Kondo coherence gap and superconductivity in the $Ce_{1-x}La_xRhSb$ system

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CeRhSb is a mixed valent Ce-based compound which shows a rapid rise in resistivity at low temperatures. This resistivity rise has been attributed to the opening of a gap in the electronic density of states. On the other hand, isostructural LaRhSb is a superconductor with T_c of about 2.5 K. We have investigated the system $Ce_{1-x}La_xRhSb$ to study the effect of La substitution for Ce on the gap formation in CeRhSb, and the effect of Ce substitution for La on the superconductivity in LaRhSb. It is observed that the rapid rise in resistivity, and hence the gap formation, is suppressed even when a small amount of La is substituted for Ce in CeRhSb, though susceptibility continues to show mixed valent behavior. This suggests that a coherent Kondo lattice state is essential for the gap formation in CeRhSb. On the La rich side, superconductivity is suppressed even by 0.5% replacement of La by Ce. In the intermediate region of substitution, a gradual transformation from a mixed valent to a Curie-Weiss behavior in the susceptibility is observed.

I. INTRODUCTION

Many rare-earth intermetallic compounds, in particular, those containing Ce, Eu, and Yb are known to show anomalous properties, such as lattice volume anomaly, Kondo effect, mixed-valent behavior, heavy-fermion behavior, etc. (see, for instance, Refs. 1–3). This has been attributed to the hybridization between the $4f$ electrons of the rare earth and the conduction electrons. At high temperature, the valence fluctuating and heavy-fermion systems are thought to consist of uncorrelated $4f$ electrons each of which independently scatter conduction electrons through the Kondo interaction. The low-temperature ground state of such systems is strongly correlated, usually metallic and, in some cases, may exhibit superconductivity or magnetism. However, during the past few years, a few cerium based compounds have been discovered which exhibit an insulating ground state with a small energy gap.[4–6] One such system is CeRhSb which shows an insulating behavior with a gap energy of about 4 K.[6] The magnetic susceptibility of CeRhSb shows non-Curie-Weiss behavior in the temperature range of 2 to 300 K. It is weakly temperature dependent and shows a broad maxima at about 120 K. Such a behavior of susceptibility, coupled with the lattice volume anomaly, is characteristic of mixed-valent Ce-based compounds. The electric resistivity of CeRhSb behaves in an unusual fashion. It is metallic at room temperature, passes through a minima at about 8 K and then rises rapidly at low temperatures. The low-temperature rapid rise in resistivity has been attributed to a gap formation in the electronic density of states at the Fermi level. From the activation-type behavior of the resistivity, the gap energy Δ has been estimated to be about 4 K. On the other hand, the isostructural La containing compound, LaRhSb, has been found to be a superconductor with a transition temperature of about 2–2.7 K.[7,8]

In view of the contrasting behavior of CeRhSb and LaRhSb, it is of interest to examine the solid solution, $Ce_{1-x}La_xRhSb$, to see the effect of La substitution on gap formation in CeRhSb and the changes in the mixed-valent character of Ce ions across the series. On the La end, it is also of interest to see how the superconductivity in LaRhSb is affected with increased substitution of Ce. We present here the results of such studies. Our measurements indicate that the gap in CeRhSb is rapidly suppressed even by substitution of a small amount of Ce by La though the susceptibility continues to show a mixed-valent behavior for Ce ions. However, superconductivity is not observed down to 2 K even in those $Ce_{1-x}La_xRhSb$ samples in which the gap formation is suppressed. Further, superconductivity in LaRhSb is suppressed even for small Ce substitution.

II. EXPERIMENT

Polycrystalline samples of $Ce_{1-x}La_xRhSb$ ($x=0$, 0.1, 0.2, 0.4, 0.6, 0.8, and 1) were prepared by arc melting of the stoichiometric amounts of the constituent elements in a continuous flow of argon gas. The purity of Rh and Sb elements was better than 99.99%. The La and Ce used were of high purity, procured form the Materials Preparation Center, Ames Laboratory. The samples were annealed at a temperature of 950 °C for seven days. The low Ce concentration samples $Ce_{1-x}La_xRhSb$ ($x=0.99$, 0.995) were prepared from master alloys of LaRhSb and CeRhSb by melting them together in appropriate proportions. Powder x-ray-diffraction patterns of the compounds were obtained in the range $10° < 2\theta < 70°$ using CuK_α radiation. Electrical resistivity measurements were carried out using a standard four-probe dc technique and a computer controlled data-acquisition system in the temperature range 2–300 K. dc magnetic susceptibility measurements were made using the superconducting quantum interference device magne-

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tometer in the temperature range 5–300 K in an applied field of 5 kOe. ac magnetic susceptibility measurements on the La-rich samples were made in the temperature range of 1.2–30 K using the mutual inductance bridge method.

III. RESULTS AND DISCUSSIONS

All the observed x-ray reflections could be indexed on the basis of an orthorhombic ϵ-TiNiSi-type structure (space group *Pnma*). This is a well-ordered structure in which the La(Ce), Rh, and Sb occupy well-defined lattice sites. The lattice parameters obtained from a least-squares analyses of the observed d or 2θ values are given in Table I. The lattice parameters and unit-cell volume obtained for all these compounds are plotted in Fig. 1 as a function of the fraction of the La ion. The lattice parameters are also given in Table I. The unit-cell volume is thus found to obey the usual Vegard's law.

Figure 2 shows the plot of resistivity versus temperature for various samples in the $Ce_{1-x}La_xRhSb$ series in the temperature range of 2–300 K. We first discuss the case of CeRhSb and the effect of small La substitution in this compound. The resistivity of CeRhSb shows a broad maxima at about 110 K and then decreases with decreasing temperatures. It passes through a minimum and then shows a rapid rise at low temperatures. The temperature of the minima and the overall temperature variation of resistivity are somewhat sample dependent. The low-temperature rapid rise in resistivity has been interpreted in terms of opening of a gap in the electronic density of states. At low temperatures, the resistivity follows an activation behavior $\rho=\rho_0\exp(\Delta/kT)$ with Δ of about 4 K. The temperature dependence of the magnetic susceptibility in an applied field of 5 kOe is shown in Figs. 4 and 5. For CeRhSb, the susceptibility passes through a broad maximum at about 120 K. There is a minimum at around 2.5 K below which there is small rise down to 2 K. This rise is probably due to Ce^{3+} ions stabilized by lattice defects. On substituting small amount of La for Ce, the susceptibility of $Ce_{0.9}La_{0.1}RhSb$ continues to show mixed-valent behavior in agreement with the single-ion nature. The resistivity versus temperature curve for $Ce_{0.9}La_{0.1}RhSb$ also exhibits a weak maxima at about 100 K. However, unlike CeRhSb, the sharp rise in resistivity at low temperatures is considerably suppressed.

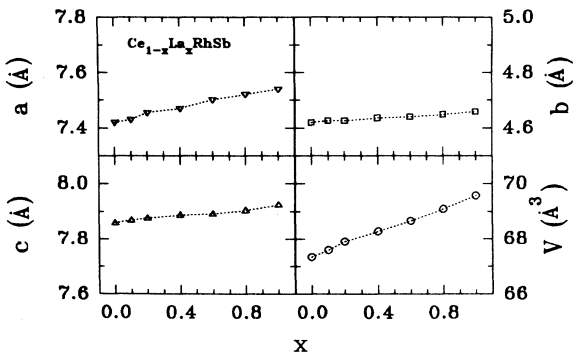

FIG. 1. Lattice parameters, a, b, c, and the unit-cell volume, V, as a function of x in $Ce_{1-x}La_xRhSb$.

With further increase in substitution of La in place of Ce, the rapid rise in resistivity is found to be suppressed completely and the system shows the usual metallic behavior. This strongly suggests that the gap formation is a coherence effect. Any disruption in the coherence due to disorder in the lattice smears or suppresses the gap formation. However, magnetic susceptibility, being a single-ion effect, continues to exhibit mixed-valent behavior. Similar observations have been made for small substitution of La (Ref. 6) and different rare-earth ions in CeRhSb (Ref. 9) and for La substitution in the $Ce_3Bi_4Pt_3$ system.[10]

Figure 3 shows the plot of $\ln(\rho)$ vs $1/T$ for CeRhSb and $Ce_{0.9}La_{0.1}RhSb$, respectively. The linear relationship holds in a very small temperature range between 2 and 5 K. From the linear region of these curves, the gap energy is estimated to be about 4 and 0.28 K, respectively.

The susceptibility of the compounds showing mixed-valent behavior ($x=0$, 0.1) has been analyzed on the basis of the Coqblin-Schrieffer model. Based on the Bethe-ansatz solution of the Coqblin-Schrieffer Hamiltonian, Rajan[11] has calculated the magnetic susceptibility (χ) for arbitrary values of the moment $J(=\frac{1}{2},\ldots,\frac{7}{2})$. For $T=0$ and $H=0$, $\chi(0)$ is given analytically by

$$\chi(0)=N(N^2-1)g_j\mu_B^2/24\pi k_B T_0 .$$

Here N is the degeneracy and is equal to $2J+1$ which is 6 in the case of Ce. T_0 is the strong-coupling scale and is

TABLE I. Lattice parameters, a, b, and c, effective paramagnetic moment, μ_{eff}, paramagnetic Curie temperature, θ_p, superconducting transition temperature, T_c, temperature-independent susceptibility, χ_0, strong-coupling scale, T_0, zero-field and zero-temperature susceptibility, $\chi(0)$, and impurity fraction n in $Ce_{1-x}La_xRhSb$ compounds as a function of x.

x	a (Å)	b (Å)	c (Å)	μ_{eff} (μ_B)	θ_p (K)	χ_0 (emu/mol)
0.0	7.420	4.619	7.859	$n\approx0.0001$	$T_0\approx466$	$\chi(0)\approx0.0019$
0.1	7.430	4.626	7.869	$n\approx0.0007$	$T_0\approx465$	$\chi(0)\approx0.0022$
0.2	7.455	4.626	7.876	$n\approx0.145$	$T_0\approx400$	$\chi(0)\approx0.0006$
0.4	7.470	4.636	7.888	2.68	−208	0.0003
0.6	7.502	4.639	7.892	2.53	−200	0
0.8	7.521	4.648	7.905	2.75	−152	0.0004
1.0	7.541	4.658	7.924		$T_c\approx2.5$	

related to the Kondo temperature through the Wilson number. Thus, at $T=0$, χ is temperature independent and shows Pauli-like behavior due to the screening of the magnetic impurities. Besides, a maxima in susceptibility is observed below T_0 (for $J>\frac{1}{2}$) which increases with increasing J. The fit of the observed susceptibility on the basis of the Coqblin-Schrieffer model is shown in Fig. 4. A term nC/T was added to account for the presence of a small amount (n) of Ce^{3+} ions (Curie-constant C). The parameters obtained from the fit for these and some other compositions are given in Table I.

The variation of susceptibility with temperature for intermediate compositions, namely, $Ce_{0.8}La_{0.2}RhSb$, $Ce_{0.6}La_{0.4}RhSb$, $Ce_{0.4}La_{0.6}RhSb$, and $Ce_{0.2}La_{0.8}RhSb$ is shown in Fig. 5. The maxima in the susceptibility is weakened and eventually suppressed and Curie-Weiss–type behavior sets in albeit with a large negative θ_p. The temperature range over which the Curie-Weiss behavior is observed increases with increasing La concentration. The low-temperature rise in the susceptibility is still observed. The component $Ce_{0.2}La_{0.8}RhSb$, shows

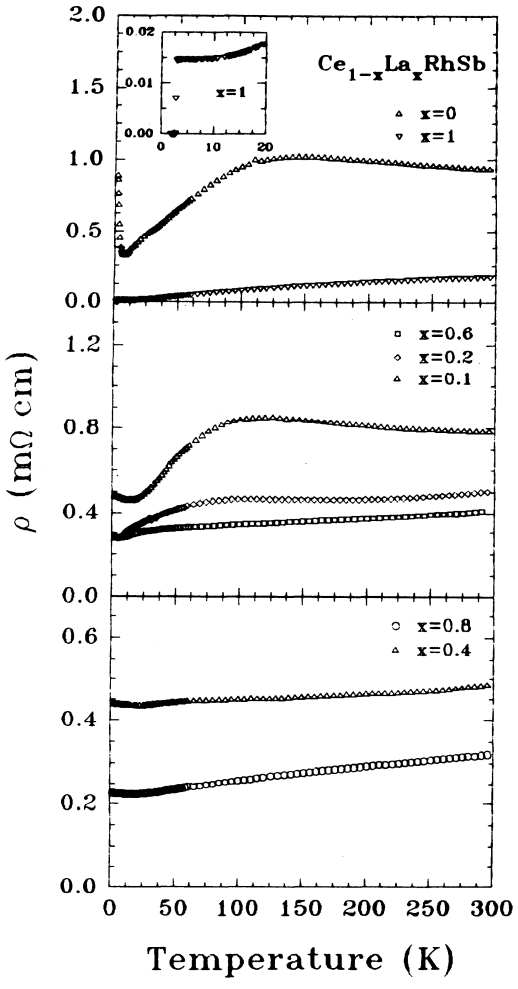

FIG. 2. Electrical resistivity of $Ce_{1-x}La_xRhSb$ as a function of temperature for various values of x. Inset gives the resistivity of LaRhSb at low temperatures showing the superconducting transition in this compound.

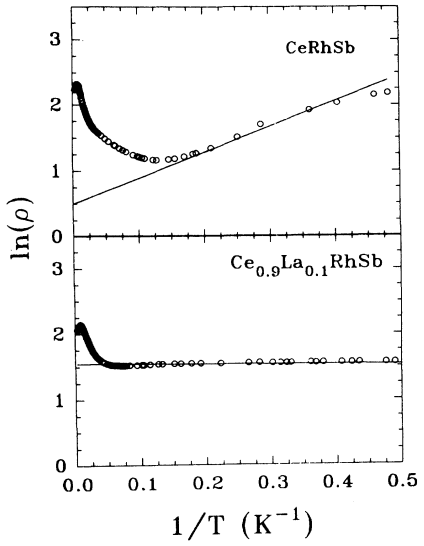

FIG. 3. Plot of $\ln(\rho)$ versus $1/T$ for CeRhSb and $Ce_{0.9}La_{0.1}RhSb$. The solid line is a fit to the equation, $\ln\rho=\rho_0\exp(\Delta/kT)$.

Curie-Weiss behavior over the temperature range 50–300 K. Using the Curie-Weiss fit,

$$\chi=C/(T-\theta_p)+\chi_0\ ,$$

for this compound, χ^{-1} vs T is shown in Fig. 5. Here, χ_0 is the temperature-independent susceptibility, C is the Curie constant, and θ_p is the paramagnetic Curie temperature. The results of susceptibility analyses on this and other compounds of $Ce_{1-x}La_xRhSb$ series are largely summarized in Table I. The μ_{eff} values are close to that of the free Ce^{3+} ion and the large θ_p signifies the presence of Kondo-type interactions.

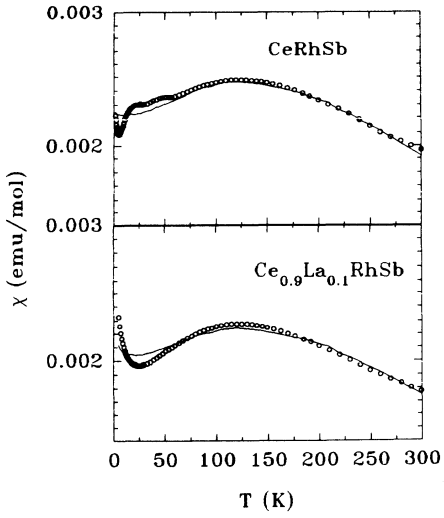

FIG. 4. Magnetic susceptibility, χ, of CeRhSb and $Ce_{0.9}La_{0.1}RhSb$ as a function of temperature. The solid line shows the fit to the Coqblin-Schrieffer model.

As remarked earlier, many of the mixed-valent cerium-based compounds, e.g., $CeRu_3B_2$, $CeOs_3B_2$, and heavy-fermion compound, namely $CeCu_2Si_2$, exhibit a superconducting ground state.[12,13] Observation of superconductivity in the last mentioned compound is even more interesting since its La analog, $LaCu_2Si_2$, is not superconducting down to mK.[13] In the case of LaRhSb, superconductivity is observed with T_c of about 2–2.7 K. Since CeRhSb is strongly mixed valent, the cerium ion moment is largely quenched. Thus CeRhSb is like LaRhSb in the sense that effectively both have nonmagnetic rare-earth atoms. Yet superconductivity is seen only in LaRhSb but not in CeRhSb. Instead, CeRhSb exhibits semiconducting behavior at low temperatures overcoming any superconducting interactions inherent in the lattice.

We have examined the occurrence of superconductivity in the $Ce_{1-x}La_xRhSb$ system. Considering that LaRhSb is superconducting, one may expect that when gap formation is suppressed, superconductivity may appear in the $Ce_{1-x}La_xRhSb$ system. However, resistivity measurements on these samples reveal only metallic behavior and no superconductivity down to 2 K (the lowest temperature attainable in our resistivity setup). Moreover, on the La-rich end, even 0.5% substitution of Ce for La suppresses the superconducting temperature and no superconductivity is seen down to 1.2 K in the ac susceptibility measurements (Fig. 6). This is similar to the situation in the archetypal ($LaAl_2$:Ce) (Ref. 14) system where again superconductivity is suppressed by small

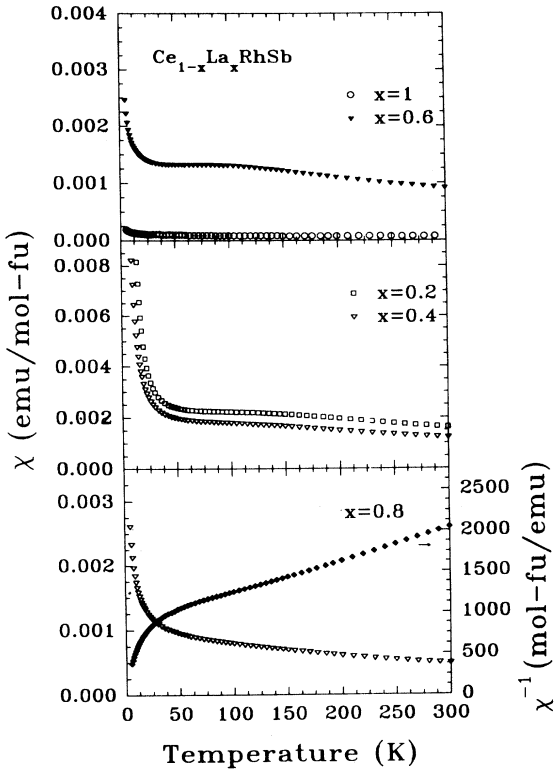

FIG. 5. Magnetic susceptibility, χ, as a function of temperature for $Ce_{1-x}La_xRhSb$ ($x=0.2$, 0.4, 0.6, 0.8) and for LaRhSb.

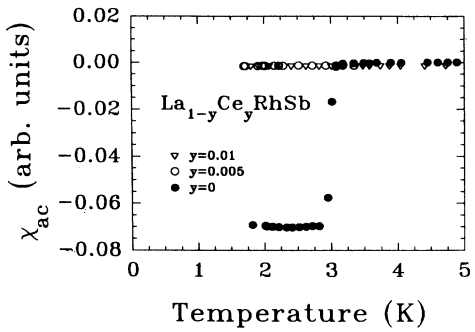

FIG. 6. ac susceptibility, χ_{ac}, as a function of temperature for $La_{1-y}Ce_yRhSb$ for $y=0.0$, 0.005, and 0.01.

Ce substitution. This is most likely due to the Kondo scattering of conduction electrons by the Ce-4f electrons which results in strong pair breaking. The RRhSb (R=La and Ce) system is unique so far in the sense that the La compound is superconducting and the Ce compound shows insulating behavior due to the gap formation. The interplay, if any, of these two phenomenon is very intriguing and warrants further studies. It would be of considerable interest to search for superconductivity in the $Ce_{1-x}La_xRhSb$ system at still lower temperatures and also under pressure.

Finally, we would like to point out the complexity of the situation and some of the problems associated with the interpretation of low-temperature rise in resistivity in CeRhSb as being due to the gap formation. The resistivity increases by a factor of about 5 on decreasing the temperature from 8 to 2 K. More recent studies[15] down to still lower temperatures show a continued increase but at a slower rate reaching a factor of about 8 at 0.1 K. Thus the resistivity increase is not a few orders of magnitude as would be expected in the case of a true gap. Besides, the resistivity follows $\ln(\rho)-1/T$ behavior in a narrow temperature interval and shows considerable deviation at lower temperatures. Heat capacity (C) at best show a change of slope in C/T vs T^2 curve at about 7 K and does not follow the activated behavior.[16] The situation in the isostructural compound CeNiSn, which also shows features reminiscent of a gap, is even more complex. Studies on single crystal CeNiSn reveal that there are anomalies in the specific heat at low temperatures which are not well understood. These factors suggest that the physics of such materials is more complex than the simple gap formation. Besides, some of the properties are sample dependent suggesting that metallurgical considerations may also be important. Therefore, the above interpretation of suppression of gap in CeRhSb by La substitution in terms of the coherence effect may be an oversimplification and clearly further work is necessary to fully elucidate the behavior of such compounds.

IV. CONCLUSIONS

In conclusion, it has been shown that the gap formation in CeRhSb is rapidly suppressed on replacement of a small amount of Ce by nonmagnetic La, though suscepti-

bility continues to show mixed-valent behavior. This suggests that a well-ordered Ce lattice, i.e., a coherent Kondo lattice state, is essential for the low-temperature gap formation in this compound. With increased La concentration, the susceptibility of the compounds in the solid solution $Ce_{1-x}La_xRhSb$ gradually changes from mixed-valent type to Curie-Weiss type. Superconductivity is suppressed even for small (0.5%) concentrations of Ce in LaRhSb. Moreover, superconductivity is not observed in the solid solutions, $Ce_{1-x}La_xRhSb$, down to the lowest temperature of measurement (2 K) even after gap formation is suppressed.

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