

Anisotropic physical properties of the Kondo semiconductor CeRhSb

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Measurements of resistivity ρ , thermopower S , and magnetic susceptibility χ are reported on single-crystal CeRhSb. Only along the orthorhombic a axis, $\chi(T)$ exhibits a pronounced peak at 13 K and $\rho(T)$ has a shoulder at around 20 K. These anomalies and the relations $\rho_c > \rho_b > \rho_a$ and $\chi_a > \chi_b > \chi_c$ resemble those in the isostructural Kondo semiconductor CeNiSn. However, the anisotropy in $\rho(T)$, $\chi(T)$, and $S(T)$ is still weaker than that in CeNiSn. The magnetic contribution to the specific heat divided by temperature C_m/T reveals a maximum of 0.1 J/K² mol near 10 K and decreases linearly with decreasing temperature. These results indicate that the gap formation in CeRhSb and CeNiSn originates from a similar type of hybridization of $4f$ states with a conduction state.

The Ce-based compounds CeNiSn (Refs. 1–3), CeRhSb (Refs. 4–6), and Ce₃Bi₄Pt₃ (Refs. 7 and 8) form a class of materials called Kondo insulators or semiconductors, and are characterized by a small energy gap in the electronic excitation spectrum. The gap formation is generally believed to originate in the hybridization between the $4f$ states and a conduction band near the Fermi level.⁹ The energy gap estimated from transport properties is several kelvins for both CeNiSn and CeRhSb. CeNiSn crystallizes in an orthorhombic structure, which is closely related to the ϵ -TiNiSi-type structure.¹⁰ CeRhSb is assumed to be isostructural,^{4,6} but it has not been determined yet whether or not Rh and Sb atoms are crystallographically ordered in the ϵ -TiNiSi-type structure. Magnetic, transport, and elastic properties of CeNiSn are strongly anisotropic as expected from the low crystal symmetry.^{1–3} The magnetic susceptibility along the a axis χ_a is much larger than χ_b and χ_c , and exhibits a pronounced peak at 12 K. Below this temperature, antiferromagnetic correlations with characteristic energy of 2.5 and 4.5 meV develop.^{11,12} Furthermore, an anisotropic gapping of the Fermi surface has been inferred from the anisotropic transport properties in the gapped state below 7 K.

On the other hand, physical properties of CeRhSb have been so far reported on polycrystalline samples.^{4–6} Both the resistivity and magnetic susceptibility have a broad maximum at around 120 K, which is a characteristic of a Ce-based valence fluctuating system. As the temperature is decreased below 10 K, the resistivity and Hall coefficient show semiconducting behavior, suggesting gap formation as similar in CeNiSn. Recently, a V-shaped structure of the pseudogap has been proposed based on the T^3 dependence of the nuclear-lattice relaxation rate of ¹¹⁹Sr in CeNiSn and of ¹²³Sb in CeRhSb.^{13,14} For better understanding of the mechanism of gap formation, it is important to compare anisotropic properties between the two systems. We have prepared single-crystal CeRhSb and present the results of magnetic, transport, and calorimetric measurements in this paper.

Polycrystalline samples of CeRhSb were prepared from Ames Laboratory Ce by arc-melting in a purified argon atmosphere. An excess amount of Sb by approximately 0.6 at. % was added so as to compensate the weight loss during the melting. The samples were then loaded in a molybdenum crucible to grow a single crystal by using the Bridgman technique. The resulting ingot possessed single-crystal grains up to 3 mm across. The quality of the crystals was checked by Laue photos, metallographic examination, and electron-probe microanalysis. Impurity phases of Ce₂Sb and CeRh₂Sb₂ were detected with a total volume fraction less than 1%. By powder x-ray-diffraction analysis, we observed the reflections of (403) and (210) from the polycrystalline sample of CeRhSb. These reflections are not allowed for the CeCu₂-type structure. Thus we confirm that Rh and Sb atoms in CeRhSb are crystallographically ordered in the ϵ -TiNiSi-type structure.

A crystal in the shape of 3-mm-edge cube was used for the magnetic measurements. Susceptibility measurements from 2 to 300 K were done in a magnetic field of 5.5 T by using a superconducting-quantum-interference-device magnetometer. Magnetization measurements were performed by using a vibrating sample magnetometer in fields up to 15 T which were produced by a water-cooled magnet. Bar-shaped samples with typical dimensions of 0.3 × 0.4 × 3 mm³ were used for resistivity and thermoelectric power measurements from 1.3 to 300 K. A polycrystalline sample annealed for 8 days at 1000 °C was used for specific-heat measurements from 1.3 to 60 K.

Figure 1 represents the temperature dependence of the resistivity $\rho(T)$ along the three principal axes. The three curves of $\rho(T)$ are characterized by a broad maximum at around 120 K and a rapid rise below 8 K. The overall temperature dependence agrees with the result reported for a polycrystalline sample.^{4,5} The anisotropy of $\rho(T)$ becomes evident at temperatures below 80 K. We notice a shoulder in $\rho_a(T)$ near 20 K, which is reminiscent of a peak in $\rho_a(T)$ at

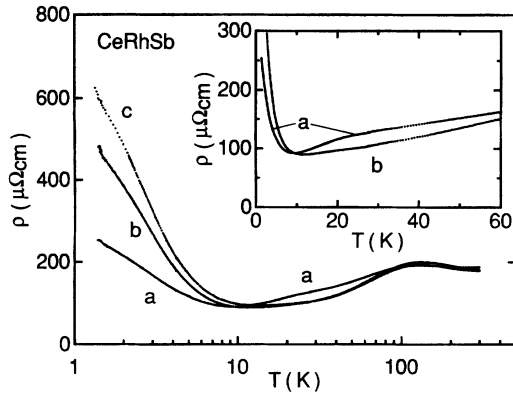


FIG. 1. Electrical resistivity vs temperature for CeRhSb along the three principal axes. The inset shows the low-temperature part in a linear scale.

12 K found for CeNiSn.¹ Furthermore, the relation $\rho_c > \rho_b > \rho_a$ holds in the gapped state below 8 K, as similar to the case of CeNiSn.

The thermoelectric power $S(T)$ shown in Fig. 2 exhibits weakly anisotropic temperature dependence. Both $S_b(T)$ and $S_c(T)$ have a shoulder at around 150 K and a huge broadened maximum near 20 K, followed by a strong decrease below 10 K. The characteristic features and the absolute value agree with those of a polycrystalline sample.⁵ The temperature of the shoulder is close to that of the maxima of $\rho(T)$ and of magnetic susceptibility as shown later. This indicates that the shoulder originates in single-site spin fluctuations with a characteristic energy of 150 K. We note that $S(T)$ of typical valence-fluctuating compounds CePd₃ and CeSn₃ has a large maximum at around 150 K.¹⁵ Whereas $S(T)$ of the two compounds goes to zero monotonically with decreasing temperature, $S(T)$ of CeRhSb has the maximum near 20 K. This maximum can be interpreted as a result of formation of renormalized bands near the Fermi level, because the specific-heat data indicate a significant mass enhancement at temperatures below 20 K as will be shown later. In $S_a(T)$, a sharp structure appears at 2 K. We recall here that both $S_a(T)$ and $S_c(T)$ of CeNiSn exhibit a sharp

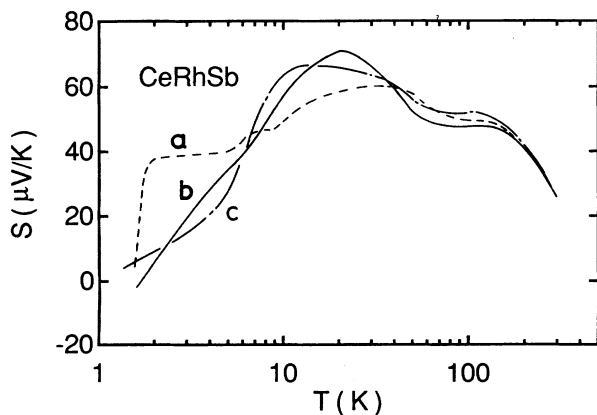


FIG. 2. Thermoelectric power vs temperature for CeRhSb along the three principal axes.

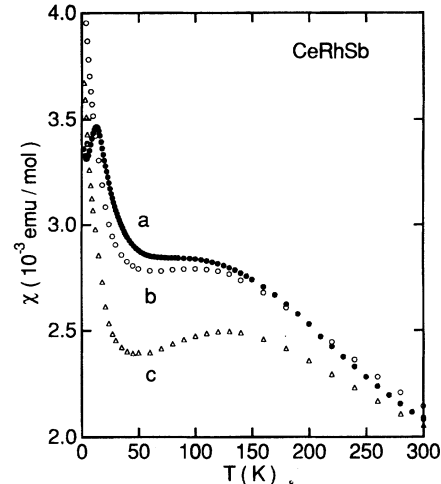


FIG. 3. Magnetic susceptibility vs temperature for CeRhSb along the three principal axes.

peak at 3 K, which arises from the residual density of states within the energy gap.¹ Following this idea, the structure in $S_a(T)$ of CeRhSb can be attributed to the residual density of states.

As shown in Fig. 3, the magnetic anisotropy of CeRhSb is apparent in the temperature dependence of susceptibility $\chi(T)$. A relation $\chi_a > \chi_b > \chi_c$ is noticed at temperatures below the broad maximum near 130 K. This relation is common among isostructural compounds CeRhSb, CeNiSn, and CePtSn.^{1,16} The magnetic anisotropy of CePtSn is dominated by the strong crystal-field acting of the trivalent Ce ions.¹⁶ When hybridization of 4*f* electronic states with conduction electronic states is increased, the magnetic anisotropy arising from the crystal field may be weakened as observed in CeRhSb. Most notable in Fig. 3 is the pronounced peak of $\chi_a(T)$ at 13 K, which closely resembles the peak of $\chi_a(T)$ at 12 K for CeNiSn. The Knight shift of ¹¹⁹Sn in CeNiSn exhibits a similar peak in applied fields along the *a* axis.¹³ The peaking is thought to reflect the development of antiferromagnetic correlations.^{11,12}

We direct our attention to the upswing of χ below 50 K. Such an upswing has been observed in a polycrystal CeRhSb (Refs. 4 and 5) as well as single crystals of CeNiSn (Ref. 1) and Ce₃Bi₄Pt₃.^{7,8} It was attributed to the presence of trivalent Ce ions in impurity phases or lattice imperfections. However, as in the case of CeSn₃,^{17,18} the contribution from the Ce 5*d* electrons to the upswing cannot be excluded. For the present CeRhSb crystal, we found impurity phases of Ce₂Sb and CeRh₂Sb₂. Ce₂Sb orders antiferromagnetically at 9.5 K,¹⁹ while the magnetic property of CeRh₂Sb₂ has not been reported as far as we know. In order to estimate the concentration of trivalent Ce impurities in the present sample, we assumed that intrinsic susceptibilities χ_b and χ_c become independent of temperature below 50 K. This assumption is based on the fact that the Knight shift of ¹¹⁹Sn in CeNiSn along the *b* and *c* axes rather weakly depends on temperature below 50 K.¹³ The impurity susceptibilities thus obtained lead to Curie constants which correspond to a trivalent Ce impurity concentration of 1.2%.

Figure 4 displays the magnetization curves taken at 4.2 K.

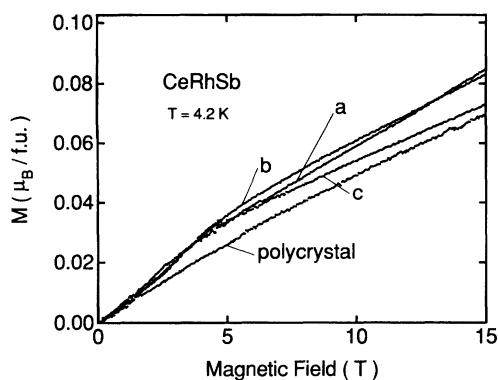


FIG. 4. Magnetization curves of polycrystal and single-crystal CeRhSb in fields along the three principal axes at 4.2 K.

The three curves for the single crystal show a change in the slope around 5 T and increase linearly with increasing field. In the highest field of 15 T, the a -axis magnetization M_a attains a value of $0.085\mu_B/\text{f.u.}$, which is half of that of CeNiSn. The change in the slope near 5 T is rather weak for the polycrystalline sample compared to the single crystal. Therefore, the anomaly near 5 T can be attributed to paramagnetic impurities of trivalent Ce ions. The saturation moment of impurities is estimated by a linear extrapolation of the data of $M_b(H)$ and $M_c(H)$ from above $H=10$ T to 0 T. Assuming the saturation moment of $2.14\mu_B$ for the trivalent Ce impurity, the concentration is estimated to be 0.8%. This value is comparable to that estimated from the aforementioned analysis of the magnetic susceptibility. Recently, magnetization measurements have been performed up to 35 T on a powdered sample at 1.3 K.²⁰ In the fields above 30 T, the magnetization curve shows a metamagneticlike increase, suggesting that the gap in CeRhSb is closed near 40 T.

The specific heat divided by temperature C/T is plotted vs T^2 in the inset of Fig. 5. A downward deviation from the linear relation starts below about 12 K and becomes evident below 7 K. This implies a significant reduction of the density of states at the Fermi level. A linear extrapolation of the data above 12 K yields a value $C/T=0.1$ J/K² mol at $T=0$ K. The enhanced Sommerfeld coefficient signals the formation of a heavy quasiparticle band antecedent to the gap opening. The magnetic contribution to the specific heat C_m was obtained by means of subtraction of the phonon contribution, which was estimated from the data of LaRhSb. As shown in Fig. 5, C_m/T exhibits a pronounced maximum at $T_{cm}=10$ K and decreases linearly with decreasing temperature. For CeNiSn, the maximum with a larger value of 0.17 J/K² mol is located at a lower temperature of 6.5 K.²¹ By comparing

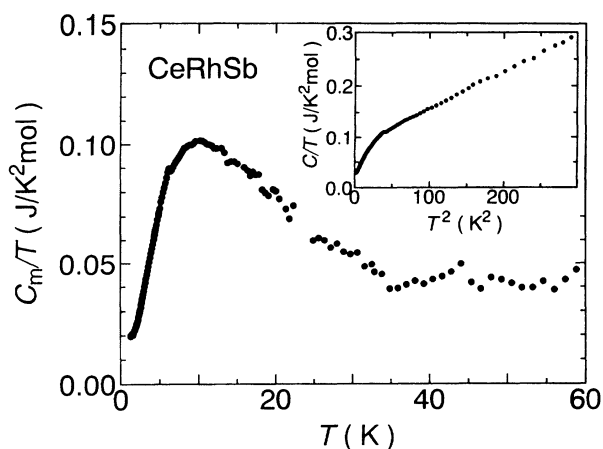


FIG. 5. Magnetic contribution to specific heat divided by temperature C_m/T vs T for CeRhSb. The inset shows C/T vs T^2 .

the magnetic entropy with the value calculated for a single Kondo impurity,²² the Kondo temperature T_K is estimated to be 96 K and 54 K for CeRhSb and CeNiSn, respectively. It is noteworthy that the ratio T_{cm}/T_K is approximately 0.1 for the two compounds.

In summary, we have reported a set of measurements of resistivity, thermopower, magnetic susceptibility on single-crystal CeRhSb, and specific heat on the polycrystal. The combined results indicate that a pseudogap opens in the quasiparticle band at temperatures below 10 K. The fact that the anisotropy in the transport and magnetic properties of CeRhSb in the gapped state is weaker than that of CeNiSn suggests relatively weak anisotropy of the gap in CeRhSb. However, the common relationships $\rho_c > \rho_b > \rho_a$ and $\chi_a > \chi_b > \chi_c$ are found for the two compounds. It is also common that $\chi(T)$ and $\rho(T)$ exhibit a peak or shoulder at 12–20 K only along the a axis. The strong similarities suggest that the formation of the pseudogap in CeRhSb and CeNiSn originates from a similar type of hybridization of $4f$ states with a conduction state. For CeNiSn, development of antiferromagnetic correlations below 15 K has been revealed by recent neutron-scattering experiments.^{11,12} We therefore infer that similar spin correlations develop in CeRhSb and it is closely related to the gap formation.

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