Superconductivity in LaRhAl and mixed valent behavior in CeRhAl

N. Harish Kumar and S. K. Malik
Tata Institute of Fundamental Research, Colaba, Mumbai 400 005, India
(Received 13 December 1999)

We have carried out magnetic susceptibility and electrical resistivity measurements on LaRhAl and CeRhAl that reveal that LaRhAl is superconducting with superconducting transition temperature of about 2.4 K, while CeRhAl shows mixed valent behavior of the cerium ions and is neither magnetically ordered nor superconducting down to 1.7 K.

INTRODUCTION

In our laboratory we have been carrying out a systematic investigation of magnetic, electronic, and transport properties of equiatomic ternary rare-earth (R) intermetallic compounds of the type RTX where T is a transition metal and X is an s-p element. These compounds are found to crystallize in various structure types and exhibit a variety of interesting behavior depending upon the elements involved. For instance, the compounds CeRhIn (Ref. 1) and CeIrAl (Ref. 2) exhibit mixed valent behavior of the Ce ions. The compound CeRhSb is also a mixed valent Ce-based compound in which a gap opens in the electronic density of states at low temperatures.[3] Such gap-forming compounds are known as Kondo insulators and only a few such Ce compounds are known in the literature, e.g., CeNiSn (Ref. 4) and $Ce_3Bi_3Pt_3$.[5] In contrast to the low-temperature semiconducting behavior of CeRhSb the compound LaRhSb is superconducting with T_c of about 2.1 K.[6] In view of the very interesting and contrasting behavior of LaRhSb and CeRhSb, we have examined the properties of other similar compounds as regards the occurrence of superconductivity and/or Kondo insulating behavior. Recently, a new series of compounds with the formula RRhAl has been reported.[7] In this paper, we report the results of our studies on LaRhAl and CeRhAl. The compound LaRhAl is found to exhibit superconductivity with a transition temperature of about 2.4 K. However, though CeRhAl shows mixed valent behavior, it is neither superconducting/magnetic nor does it show a rapid rise in resistivity at low temperatures seen in Kondo insulators.

EXPERIMENTAL DETAILS

The samples of LaRhAl and CeRhAl were prepared by arc melting the stoichiometric amounts of the constituent elements on a water-cooled copper hearth in argon atmosphere. The La and Ce metals were obtained from the Materials Preparation Center, Ames Laboratory, and had a purity of 99.99% with respect to other rare-earth elements. The Al metal was obtained from Leico Industries, and had a stated purity of 99.999%. The Rh metal was procured from Arora-Mathey and was at least 99.9% pure. The alloy buttons were melted at least four times and turned over after every melting to ensure homogeneous mixing. Powder x-ray diffraction patterns were obtained using Cu $K\alpha$ radiation. Magnetization measurements were carried out using a superconducting quantum interference device magnetometer (Quantum Design). The LaRhAl sample was cooled to 1.7 K in zero applied field and the magnetization was measured on warming the sample from 1.7 K in low applied fields. Magnetization-field isotherm was also obtained on a zero-field-cooled sample at 1.7 K. Magnetic susceptibility of CeRhAl was measured in an applied field of 5 kOe in the temperature range of 1.7–300 K. Four-probe electrical-resistivity measurements were carried out up to 300 K on a rectangular slab of the sample using an automated resistivity set up.

RESULTS AND DISCUSSION

It has been reported[7] that LaRhAl and CeRhAl crystallize in the orthorhombic $Pd_2(MnPd)Ge_2$ structure, space group *Pnma* (No. 62). Powder x-ray diffraction patterns of LaRhAl and CeRhAl prepared in our laboratory confirm these findings. The lattice parameters obtained by us from a Rietveld analysis of the x-ray diffraction data are as follows: LaRhAl, $a=7.246(1)$ Å, $b=4.256(1)$ Å, and $c=16.256(2)$ Å; for CeRhAl, $a=7.099(1)$ Å, $b=4.210(1)$ Å, and $c=15.934(2)$ Å. These lattice parameters are in good agreement with those reported in Ref. 7 for the same materials. It has been observed [7] that LaRhAl and CeRhAl adopt a different orthorhombic structure type than the remaining RRhAl compounds ($R=$rare-earth and Y). While the other RRhAl compounds crystallize in the orthorhombic TiNiSi-type structure, those with La and Ce form in $Pd_2(MnPd)Ge_2$-type structure, which is a combination of TiNiSi-type structure and ZrNiAl- type structure with the c-lattice parameter almost double of that in the TiNiSi-type RRhAl compounds. However, neither the size nor the valence of the rare-earth ion appears to be the consideration in deciding the structure type. Though there are two inequivalent rare-earth sites in LaRhAl and CeRhAl, the immediate surroundings of the rare-earth ions are nearly the same in the two structure types. A comparison of the unit-cell volume per formula unit in the RRhAl series[7] shows a volume smaller than that expected on the basis of lanthanide contraction for CeRhAl suggesting that Ce may be in a non-3+ state in this compound.

Figure 1 shows a plot of magnetic susceptibility versus temperature for LaRhAl in the temperature range of 1.7–4 K measured in various low applied fields ranging from 20 to 70 Oe. An onset of diamagnetism is observed at about 2.4 K indicating that the sample is going into a superconducting state below this temperature. This is confirmed by electrical

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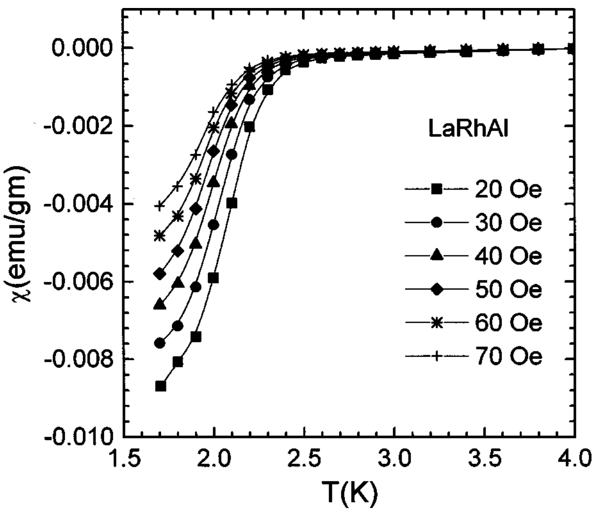

FIG. 1. Low-field (20–70 Oe) magnetic susceptibility of LaRhAl in the temperature range 1.7–4 K in a zero-field-cooled state.

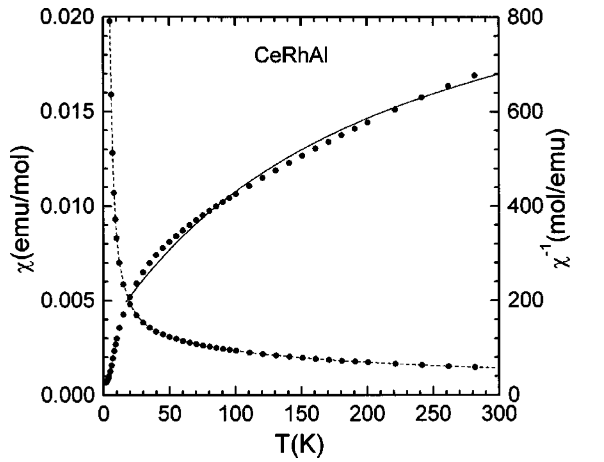

FIG. 3. Magnetic susceptibility (χ) and χ^{-1} versus temperature for CeRhAl. The solid line is a fit to the modified Curie-Weiss law. The dashed line is a guide to the eye.

resistivity measurements also (see below). Figure 2 shows a plot of magnetization (M) versus field (M-H) at 1.7 K. The M-H loop is typical of a type-II superconductor.

In the LaRhX series of compounds studied in our laboratory, those with $X=$Al and Sb have been found to be superconducting with transition temperatures of 2.4 and 2.1 K, respectively. It is likely that some other members of this series may also exhibit superconductivity. A comparison of the unit-cell volume per formula unit reveals that LaRhAl has a higher volume and also a higher T_c than LaRhSb. Further, we have found that LuRhSb, isostructural to LaRhSb but with a still lower volume, is not superconducting down to 1.7 K. Thus, there seems to be a correlation between the volume and the T_c similar to that seen in other systems, such as in superconducting Heusler alloys,[8] Chevrel phase compounds,[9] etc. It is possible that LuRhSb may exhibit superconductivity at still lower temperatures.

As mentioned above, in the RRhSb series, LaRhSb is superconducting while CeRhSb shows a rapid rise in resistivity at low temperatures attributed to the opening of a gap in the $4f$ electron density of states of the mixed valent Ce ions. In view of the observation of superconductivity in LaRhAl, it was interesting to examine the magnetic and resistivity behavior of CeRhAl. As already mentioned, the unit-cell volume of CeRhAl suggests that Ce ions are in a mixed valent state in this compound[7] similar to the situation in CeRhSb. This is borne out by the magnetic susceptibility measurements shown in Fig. 3. The susceptibility of CeRhAl follows modified Curie-Weiss behavior ($\chi=\chi_0+C/T-\theta_p$) in the temperature range 20–300 K with $\chi_0=0.000\,94$ emu/mol, $\theta_p=-24.8$ K, and an effective paramagnetic moment of $1.17\mu_B$ the latter of which is considerably smaller than the Ce^{3+} free ion value of $2.54\mu_B$ indicating the possibility of a mixed valent state for cerium ions. The large and negative value of θ_p is indicative of the presence of Kondo-type interactions in this compound. Since there are two inequivalent Ce sites in the CeRhAl structure, the possibility exists that only one of them is in a mixed valent state while the other is in a 3+ state. Our magnetization-field isotherms and low-field temperature dependence of magnetization of CeRhAl show the presence of a small ferromagnetic impurity with Curie temperature of about 6 K. The impurity fraction is estimated to be 2%. Therefore, the rapid rise in susceptibility at low temperatures may be due to the presence of this small

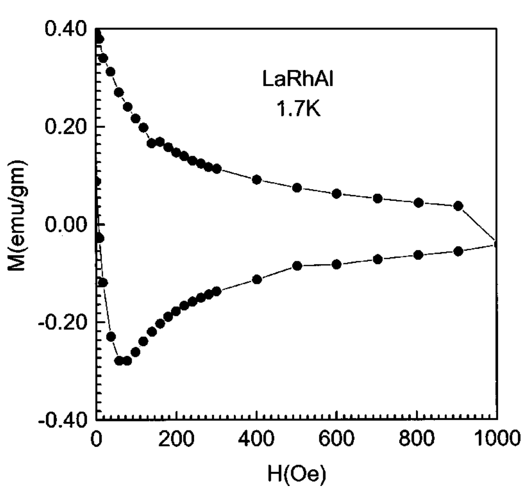

FIG. 2. Magnetization-field (M-H) hysteresis loop for LaRhAl at 1.7 K.

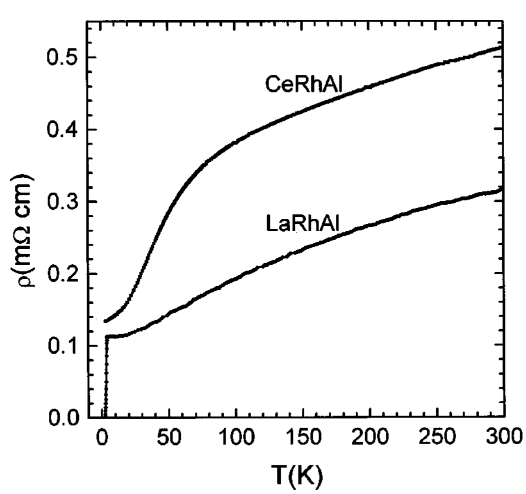

FIG. 4. Electrical resistivity versus temperature for LaRhAl and CeRhAl.

ferromagnetic impurity. However, since the impurity concentration is small and its T_C is very low, this will not affect the susceptibility and its analysis in the 20–300 K temperature range discussed above.

Figure 4 shows the plot of electrical resistivity versus temperature for LaRhAl and CeRhAl in the temperature range of 2–300 K. The resistivity of LaRhAl drops sharply and becomes nearly zero at about 2.4 K which is in very good agreement with the onset of diamagnetism in this compound. Thus, both magnetic-susceptibility and electrical resistivity measurements suggest that LaRhAl becomes superconducting below 2.4 K. Neither a rapid rise in resistivity, nor a superconducting transition is observed in CeRhAl down to 2 K. Further, there is also no magnetic ordering in this compound down to 1.7 K. Thus, in spite of the mixed valent behavior of Ce ions and the close similarities in structure type, the behavior of CeRhAl and CeRhSb is very different pointing towards the fact that some other factors may also be necessary for the formation of a Kondo insulating state in mixed valent Ce-based compounds.

In conclusion, magnetic susceptibility and electrical resistivity studies reveal that LaRhAl is superconducting with a transition temperature of 2.4 K. The isostructural CeRhAl shows mixed valent behavior of the Ce ions but is neither superconducting nor magnetically ordered down to 1.7 K. Further, no rapid rise in low-temperature resistivity is seen in CeRhAl indicating the absence of a gap formation in the electronic density of states.

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