PHYSICAL REVIEW B VOLUME 48, NUMBER 13 1 OCTOBER 1993-I

Observation of superconductivity in LaRhSb

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(Received 17 May 1993)

Low-temperature magnetic-susceptibility and heat-capacity measurements on the ternary intermetallic compound LaRhSb reveal that this compound is superconducting with transition temperature of 2.1 K. The specific-heat jump at T_c disappears in an applied field of 0.5 Tesla. The electronic-specific-heat coefficient γ is found to be 7.7 mJ/mole K^2, and the Debye temperature Θ_D to be 252 K.

In recent years, there has been a great deal of interest in the study of rare-earth-containing ternary intermetallic compounds of the type RTX where R is a rare-earth metal, T is a transition metal, and X is one of the *sp* elements (see, for instance, Refs. 1–9). These compounds crystallize in a variety of structure types, depending upon the nature of the T and X elements. Therefore, these offer the opportunity of systematic investigations of the influence of crystal structure, and of alloying various *sp* elements and transition metals on the electronic, magnetic, and transport properties of these compounds. Many of these ternary compounds, in particular, those containing cerium, exhibit unusual electronic and magnetic behavior, e.g., CeRhIn is a valence fluctuating system,[2] CdPdSn is an antiferromagnetic Kondo lattice system,[3,8,9] while CePdSb exhibits ferromagnetic ordering in the presence of possible Kondo-type interactions.[7]

Recently, studies on a series of such ternary compounds represented by the general formula RRhSb (R = La, Ce, Pr, or Nd) have been reported. In this series, the cerium-containing compound again shows very interesting properties.[6] Its susceptibility is only weakly temperature dependent and passes through a broad maximum. This behavior is typical of mixed-valence cerium compounds. The resistivity of CeRhSb behaves in an unusual fashion. It increases slightly as the temperature is decreased from 300 K, reaches a broad maximum at about 113 K, after which it starts decreasing. On a further decrease of temperature, the resistivity passes through a minimum at about 21 K and then rises sharply at low temperatures. The sudden rise in resistivity at low temperatures has been attributed to the opening of a gap in the electronic density of states at the Fermi level due to the hybridization of the Ce-4f electrons with the conduction electrons. The La analogs of such compounds serve as reference materials for estimating the non-4f contribution to various physical quantities (e.g., susceptibility, resistivity, lattice contribution to the heat capacity, etc.), since La has no electrons in the 4f shell. Therefore, in view of the unusual behavior of CeRhSb, we have examined the magnetic and transport properties of the isostructural LaRhSb in detail. From magnetic-susceptibility and heat-capacity measurements, we find that this compound becomes superconducting with a transition temperature T_c of 2.1 K.

Two different samples of the compound LaRhSb were prepared, one at the Tata Institute of Fundamental Research (TIFR) and the other at the Ames Laboratory (AL), by melting together Rh and Sb of at least 99.9% purity and pure La in an arc furnace under a continuous flow of purified argon. The La used by TIFR was purchased from Leico, USA, and had a stated purity of 99.9%, probably with respect to other rare earths only. The La used by AL was prepared by the Materials Preparation Center of the AL and had a purity of 99.8 at % with respect to *all* the elements in the periodic table (the major impurities in ppm atomic were H = 1650, O = 190, N = 128, F = 80, C = 34, and Fe = 7.6). The buttons were turned over and melted several times to ensure homogeneity. The weight loss during melting was negligible. The TIFR button was wrapped in a Ta foil and annealed in vacuum in a sealed quartz tube at 850 °C for seven days, while the AL sample was heat treated in the same manner for two weaks at 950 °C. Powder x-ray-diffraction patterns obtained using Cu K_α radiation showed only the presence of the expected LaRhSb lines. An optical metallographic investigation of the AL sample revealed a very clean microstructure with no evidence for a second phase, confirming the single-phase nature of the material. Magnetic susceptibility was measured using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design) in the temperature range of 1.8 to 30 K. The heat capacity was measured from 2 to 100 K both in zero applied field as well as in the presence of various applied fields using a standard heat-pulse calorimeter, details of which have been described elsewhere.[10]

The compound LaRhSb crystallizes in the orthorhombic ε-TiNiSi-type structure (space group *Pnma*). This is a well-ordered structure in which the La, Rh, and Sb atoms occupy unique lattice sites. The lattice parameters obtained from a least-squares fit of the observed Bragg reflections are $a = 7.547$ Å, $b = 4.696$ Å, and $c = 7.898$ Å.

Figure 1 shows the results of magnetic-susceptibility measurements in the low-temperature range in an applied field of 500 Oe taken on both TIFR and AL samples. The susceptibility in the normal state is positive (paramagnetic) and nearly temperature independent. A

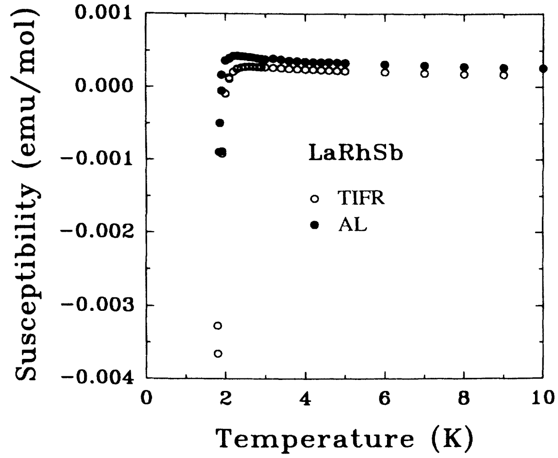

FIG. 1. Magnetic susceptibility of the TIFR and AL samples of LaRhSb below 10 K.

sharp change from positive to negative (diamagnetic) susceptibility is observed at a temperature close to 2.1 K. This signals the transition to the superconducting state.

The results of heat-capacity (C) measurements in the temperature (T) range of 1.6 to 10 K are shown in Fig. 2 for the AL sample where C is plotted versus T. The measurements were made on two different calorimeters and one can see that there is good agreement between the two sets of data (Figs. 2 and 3). A jump in the heat capacity is observed at 2.2 K, which can be suppressed in a field of 0.5 Tesla. These observations coupled with the magnetic-susceptibility results confirm that the transition is due to superconductivity. The bulk nature of the superconductivity is inferred from the magnitude of the specific-heat jump (see below). Figure 3 shows a plot of C/T vs T^2 below 6 K (36 K^2). The heat-capacity data are analyzed using the expression

$$C=\gamma T+\beta T^3 \ . \tag{1}$$

From a least-square fit of 65 data points between 1.8 and 5.5 K (3.35 and 30.5 K^2) the electronic-specific-heat coefficient γ is found to be 7.7 ± 0.2 mJ/mole K^2. From the β value, the Debye temperature obtained is 252 ± 3 K. The jump in the specific heat, ΔC, at T_c is completely delineated and the ratio $\Delta C/\gamma T_c$ is 1.53, which is slightly larger than the BCS weak-coupling limit of 1.43. This value for the ratio confirms that LaRhSb is a bulk superconductor.

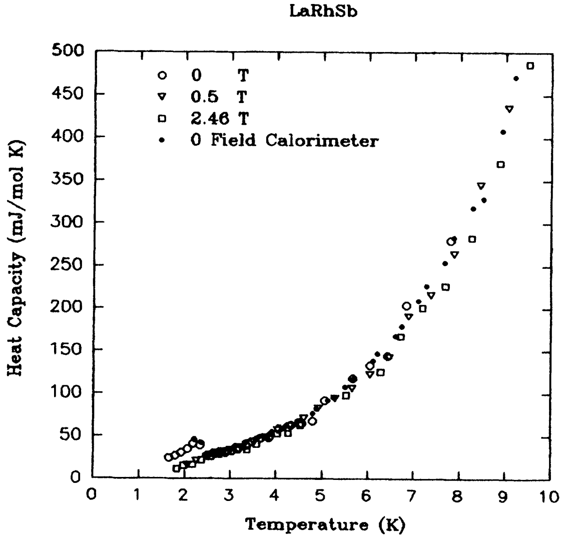

FIG. 2. Low-temperature heat capacity of the AL sample of LaRhSb from 1.6 to 10 K measured in two different calorimeters (a zero-field one and a high-magnetic-field one).

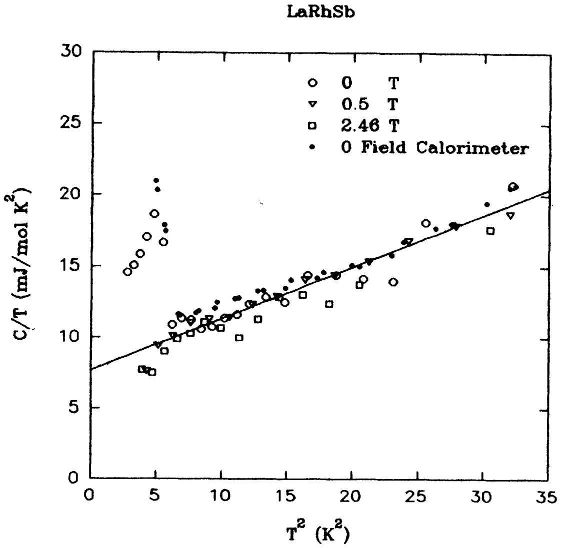

FIG. 3. A C/T vs T^2 plot of the heat capacity of the AL sample of LaRhSb from 1.6 to ~6 K (2.56 to 35 K^2) measured in two different calorimeters (a zero-field one and a high-magnetic-field one).

In the light of the observation of superconductivity in LaRhSb, the results on CeRhSb are even more interesting. The La and Ce compounds have the same outer electronic configuration and differ in the number of $4f$ electrons. While La has no electrons in the $4f$ shell, Ce normally has one electron in the $4f$ shell. Lattice volume anomaly and susceptibility measurements on CeRhSb show that Ce ions in this compound are in a strongly mixed-valence state, implying loss of magnetism of the $4f$ electrons. The susceptibility of CeRhSb does not follow the usual local-moment behavior. In this respect, CeRhSb may be thought of as an exchange-enhanced analog of LaRhSb. Superconductivity has been observed in some strongly mixed-valence cerium compounds, such as $CeRu_3B_2$ and $CeOs_3B_2$ (Ref. 11). However, superconductivity is not observed in CeRhSb down to about 2 K; instead its resistivity shows a sharp rise at low temperatures, overcoming the superconducting interactions presumably inherent in the system. To our knowledge, RRhSb is the only system in which the La compound is superconducting but the Ce compound behaves like an insulator (termed Kondo insulator). Thus, the behavior of the RRhSb phases are quite intriguing and need further investigation.

The Ames Laboratory is supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy through Iowa State University under Contract No. W-7405-ENG-82.

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