Effect of magnetic fields on the Kondo insulator CeRhSb: Magnetoresistance and high-field heat capacity measurements

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(Received 10 June 1996; revised manuscript received 9 January 1997)

The compound CeRhSb is a mixed valent Ce-based compound which shows a gap in the electronic density of states at low temperatures. The gap manifests by a rise in electrical resistivity—below about 8 K from which the gap energy is estimated to be about 4 K. We have carried out heat capacity measurements on this compound in various applied fields up to 9.85 T. The magnetic contribution to the heat capacity, ΔC, is found to have a maximum in $\Delta C/T$ vs T at 10 K, below which $\Delta C/T$ is linear with T. This is attributed to the fact that below this temperature, in the gapped state, the electronic density of states decreases linearly with decreasing temperature. On application of a magnetic field, the electronic specific heat coefficient γ in the gapped state increases by ~ 4 mJ/mol K^2. The maximum in $\Delta C/T$ vs T is observed in all fields, which shifts to lower temperatures ~ 1 K at 5.32 T and raises again at 9.85 T to about the same values as at $H=0$ T. This suggests that the gap exists for all fields up to 9.85 T. Above 10 K, in the mixed-valent state, $\Delta C/T$ vs T decreases with increasing temperature in zero field. There is hardly any effect of application of field in the mixed-valent state, since the applied fields are too small to change the already large density of states at the Fermi level. We have also carried out magnetoresistance measurements on CeRhSb up to fields of 5.5 T at 2, 4.5, 10, 20, and 30 K. The magnetoresistance in CeRhSb is positive at temperatures of 4.5 K and above, in applied fields up to 5.5 T. At 5.5 T, the magnetoresistance is maximum at 4.5 K (6%) and decreases with increasing temperature. The observation of the maximum is consistent with the observation of a maximum in $\Delta C/T$ vs T and is due to a change in the density of states. At a temperature of 2 K, a negative magnetoresistance is observed for magnetic fields greater than ~ 3.5 T which suggests reduction in the gap. [S0163-1829(97)15517-5]

INTRODUCTION

Many lanthanide intermetallic compounds show interesting properties, such as the Kondo effect, heavy fermion behavior, mixed-valent behavior, etc. (see, for instance, Refs. 1 and 2). This has been attributed to the hybridization between the lanthanide $4f$ electrons and the conduction electrons. In the single impurity Kondo model, it has been shown that, due to this hybridization, a Kondo resonance develops at the Fermi level below a critical temperature, T_K, called the Kondo temperature. This implies that below T_K, the density of states at the Fermi level is enhanced. The development of the Kondo resonance is manifested by a minimum followed by a rise in the electrical resistivity with a decrease in temperature. Such a resonance also forms in a Kondo lattice (containing a high concentration of magnetic impurities). However, in the case of the Kondo lattice, there exist two temperature scales: one is the usual Kondo temperature and the other is the coherence temperature, $T_{\rm coh}$, where $T_{\rm coh}$ is smaller than T_K. At T_K, the usual minimum followed by a rise in resistivity is observed with decreasing temperature, until at a characteristic temperature, $T_{\rm coh}$ the resistivity shows a drop with decreasing temperature. This drop results from the development of a coherent state in the Kondo lattice, due to the periodic arrangement of magnetic impurities resulting in a coherent scattering by Kondo impurities. For such a coherent lattice, if the hybridization is strong, charge transfer between the $4f$ level and the conduction band is possible (as observed in mixed-valent systems). The Kondo resonance in such mixed-valent systems, then splits into two peaks and hence (at $T=0$ K) a gap forms in the electronic density of states, at the Fermi level. This gap, however, exists only at $T=0$ K and is therefore called a pseudogap. With increasing temperature, the electronic density of states increases linearly and the gap develops into a minimum. This minimum in the electronic density of states finally disappears at the critical temperature, $T_{\rm coh}$, due to increase in the incoherent scattering. Above $T_{\rm coh}$, a Lorentzian density of states develops at the Fermi level, the height of which decreases logarithmically with increasing temperature as in normal Kondo systems. Thus the electronic density of states in such mixed-valent, gap-forming compounds shows a maximum at $T=T_{\rm coh}$, since both above and below this characteristic temperature, the electronic density of states decreases with temperature. Such systems, the so-called Kondo insulators, are of great theoretical and experimental interest. As of now, only a few such systems have been reported—some of the Ce-based mixed-valent, gap-forming compounds being $Ce_3Bi_4Pt_3$,[3] CeNiSn,[4] and CeRhSb.[5]

The compound CeRhSb forms in the orthorhombic ϵ-TiNiSi type structure. Earlier observations[5,6] of a lattice volume anomaly and a broad shallow maximum in the otherwise weakly temperature dependent magnetic susceptibility place this material in the class of mixed valent cerium based compounds. Its electrical resistivity is similar to that of

metallic systems at 300 K and decreases with decreasing temperature between 300 and ~8 K. However, the most interesting feature in resistivity occurs between 2 and 8 K, where it rises suddenly. (The temperature where the resistivity minimum occurs is 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. The resistivity, ρ, largely follows the behavior $\rho = \rho_0 \exp(-\Delta/k_B T)$ in the temperature interval 2–8 K from which the energy gap, Δ, is estimated to be about 4 K.[7] Thermoelectric power measurements on CeRhSb (Ref. 8) reveal a broad maximum at ~10 K, below which there is a sharp drop down to low temperatures. Hall effect measurements also show a large positive upturn below 10 K.[9] All of these results reveal a sharp decrease in carrier concentration below 10 K, which is consistent with the above interpretation of opening of a gap. The heat capacity of CeRhSb in a zero magnetic field was earlier reported in Refs. 10 and 11. The study of the influence of 14 T magnetic field on a low temperature ($T<8$ K) heat capacity of CeRhSb (Ref. 10) was inconclusive.

In order to further understand the nature of the ground state of CeRhSb, we have carried out heat capacity measurements on this compound and its La analog in various applied fields from 0 to 9.85 T in the temperature range of 1.8 to 30 K. The results of this study are presented below.

EXPERIMENTAL DETAILS

The samples of CeRhSb and LaRhSb were prepared by melting together stoichiometric amounts of the constituent elements in an arc furnace under purified argon. High purity (99.9+ wt. %) Ce and La metals were obtained from the Materials Preparation Center, Ames Laboratory. The Rh and Sb metals were purchased from commercial sources and had a stated purity of better than 99.9 wt. %. The alloy ingots were melted several times to ensure proper homogeneity and then were wrapped in tantalum foils for annealing in vacuum at 950 °C for one week. X-ray diffraction studies showed that, within a 5% resolution, the samples were single phase materials crystallizing in the orthorhombic ε-TiNiSi structure (space group *Pnma*). Metallographic examination also revealed the single phase nature of the samples with an upper limit for any extraneous phase of 1%. The lattice parameters obtained from a least squares fit of the observed 2θ values are (within an error limit of ± 0.005 Å):

LaRhSb: $a = 7.541$ Å, $b = 4.658$ Å, $c = 7.924$ Å,

CeRhSb: $a = 7.420$ Å, $b = 4.619$ Å, $c = 7.859$ Å.

The samples were further characterized by magnetic susceptibility measurements using a SQUID (superconducting quantum interference device) magnetometer and by the four probe electrical resistivity measurements. Heat capacity measurements were carried out in an adiabatic heat pulse calorimeter in the temperature range of 1.8 to 30 K both in zero field as well as in the presence of various applied fields ranging up to 9.85 T.[12] Magnetoresistance measurements were made in applied fields up to 5.5 T with the field applied parallel to the direction of the current.

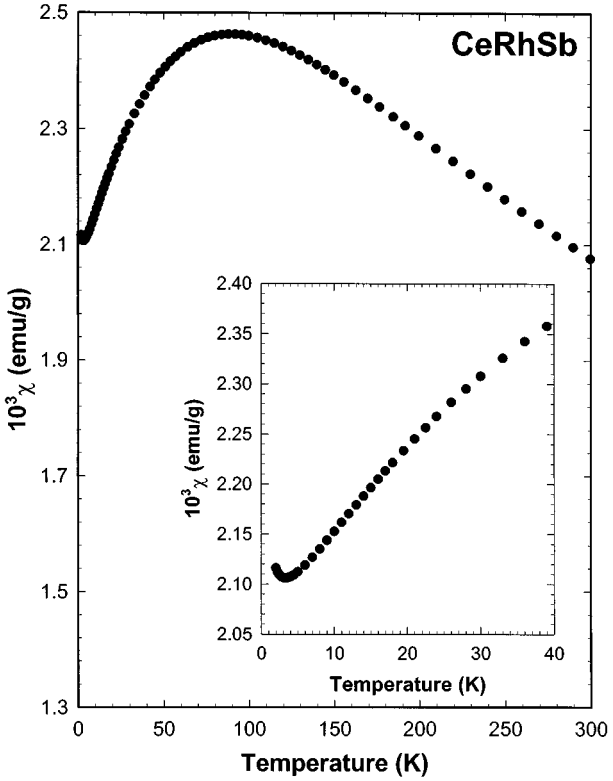

FIG. 1. Plot of the magnetic susceptibility, χ, vs temperature. The inset shows the magnetic susceptibility at low temperatures.

RESULTS AND DISCUSSION

Figure 1 shows the plot of magnetic susceptibility as a function of temperature on the present sample prepared using Ames Laboratory (AL) high purity cerium. The general features of the susceptibility are the same as reported earlier,[6] namely a broad maximum in the susceptibility, at ~90 K characteristic of mixed-valent Ce-based compounds and a rise at low temperatures (~3 K, inset Fig. 1.) In the present sample, however, the low temperature rise is less pronounced than for the earlier sample.[5] The temperature dependence of resistivity of the AL sample is shown in Fig. 2. The features are again similar to those reported earlier.[5] There is a broad maximum in the resistivity at ~150 K followed by a minimum at ~8 K and a sharp rise at low temperatures (see inset Fig. 2). Below 8 K, resistivity largely follows the activated behavior mentioned earlier in the Introduction, from which the energy gap, Δ, is obtained and calculated to be 4 K. However, there are slight deviations from the activated behavior suggesting the presence of a residual density of states in the gap and/or the anisotropic nature of the gap, i.e., the density of states at the Fermi level is not zero as in an ideal insulator. Hence the gap is not a true gap but is a pseudogap as described above. This observation is corroborated by heat capacity measurements, as will be described below.

Figure 3 shows the plot of heat capacity, C, vs temperature, T, for CeRhSb and LaRhSb in the temperature range 1.8–20 K. A linear least squares fit of the LaRhSb heat capacity data in the form of C/T vs T^2 plot for $T^2 \leqslant 50$ K^2(T$\leqslant$7K) gives an electronic specific heat constant, γ, of 7.2 ± 0.3mJ/mol K^2 and a Debye temperature, θ_D, of

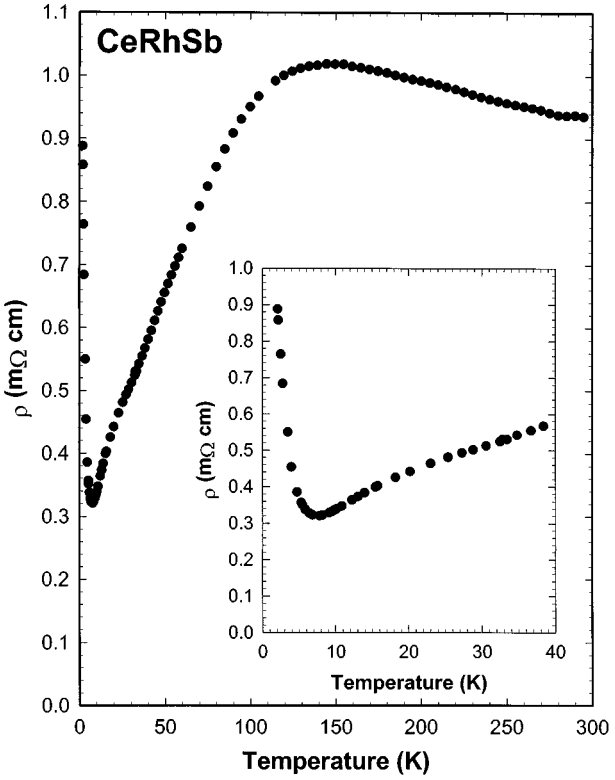

FIG. 2. Plot of the resistivity, ρ, vs temperature. The inset shows the resistivity at low temperatures.

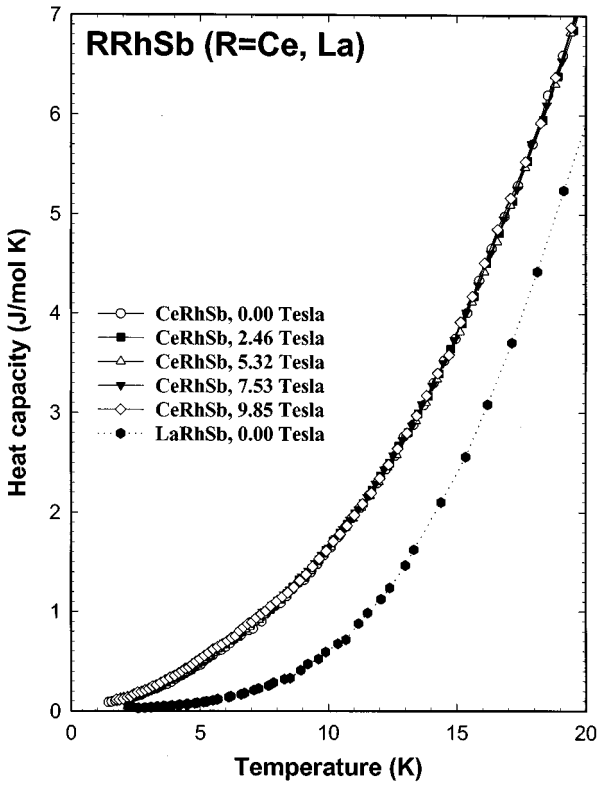

FIG. 3. Plot of heat capacity, C, vs T for CeRhSb in various magnetic fields, and for LaRhSb at zero magnetic field.

240 ± 9K. The heat capacity of CeRhSb in various applied fields is also presented in Fig. 3. It is observed that in all fields, the C vs T curves for CeRhSb vary smoothly from ~ 1.5 to 20 K, with no anomalies evident, unlike the resistivity (Fig. 2) and magnetic susceptibility (Fig. 1) results.

We will first discuss the zero field heat capacity results. The magnetic contribution to the heat capacity, ΔC, for CeRhSb is obtained by subtracting the lattice contribution, which is approximated by the heat capacity of the isostructural, nonmagnetic analog LaRhSb. A plot of $\Delta C/T$ vs T [Fig. 4(a)] shows a broad maximum at 10 K. Such a maximum in the heat capacity has been observed in other nonmagnetic Kondo lattice systems at low temperatures, like $CeAl_3$, and has been attributed to the effect of coherence. (This feature is in striking contrast to the single ion Kondo effect, where no such maximum is observed.) Both above and below this temperature, $\Delta C/T$ decreases with temperature. Thus the coherence temperature in this compound should correspond to about 10 K. Below $T = 10$ K, in the gapped state, $\Delta C/T$ shows a nearly linear variation with T [Fig. 4(a)]. This is consistent with the prediction that the gap develops as a result of the mixed-valent nature of the lattice, splitting the Kondo resonance into two peaks with a dip in between, showing a clear minimum with decrease in temperature. Thus the density of states varies linearly with temperature so that the heat capacity also shows a linear behavior from ~ 2 to ~ 7 K at all fields [Fig. 4(a)]. The nonactivating behavior of $\Delta C/T$ is consistent with the slight deviation from activated behavior seen in the resistivity suggesting some residual density of states or anisotropy in the gap. On extrapolating to 0 K, the plot of $\Delta C/T$ vs T [Fig. 4(a)] gives an intercept (electronic specific heat coefficient, γ) of 30 mJ/mol K^2, which is about four times larger than that of LaRhSb implying an enhanced value of the density of states at the Fermi level. The nonzero value of γ probably implies that the Fermi level is not in the gap. Above 10 K also $\Delta C/T$ is quite large (ranging from 75 to 105 mJ/mole K^2), which is understandable, since the compound is in the mixed-valent state, so that the density of states is large.

We now discuss the effect of magnetic field on the heat capacity of CeRhSb. As seen from Figs. 4(a) and 4(b), the maximum in the $\Delta C/T$ vs T (~ 10 K for the zero field curve) curve is found to shift towards lower temperatures with an increase in the applied field up to $H = 7.53$ T and then it starts to decrease back towards its $H = 0$ T value. In order to understand the observed behavior, two temperature regimes have to be considered—one below 10 K—where the compound is in the Kondo insulator regime and the second above 10 K where it is in a mixed-valent state. In the mixed-valent state, the density of states, N_E, at the Fermi level is large. As in the resonance level model of Schotte and Schotte,[9] the density of states can be assumed to be of the form $N_E = \Gamma[\pi(E^2 + \Gamma_0^2)]$, where $\Gamma_0 = k_B T_K$ is the peak width. The magnetic field broadens the peak, which is evident in Fig. 4(b), i.e., compare the solid line ($H = 0$ T data) with the dashed-dotted line ($H = 7.53$ T data), and the field dependent width, Γ, is given by $\Gamma^2 = \Gamma_0^2 + \mu_B^2 B^2$. The compound CeRhSb being a mixed-valent compound, is a high T_K (~ 100 K) system, so that the applied fields up to 9.85 T are negligible compared to Γ_0. An estimate of the change in the electronic density of states due to an applied field can be

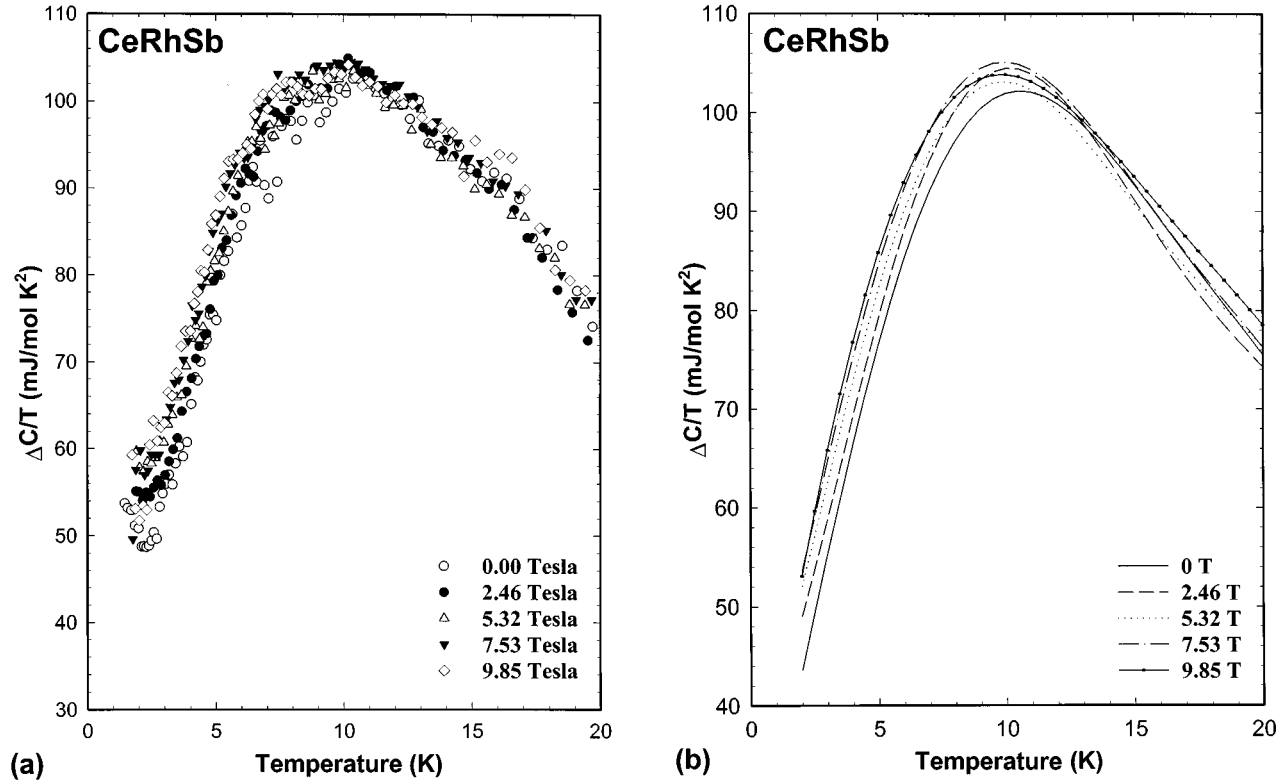

FIG. 4. The difference $\Delta C/T = C_{\mathrm{CeRhSb}}/T - C_{\mathrm{LaRhSb}}/T$ as function of temperature and magnetic field shown as the raw experimental data (a) and as smoothed curves for clarity (b). Each smoothed curve represents the actual experimental data fitted using a sixth order polynomial with accuracy better than 1.5–1.8 mJ/mol K^2.

obtained by assuming a T_K of about 100 K when $\Gamma_0 = 100k_B$. In a field of 10 T, $\Gamma^2 = (10^4 + 50)k_B^2$. Thus the effect of the applied field is negligibly small ($<1\%$ change) and hardly changes the density of states.

Below 10 K, it is expected that the temperature at which the coherence sets in (the position of the maximum in the $\Delta C/T$ vs T curve) should be shifted to lower values with increasing in applied field and for a critical value of field, $H_{\mathrm{coh}}(=k_B T_{\mathrm{coh}}/\mu_B)$, no maximum should be observed. Our measurements clearly show the shift of the linear portion of $\Delta C/T$ vs T line below the peak to lower temperatures with an increase in applied field: compare the solid line in Fig. 4(b) ($H=0$ T) with the solid line with dots ($H=9.85$ T). The limited data reported by Andraka[10] at 0 and 14 T are consistent with our results, especially below 5 K. The actual peak, however, shifts from 10.5 K at $H=0$ T to 9.5 K at $H=5.32$ T and then increases to 10.2 K at $H=9.85$ T Assuming $T_{\mathrm{coh}}=10$ K as obtained from the position of the maximum, H_{coh} is estimated to be about 13.5 T. The applied fields up to 9.85 T are not high enough to suppress the gap formation, and hence the maximum. Gap formation continues to be observed though over smaller temperature regimes with increasing field. It would be interesting to carry out high field heat capacity measurements (~ 15 T or more) using the same alloy to look for gap suppression in this compound. The γ value is found to increase from a value of 30 mJ/mol K^2 in zero field to 35.5 at $H=5.32$ T and then fall off to a value of 33 mJ/mol K^2 in a field of 9.85 T, showing the increase in the density of states in the gap due to field.

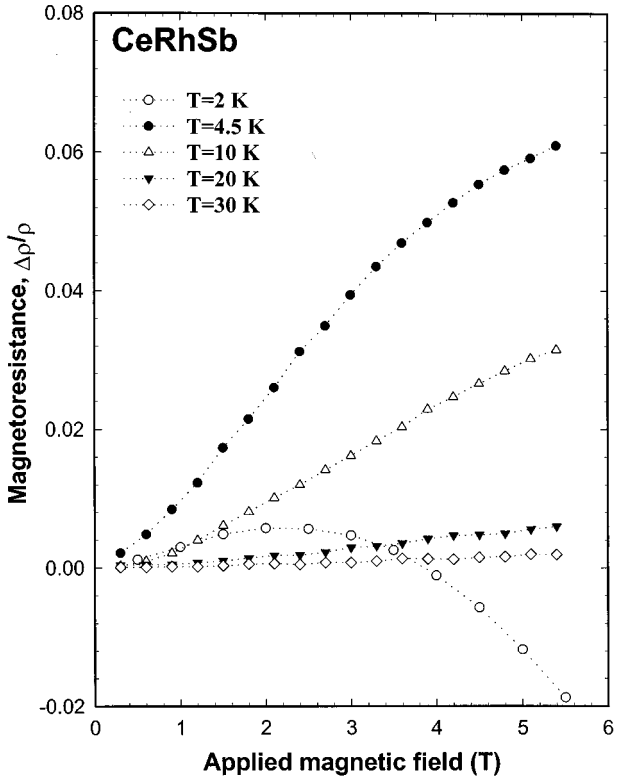

FIG. 5. Plot of magnetoresistance, $\Delta\rho/\rho$, for CeRhSb at various temperatures.

The results of magnetoresistance measurements on CeRhSb at various temperatures are shown in Fig. 5 as a plot of $\Delta\rho/\rho$ vs field at several temperatures. At 2 K, a small positive magnetoresistance is observed for small fields up to 3.5 T. This is due to the coherent state of the lattice. A sign change is observed at around 3.5 T (the magnetoresistance becomes negative) indicating the disruption of coherence (and hence the gap). No such sign change in magnetoresistance is observed at the higher temperatures. The magnetoresistance is positive for all temperatures 4.5 K and above. Furthermore, the percentage of magnetoresistance at 5.5 T (highest available field in our measurements) is largest at 4.5 K and decreases with increase in temperature. The measured magnetoresistance is about 6% at 4.5 K, 3% at 10 K, 0.5% at 20 K, and negligible at 30 K. Thus at 5.5 T, both above and below 4.5 K, the magnetoresistance decreases with temperature. Since magnetoresistance measurements also are sensitive to the density of states at the Fermi level, it is quite clear that these results are consistent with the observed heat capacity behavior which also shows a maximum, but the temperatures of the two maxima are quite different: $\sim$4.5 and 10 K.

The influence of the applied magnetic field on CeRhSb indicates that a field of 9.85 T is not strong enough to suppress the gap. This may be contrasted with the situation in the isostructural Kondo insulator CeNiSn,[13–15] where studies on single crystal have shown suppression of the gap with the application of magnetic field along certain crystallographic directions which result in large γ values. It was observed that in a field of 12 T, the value of C/T is strongly enhanced for H parallel to a direction and is almost unchanged for H parallel to c. The magnetoresistance in CeNiSn also showed a strong field dependence along the a direction.

CONCLUSION

In this paper we have presented an extensive set of heat capacity measurements over a wide temperature range as a function of magnetic fields up to 10 T, plus the magnetoresistance (up to 5 T) and the low field magnetic susceptibility on a single, well characterized sample of CeRhSb. As a result we find that the magnetic contribution to the heat capacity, ΔC, shows a maximum at around 10 K in zero field. This maximum is due to the coherence effect in the lattice which also leads to gap formation in this compound. Both above and below 10 K, $\Delta C/T$ decreases with temperature. Below 10 K, in the gapped state, $\Delta C/T$ decreases linearly with decreasing temperature due to linear decrease in the density of states with temperature. The electronic specific heat coefficient γ in the gapped state ($\Delta C/T$ extrapolated to $T\rightarrow 0$ K) increases by 3 to 4 mJ/mol K^2 on application of a 5.32 T field or greater. Magnetoresistance measurements show a positive behavior at temperatures above 4.5 K. It is maximum at 4.5 K (6%) in a 5.5 T field. At 2 K the magnetoresistance is negative in high fields above 3.5 T due to disruption of coherence and hence reduction in the gap.

ACKNOWLEDGMENTS

The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the Office of Basic Energy Sciences, Division of Material Sciences.

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