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Evidence of pseudogap formation in a new valence-fluctuating compound: CeRhSb

S. K. Malik
Tata Institute of Fundamental Research, Bombay 400 005, India

D. T. Adroja
Indian Institute of Technology, Powai, Bombay 400 076, India

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The compound CeRhSb, crystallizing in the orthorhombic $CeCu_2$-type structure, has been synthesized. Its unit-cell volume is anomalous in relation to that of isostructural *R*RhSb (R = rare earth) compounds. Its magnetic susceptibility is weakly temperature dependent and exhibits a broad maximum at about 113 K, characteristic of valence-fluctuating Ce compounds. The resistivity also shows a broad maximum at 113 K followed by a rapid rise below 21 K. The latter indicates a gap formation in the electronic density of states. The gap energy is estimated to be about 4 K. Thus CeRhSb appears to represent a valence-fluctuating cerium compound in which a pseudogap develops in the electronic density of states at low temperatures.

In recent years, equiatomic ternary intermetallic compounds containing cerium have been the subject of intensive studies because of the anomalous physical properties which these compounds exhibit, such as the Kondo effect, heavy-fermion behavior, magnetic ordering with anomalously high-ordering temperature, valence-fluctuation behavior, etc.[1-12] Such properties are thought to arise from the strong hybridization between the localized $4f$ electrons and the conduction electrons, and are associated with the formation of a many-electron state in the proximity of the Fermi level. Among the valence-fluctuating compounds, SmB_6, SmS, and YbB_{12} are known to develop an energy gap in the density of states.[13-15] In the Ce-based valence-fluctuating compounds, this phenomenon of gap formation has been observed only in CeNiSn (Refs. 8 and 11) and Cu-doped $CePd_3$.[16] In this paper we present the results of magnetic-susceptibility and electrical-resistivity measurements on a new equiatomic ternary compound (CeRhSb), which suggest that this may represent a valence-fluctuating Ce-based compound with a pseudogap in the electronic density of states. This compound exhibits some interesting properties reflecting the hydridization between the $4f$ electrons and the conduction electrons near the Fermi level, similar to the behavior seen in the Kondo-lattice or mixed-valent compounds.

Polycrystalline samples of CeRhSb (and also other *R*RhSb, R = La, Pr, and Nd) were synthesized by arc melting of the stoichiometric amounts of the constituent elements of purity better than 99.99% in a continuous flow of high-purity argon gas. The weight loss during melting was negligible. Electrical-resistivity measurements were carried out between 4.2 and 300 K using a standard four-probe dc technique and a computer-controlled data-acquisition system. Magnetic-susceptibility measurements were made using either the Faraday method or a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 2–300 K, in an applied field of 6 kOe.

Powder x-ray-diffraction analyses of the *R*RhSb (R = La, Ce, Pr, and Nd) compounds reveal their single-phase nature. All the observed reflection ($20° < 2\theta < 70°$) can be indexed on the basis of an orthorhombic unit cell. Comparison of the x-ray patterns of these compounds with those of other reported *RTX* (R = rare earth, T = transition metal, X = metalloid) compounds reveal great similarity with the x-ray patterns of compounds crystallizing in the orthorhombic $CeCu_2$- or TiNiSi-type structures, both containing four formula units per unit cell. Further, the observed reflections of *R*-RhSb compounds satisfy the condition, $h+k+l=2n$, where n is an integer. These are the allowed reflections for the $CeCu_2$-type structure. This strongly suggests that the *R*RhSb compounds form in the orthorhombic $CeCu_2$-type structure. However, it may be noted that the $CeCu_2$- and TiNiSi-type structures are closely related; the former is a disordered structure, in which only two crystallographic inequivalent sites exist, whereas the latter is an ordered structure in which three crystallographic inequivalent sites exist. Detailed neutron-diffraction work is required to confirm the site occupancy and the exact structure type of these compounds. The lattice parameters obtained from the observed d values are as follows. LaRhSb: $a=4.646$ Å, $b=7.547$ Å, $c=7.898$ Å; CeRhSb: $a=4.609$ Å, $b=7.416$ Å, $c=7.846$ Å; PrRhSb: $a=4.596$ Å, $b=7.391$ Å, $c=7.848$ Å; and NdRhSb: $a=4.584$ Å, $b=7.329$ Å, $c=7.838$ Å. The typical error in each lattice parameter is estimated to be 0.004 Å.

The unit-cell volume of *R*RhSb (R = La, Ce, Pr, and Nd) compounds (normalized to one formula unit of *R*RhSb) obtained in the present work is plotted in Fig. 1 as a function of the rare-earth ion. The estimated errors in the unit-cell volumes are smaller than the size of the symbol used in Fig. 1. It is seen that the unit-cell volume of CeRhSb shows deviation from that expected on the basis of usual lanthanide contraction suggesting that Ce ions in this compound are not in the Ce^{3+} state, but may be in a mixed-valent state. The mixed-valent nature of cerium ions in CeRhSb is borne out by the magnetic susceptibility and electrical-resistivity measurements discussed below.

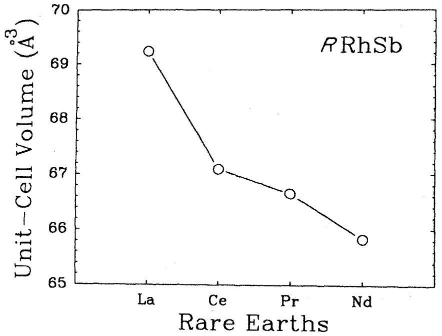

FIG. 1. Unit-cell volume (normalized to one formula unit) of *R*RhSb (*R* = La, Ce, Pr, and Nd) compounds as a function of the rare-earth ion.

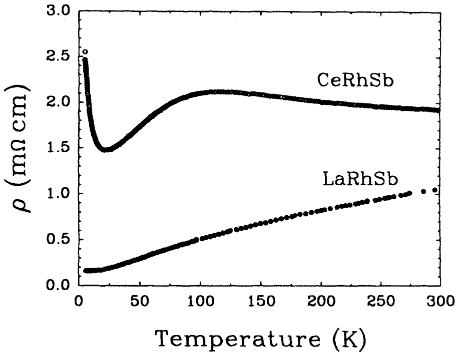

FIG. 3. Temperature dependence of the electrical resistivity of CeRhSb and LaRhSb.

The temperature dependence of the magnetic susceptibility of CeRhSb is shown in Fig. 2. The susceptibility passes through a broad maximum at about 113 K followed by a small rapid rise at low temperatures. Such a maximum in the susceptibility is a common feature of the Ce- and Yb-based valence-fluctuating compounds.[4,17,18] The low-temperature rise is most likely due to the presence of a small amount of static Ce^{3+} ions stabilized by lattice defects. Earlier bulk susceptibility measurements on the mixed-valent compound, CeRhIn, also showed a low-temperature rise which, however, was not observed in the microscopic measurement of the ^{140}Ce susceptibility in the same compound using the perturbed angular correlation technique.[19]

Figure 3 shows the temperature dependence of the electrical resistivity of CeRhSb and LaRhSb between 4.2 and 300 K. The values of room-temperature resistivities of CeRhSb and LaRhSb are 1.9 and 1.06 mΩ cm, respectively, which are somewhat high but of the same magnitude as observed in the case of the mixed-valent compound, $CeIr_2Si_2$.[17] The resistivity of CeRhSb increases as the temperature decreases from 300 K and reaches a maximum at about 113 K, then decreases with decreasing temperature and exhibits a minimum at 21 K. Below 21 K, the resistivity shows a rapid rise which continues down to the lowest temperature of measurements. On the other hand, the resistivity of LaRhSb shows the usual metallic behavior throughout the temperature range investigated (Fig. 3). The weakly temperature-dependent susceptibility of CeRhSb implies relatively broad 4*f* levels compared to the crystalline electric-field splittings normally encountered in similar compounds.[5] Further, the crystalline electric fields only tend to decrease the spin-disorder resistivity from the free-ion value[20] and cannot give rise to the behavior observed in CeRhSb. The rapid rise in the resistivity of CeRhSb at low temperatures may be interpreted to imply a gap formation in the electronic density of states. To estimate the gap energy, we have plotted ln(ρ) vs $1/T$ (Fig. 4). A linear relation is observed between the two in the temperature range of 5 K to about 17 K. The gap energy estimated from the linear regime is ≃4 K. Deviation from linearity is observed below 5 K, which may indicate that, within the gap, there exists a density of states with a temperature-dependent structure.[8] The overall resistivity behavior of CeRhSb is similar to that reported for a single crystal of CeNiSn along the crystallographic *b* direction, in which the low-temperature rise of the resistivity yields a value of 5.5 K for the energy gap in the electronic density of states.[8] It is interesting to note that a 20% replacement of Ce by La in CeRhSb (i.e., $Ce_{0.8}La_{0.2}RhSb$) suppresses the rapid rise in the resistivity at low temperatures, suggesting that a crystallographically well-ordered cerium lattice is essential for the formation of such a gap.

The observed susceptibility of CeRhSb has been ana-

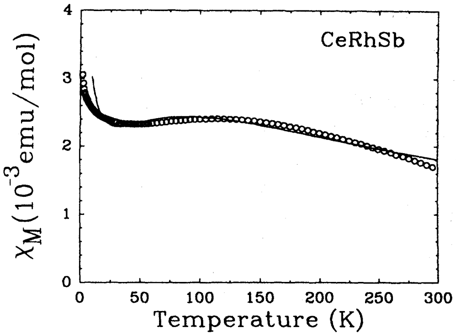

FIG. 2. Temperature dependence of the magnetic susceptibility of CeRhSb. The solid line is a fit based on the ICF model with parameters given in the text.

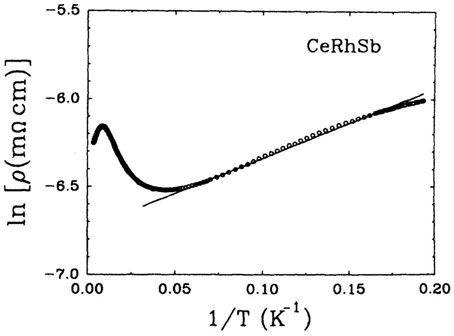

FIG. 4. ln(ρ) vs $1/T$ for CeRhSb. The solid line represents the fit with gap energy of about 4 K.

lyzed on the basis of the ionic two-level interconfiguration fluctuation (ICF) model proposed by Sales and Wholleben.[21] A Curie-Weiss term, nC/T, was added to account for the observed upturn in susceptibility at low temperatures caused by a fraction n of paramagnetic impurities which we take to be Ce^{3+}. Such an analysis of the susceptibility, details of which have been given earlier, yields the solid line in Fig. 2 with excitation energy, $E_{ex}=368$ K, spin-fluctuation temperature, $T_{SF}=87$ K, impurity concentration, $n=0.0217$, and temperature-independent susceptibility, $\chi_0=3\times10^{-4}$ (emu/mol). Since no secondary phases are detected in the sample within the x-ray limit, the 2% Ce^{3+} required to fit the susceptibility data at low temperatures may be the Ce^{3+} stabilized by lattice defects. If the impurity Ce^{3+} contribution is neglected, even then an equally good fit to the observed susceptibility is obtained down to 30 K within the framework of the Sales-Wholleben model with marginal change in parameters, namely, $E_{ex}=340$ K and $T_{SF}=87$ K. This emphasizes that the above model explains reasonably well the main feature of the susceptibility, namely, the broad peak at 113 K. The value of the Ce valence calculated from the E_{ex} and T_{SF} parameters obtained form the ICF model and using the equation of fractional occupation of the Ce^{4+} state[21] is 3.3 at 300 K.

In conclusion, the compound, CeRhSb, crystallizing in the orthorhombic $CeCu_2$-type structure has been synthesized, apparently for the first time. The unit-cell volume, magnetic susceptibility, and resistivity measurements reveal that Ce ions are in a valence-fluctuating state in this compound. Its resistivity shows a rapid rise below 21 K, which indicates pseudogap formation in the narrow band of electronic density of states. The estimated value of gap energy is about 4 K.

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