo interaction should dominate the indirect RKKY interaction in CeNiSb, compared to that in CePdSb. Since magnetic ordering is achieved at $T_C \sim T_{\mathrm{RKKY}}$, a low T_C is expected in the case of CeNiSb in comparison to that for CePdSb. Using the value of $T_K = 15$ K, an estimate of $(gJ_{sf}) \sim 0.16$ eV is obtained for both CeNiSb and CePdSb. Considering the fact that CePdSb has a larger density of states (due to a larger number of conduction electrons), J_{sf} will be smaller for this compound.

As mentioned in the Introduction, a Kondo coherence gap or hybridization gap has been observed in the orthorhombic compounds CeRhSb and CeNiSn. It is interesting to note that no such gap formation is seen in CeNiSb in which Ce ions show good local-moment behavior. It therefore seems that the crystal structure, magnetic, and transport properties of these compounds are decided by the electron-to-atom ratio. Substitution of Rh by Pd in CeRhSb increases the number of electrons per formula unit by 1. This substitution changes the structure from orthorhombic for CeRhSb to hexagonal for CePdSb. The unit-cell volume rises from 67 to 72 Å^3, resulting in a decrease in J_{sf} in CePdSb. This would mean that for the compound CeRhSb, T_K should be much higher than T_{RKKY}, in contrast to the situation in CePdSb where, T_{RKKY} should dominate over T_K. Hence it is understandable that CeRhSb should show high T_K, i.e., mixed-valent behavior and CePdSb should show high-temperature magnetic ordering. In analogy, substitution of Sn by Sb in CeNiSn also increases the number of electrons per formula unit by 1, resulting in a change in structure from orthorhombic for CeNiSn to hexagonal for CeNiSb and an increase in unit-cell volume from 66 to 70 Å^3. This results in an increase in the Kondo coupling in CeNiSn compared to that in CeNiSb so that an argument similar to that given above explains the low-temperature ferromagnetic ordering and Kondo behavior in CeNiSb compared to CeNiSn, which is a high-T_K system. Assuming a T_K of about 100 K, an estimate of (gJ_{sf}) is obtained to be about 0.23 eV for CeRhSb.

IV. CONCLUSIONS

In conclusion, we find that CeNiSb is a ferromagnetically ordered compound with $T_C \sim 4$ K. The electrical resistivity of this compound exhibits a shallow minimum at 15 K and a $\ln(T)$ behavior in the temperature range 5–15 K. Thus CeNiSb would appear to be a ferromagnetic Kondo lattice system. In comparison with the orthorhombic CeRhSb and CeNiSn, no rise in low-temperature resistivity and hence no Kondo coherence gap is observed in this compound.

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