

Magnetic-susceptibility and heat-capacity measurements on PrRhSb

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Magnetic-susceptibility (ac and dc) and heat-capacity measurements have been carried out on the compound PrRhSb. These measurements reveal two magnetic transitions in this compound— one at about 18 K and the other around 6 K. In the dc susceptibility the 18-K transition is evident as the temperature below which a magnetic correlation sets in and the susceptibility is found to be field dependent. The lower transition manifests as a peak in the susceptibility of zero-field-cooled samples which were measured in low applied fields. The electronic-specific-heat coefficient, γ , is found to be 33 mJ/mol K² between 40 and 70 K after correcting for the lattice contribution taken to be the same as in its La analog. The γ value is fairly large for a Pr compound and may be indicative of moderately heavy quasiparticles. A Kondo-type interaction of the Pr 4*f* electrons with the conduction electrons may be responsible for high-magnetic-ordering temperatures and the moderately large γ value in this compound.

I. INTRODUCTION

In the compounds containing lanthanides, the 4*f* electron of the latter can be mostly treated as localized, which interact with each other by an indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction involving conduction electrons. In such cases, the low-temperature magnetic properties are determined by the crystalline electric fields and exchange interaction with neighboring ions. Some of the lanthanides such as Ce, Sm, Eu, Yb, and Tm often exhibit valence instability caused by the hybridization of their 4*f* electrons with the conduction electrons. Compounds containing these lanthanides often show mixed-valent (valence fluctuation or intermediate valence) behavior. This is characterized by the loss of local moment, an enhanced Pauli susceptibility, and an enhanced electron specific-heat coefficient γ . The phenomenon of heavy-fermion behavior is often observed in Ce- and U-based compounds, and to a smaller extent, in Yb-based compounds. The lanthanide (and U) ions in these compounds exhibit nearly integral valent states, particularly, at high temperatures. The 4*f* (5*f*) electrons in these compounds may be considered as nearly localized with weak hybridization with the conduction electrons. The local-moment character is retained, which manifests in a temperature variation of the susceptibility, which is often of Curie-Weiss type or is influenced by the crystalline electric field. At low temperatures, the *f* electrons may form a many-body ground state characterized by even larger values of γ and susceptibility than those in mixed-valent systems. The ground state may also be nonmagnetic as in CeAl₃ (Andres, Graebner, and Ott¹) or superconducting as in CeCu₂Si₂ (Steglich *et al.*²). The observation of large effective masses of the quasiparticles and the unusual properties these systems exhibit has created a great deal of interest in these systems.

In this paper we report the results of various studies on

the ternary intermetallic compound, PrRhSb. Heat capacity and magnetic measurements show that this compound is ordered magnetically with a rather high ordering temperature of about 18 K. In fact, it shows another magnetic transition at about 6 K. Furthermore, well above 20 K the electronic specific-heat coefficient is also large—33 mJ/mol K²—which may place this compound in the realm of low effective-mass heavy-fermion systems. The compound PrRhSb belongs to the family of equiatomic ternary intermetallic compounds of the type *RTX* where *R* is a rare-earth metal, *T* is a transition metal such as Pd, Pt, Cu, Ag, Au, and Ni, etc., and *X* is an *sp* element such as Sn, Sb, Al, Ga, Bi, etc. These compounds form in a variety of structural types and show a range of interesting properties such as mixed-valent behavior in several Ce- and some Yb-based compounds,^{3,4} gap formation in the electronic density of states in CeNiSn (Ref. 5) and CeRhSb (Ref. 6), ferromagnetism in Ce-based compounds in the possible presence of Kondo-type interactions,⁷ etc. The earlier investigated RRhSb compounds of this family with *R*=La and Ce have been found to show rather interesting behavior. LaRhSb is superconducting with a T_c of about 2.1 K,⁸ while CeRhSb is a mixed-valent system, which exhibits semiconducting and/or insulating behavior at low temperatures,⁶ and now the present studies suggest PrRhSb to be a magnetically ordered Pr-based system with a moderately large electronic specific-heat coefficient.

II. EXPERIMENTAL PROCEDURES

The samples of PrRhSb and its nonmagnetic analog, LaRhSb, were prepared by arc melting the appropriate amounts of constituent elements. The La and Pr used were of high purity prepared by the Materials Preparation Center of the Ames Laboratory. The impurity levels in the La and Pr are given in Table I. Although the hy-

TABLE I. Impurity content of the lanthanum and praseodymium starting materials. The concentrations are given in parts per million (ppm) atomic.

Impurities ^a	Starting materials	
	Lanthanum	Praseodymium
H	1650	697
C	34	47
N	128	151
O	190	79
F	80	<22
Si	1.8	10
Cl	1.0	10
Fe	7.6	9.8
Ce	0.4	6
Ta	1.5	29
Pt	<0.2	<10

^aImpurities not listed are present at a concentration of less than 5 ppm atomic.

drogen concentrations are fairly high, the hydrogen is lost by evaporation during the process of making the compounds because of its high vapor pressure. The Rh and Sb were commercially obtained and had a stated purity of at least 99.99 wt. %. The alloy buttons were melted several times to obtain homogeneous mixing. Weight losses during melting were small and are attributed to the volatile nature of Sb metal. Starting from the nominal 1:1:1 stoichiometry, the final composition of the samples obtained is PrRhSb_{0.952} and LaRhSb_{0.976}. These will be referred to as PrRhSb and LaRhSb, respectively. The alloy buttons were wrapped in tantalum foils and annealed in vacuum at 950 °C for 2 weeks. The dc magnetic measurements were carried out using a commercial (Quantum Design) superconducting quantum interference device (SQUID) magnetometer in the temperature range of 2–300 K and in applied fields up to 5.5 T. The ac susceptibility measurements were made on a commercial ac susceptometer (Lake Shore) in the low-temperature range of 4–25 K. A dc bias field could also be applied in these measurements. The heat-capacity measurements were performed in an adiabatic calorimeter⁹ using a standard heat-pulse technique with or without the application of an applied magnetic field.

III. RESULTS AND DISCUSSION

The compounds LaRhSb and PrRhSb are isostructural with CeRhSb and NdRhSb and crystallize in the orthorhombic ϵ -TiNiSi (space group $Pnma$) type structure in which all the atoms occupy well-defined crystallographic sites. Both metallographic and x-ray-diffraction studies reveal that the samples are single-phase materials; the former suggests that there is less than 1% second phase present in the PrRhSb sample. Rietveld refinement of the powder x-ray-diffraction patterns of PrRhSb yield lattice parameters $a = 7.3811 \text{ \AA}$, $b = 4.6037 \text{ \AA}$, and $c = 7.8597 \text{ \AA}$ and give no evidence of any significant mixing between atoms at various crystallographic lattice sites. However, due to a slight deviation from 1:1:1 stoichiometry, a small number of vacancies and/or intermixing is possible. The

results of magnetic and heat-capacity measurements are briefly described below.

A. ac susceptibility measurements

The ac magnetic susceptibility behavior of PrRhSb was studied at various frequencies and in the presence of various dc fields. The ac field was 1.25 Oe. The results are largely independent of the frequency and are shown in Figs. 1 and 2. Figure 1 shows the plot of χ_{ac} as a function of temperature at six different frequencies in zero dc applied field. Two distinct peaks are seen in χ_{ac} —one at about 8 K and the other around 15 K, indicating the presence of two (magnetic) transitions. In addition, there is a shoulder on the high-temperature side of the 8-K peak. Application of a dc magnetic field modifies the response. Figure 2 shows the plot of χ_{ac} vs temperature in various applied fields at a frequency of 1000 Hz. The results at other frequencies are identical. It is noted that application of even a small dc field tends to broaden the transitions with a slight shift and eventually suppresses the peaks in χ_{ac} to the extent that in a 2-kOe dc field, χ_{ac} shows very weak or no features at the temperatures where the peaks are observed in zero field.

B. dc magnetization

Figures 3(a) and 3(b) show the low-temperature behavior of the dc susceptibility χ_{dc} in various applied fields. χ_{dc} shows a pronounced field dependence below a temperature of about 18 K, suggesting the onset of magnetic correlations. This temperature of 18 K is close to the higher of the two transitions (15 K) seen in χ_{ac} . When the sample is zero-field cooled (ZFC) and the magnetization measured on warming up, the susceptibility shows a peak at about 7 K in the low applied field, e.g., 50 Oe [Fig. 3(a)]. This peak progressively broadens and eventually disappears as the measuring field is increased. This is consistent with the heat-capacity measurements.

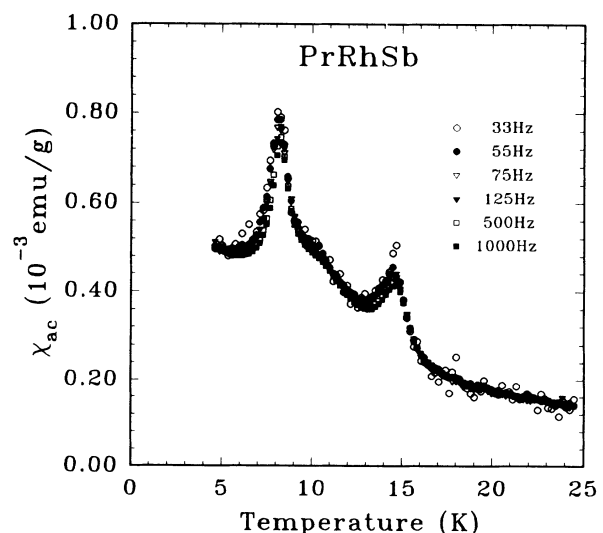


FIG. 1. Real part of ac susceptibility, χ_{ac} vs temperature for PrRhSb at different frequencies. The ac field was 1.25 Oe.

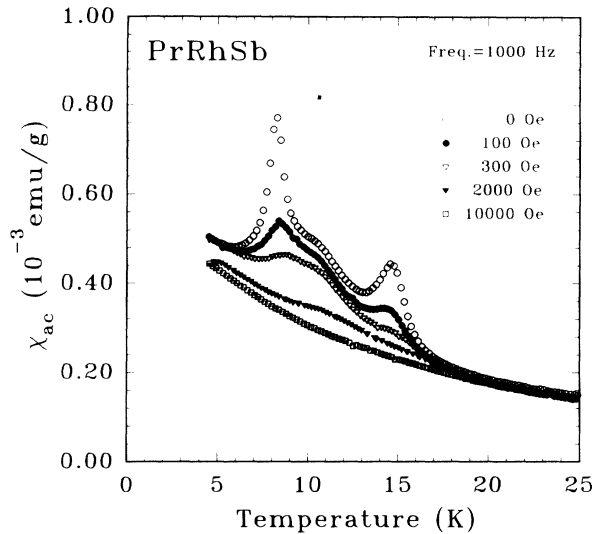


FIG. 2. Effect of dc magnetic field on χ_{ac} . The frequency is 1000 Hz and ac field is 1.25 Oe. The results for other frequencies are identical.

When the sample is cooled in applied fields of varying magnitudes ranging from 50 to 1 kOe, the low-temperature (7-K) peak in the susceptibility disappears even when the measurement field is only 100 Oe [Fig. 3(b)]. The magnetization below 18 K also shows history effects and depends on whether the sample is cooled in zero applied field or in the presence of a field.

Figure 4 shows the magnetization-field (M - H) isotherms for PrRhSb at various temperatures. At 30 K, the M - H isotherm is a straight line as would be expected for a paramagnetic system (or an antiferromagnetic system with no metamagnetic or spin-flip transition). However, at lower temperatures and high fields, the M - H curve shows small deviation from linearity, which could either be due to the usual saturation effect under the conditions of high fields and low temperatures or to a small ferromagnetic component, which could be intrinsic to PrRhSb or due to the second phase present in the sample (estimated to be about 1%). There is no hysteresis in the M - H curves. Overall the magnetization behavior suggests antiferromagnetic ordering of the Pr moments with the possibility of a small ferromagnetic or spin-glass-type component.

In the paramagnetic state between 30 and 300 K, the susceptibility of PrRhSb can be fitted to a Curie-Weiss law (Fig. 5) with effective paramagnetic moment $p_{\text{eff}} = 3.50\mu_B$ and the paramagnetic Curie temperature $\Theta_p = -1.3$ K. The p_{eff} value is close to that of the free Pr^{3+} ion. The magnitude of Θ_p is too small to make any comparison with the type of magnetic ordering. The observation of Curie-Weiss behavior may suggest that the crystalline electric-field effects are small. However, these materials are known to be highly anisotropic, and the powder average susceptibility may not be a true indicator of the presence or the absence of such effects. Neutron-diffraction studies are needed to clarify this issue. At low temperatures and moderately high fields, the susceptibili-

ty continues to rise with decreasing temperatures even below the lowest ordering temperatures [Fig. 3(a)]. This may be due to the weak antiferromagnetic state, which is easily influenced by the applied field, resulting in a large and temperature-independent susceptibility. It is also possible that the slight off stoichiometry and consequent disorder leads to a weak spin-glass type of ordering, which is again influenced by the application of the magnetic field. A rise in the susceptibility below the Néel temperature of Pr moments has been also observed in $\text{PrBa}_2\text{Cu}_3\text{O}_7$, the origin of which is not yet understood; for instance, see Malik *et al.*¹⁰ and references therein.

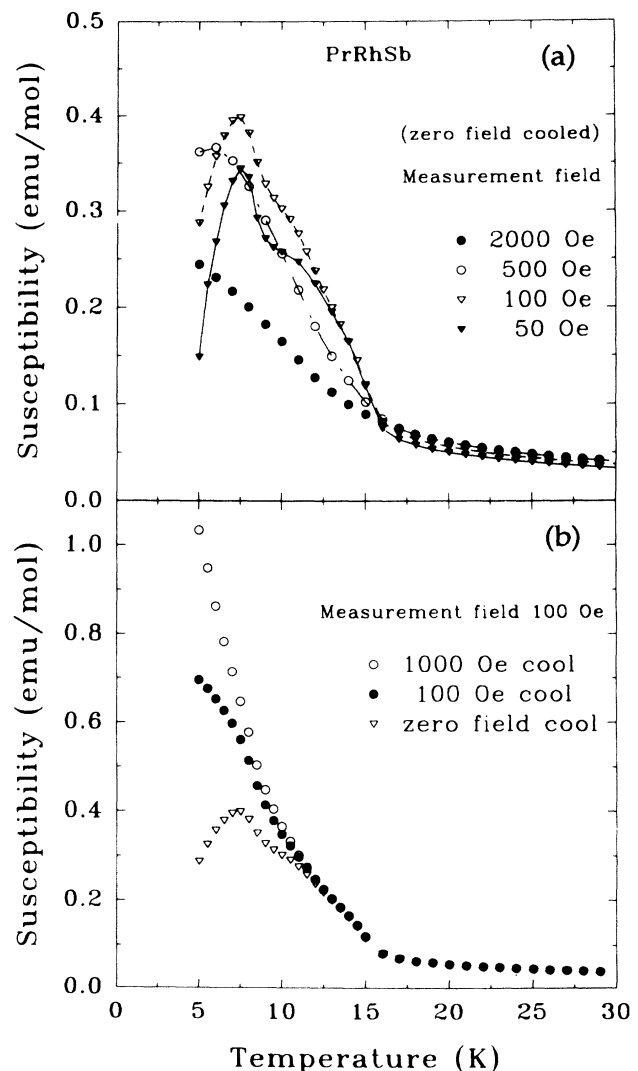


FIG. 3. Low-temperature dc magnetic susceptibility of PrRhSb as a function of temperature under a variety of conditions. (a) Zero-field-cooled runs in which the magnetization was measured on warming at four different applied fields. (b) Field-cooled samples in which the magnetization was measured on warming in an applied field of 100 Oe.

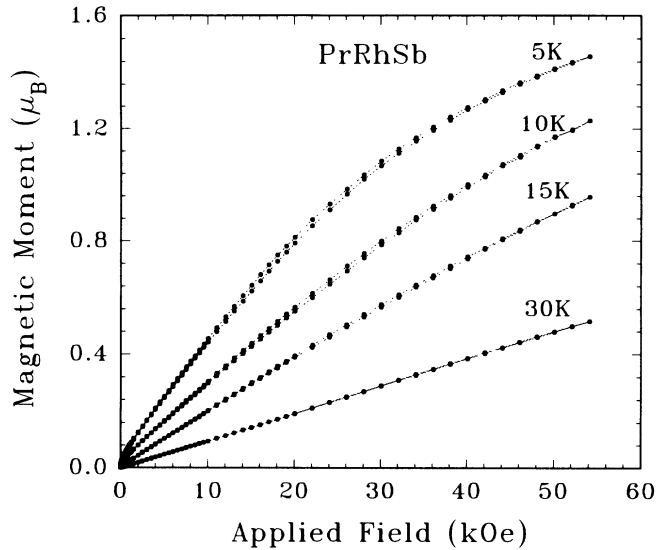


FIG. 4. Magnetization-field isotherms for PrRhSb at various temperatures.

C. Heat capacity

The results of heat-capacity measurements on this compound are shown in Fig. 6 as a plot of C/T vs T at different applied fields. Heat capacity shows two pronounced anomalies—one at about 18 K and the other around 6 K. From ac and dc magnetization studies it is inferred that both the transitions are magnetic in origin. The magnetic entropy, which is obtained by subtracting the heat capacity of LaRhSb from that of PrRhSb and assuming more-or-less ideal λ -type magnetic-ordering peaks for the two transitions, associated with the lower (6-K) heat-capacity peak is nearly the same as that associated with the higher (18-K) peak. This suggests that an equal number of spins take part in the ordering at two

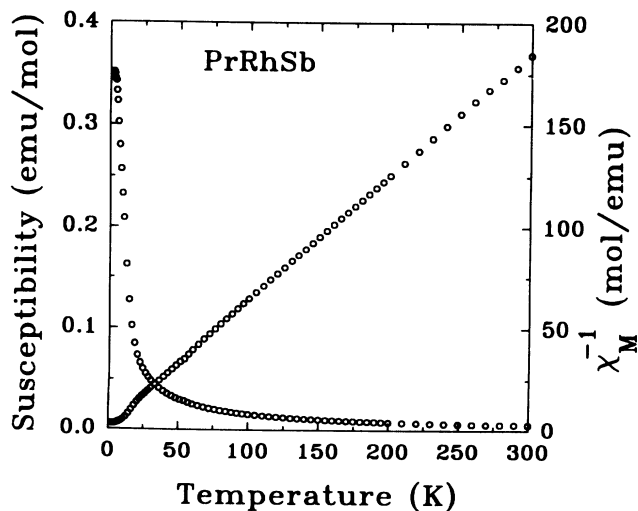


FIG. 5. Molar dc susceptibility χ_M and $1/\chi_M$ vs temperature for PrRhSb.

temperatures and that the lower ordering temperature is also magnetic in origin and cannot be due to the impurity effects. The total entropy up to 60 K is 70% of $R \ln(2J+1)$ and perhaps a small amount (15%) is tied up in spin fluctuations as is the case in some Gd compounds.¹¹

The field dependence of the heat capacity for the lower transition-temperature peak is about what one expects for a ferromagnetic substance, i.e., the height of the peak is lowered and the associated entropy is shifted to higher temperatures and actually enhances that of the upper peak. These results are consistent with χ_{ac} data. The dc magnetization measurements suggest that the lower transition has a weak antiferromagnetic component, which is overcome by the application of a small magnetic field. The fact that the magnetic field has little or no effect on the upper transition strongly supports our conclusion based on the magnetic data that the upper transition is due to the onset of antiferromagnetic ordering. However, there are features reminiscent of the spin glass or other complex type of ordering at both the transitions, and further work needs to be done to understand the magnetic and transport behavior of this compound.

The ϵ -TiNiSi structure of PrRhSb has only one type of Pr atoms, which form a zigzag chain along the a direction. The shortest Pr-Pr distance is about 3.77 Å in the ac plane. The Pr atoms in the adjacent planes are separated by a distance of about 3.9 Å. Though Pr ions are presumed to interact with each other via the indirect RKKY interaction involving conduction electrons, it is possible that there is also some direct superexchange interaction. Thus two exchange interactions between the Pr ions may be operative—the interplane and the intraplane. It is possible that the magnetic order first sets in the planes, and, on further lowering the temperature, the interplane exchange becomes important, leading to a second transition, which would then appear as a 2D-3D transition. If the signs of the two interactions are different, a competition between different types of magnetic orderings could set in leading to spin-glass-incommensurate magnetic ordering, which is strongly influenced by magnetic fields. In this picture, all the Pr ions are magnetically ordered, even at the higher transition temperature, and this may not be consistent with the observed entropy change, which occurs in two steps.

Alternatively, another possibility has been suggested by Mehta,¹² that the structure of PrRhSb is of a lower symmetry derived from that of the ϵ -TiNiSi type of structure, which results in two inequivalent Pr sites in equal proportion. This could lead to a natural explanation for the two observed magnetic transitions as due to the ordering of different types of Pr ions. Further work is necessary to understand the magnetic structure of this compound.

As remarked earlier, LaRhSb, the non-magnetic analog of PrRhSb, is found to be superconducting with a T_c of 2.1 K. From the C/T -vs- T data in various applied fields, the electronic specific-heat coefficient in this compound is found to be 7.7 ± 0.2 mJ/mol K² and the Debye temperature Θ_D is 252 ± 3 K.⁸ In the case of PrRhSb the magnetic contribution persists almost 20 K above the ordering

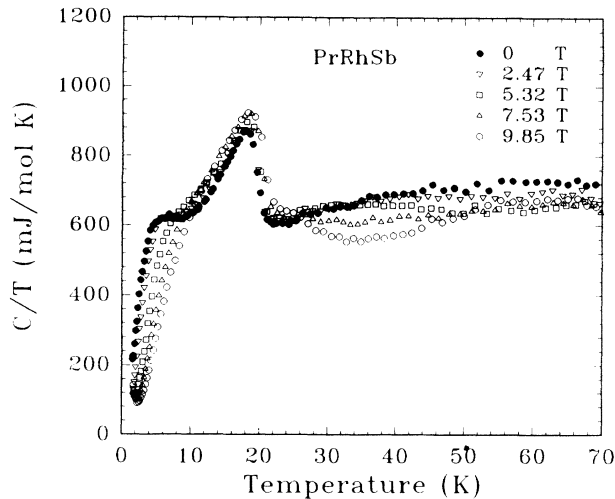


FIG. 6. C/T vs temperature (T) for PrRhSb in various applied fields showing the two peaks.

temperature. Thus, if one plots C/T vs T^2 immediately above T_N , a straight line is obtained with an intercept of about 500 mJ/mol K^2 . This, however, is not the true γ . On going well above T_N and after subtracting the lattice contribution (assuming it is the same as that of LaRhSb), one obtains a constant C/T value of about 25 mJ/mol K^2 (see Fig. 7). When the La electronic specific-heat constant is added to the constant C/T value, a value of 33 mJ/mol K^2 is obtained for γ for PrRhSb. Considering the scatter in the two sets of heat capacity data, and the subtraction of the LaRhSb results from the PrRhSb values, we estimate an error of $\pm 20 \text{ mJ/mol K}^2$ for this γ value. As noted above, the C/T -vs- T curve is essentially parallel to the T axis in the (40–70)-K temperature range, and it is hard to imagine a crystal-field scheme, which would yield a constant C/T value over such a large temperature region. Thus, it is believed that this γ value is intrinsic, and that PrRhSb may represent a possible Pr-based low effective-mass heavy-fermion system. The high magnetic-ordering temperature and the fairly large γ value would be consistent with some hybridization between the Pr $4f$ electrons and the conduction and/or the Rh $4d$ and Sb $5p$ electrons. The recent band-structure calculations on Pr metal by Temmerman, Szotek, and Winter¹³ show that the unoccupied $4f$ bands just above the Fermi level are strongly hybridized with the s ,

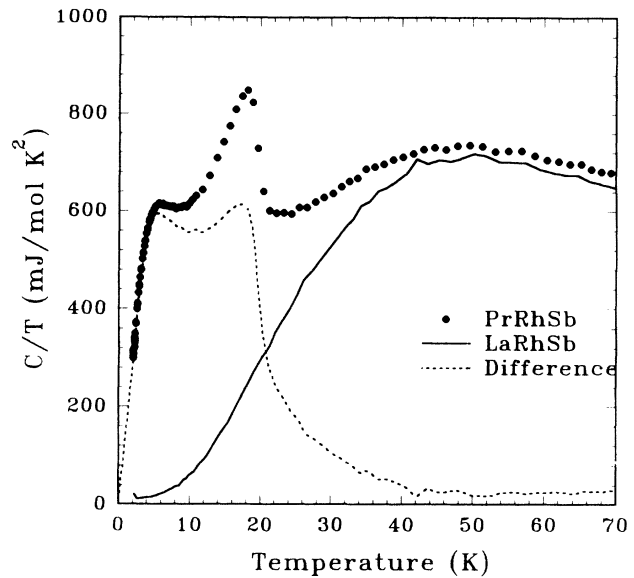


FIG. 7. C/T vs T for LaRhSb and PrRhSb and the difference between the two.

p , and d bands. Such a model might also be applicable to PrRhSb and could account for the observed behaviors noted above.

In conclusion, we have studied the magnetic and thermal behavior of PrRhSb. This compound seems to order magnetically and shows two magnetic transitions, the higher one at about 18 K and lower one at about 6 K. Above the higher ordering temperature an apparently large electronic specific-heat coefficient is observed. The present results on PrRhSb, the observation of superconducting in LaRhSb with T_c of 2.1 K, and the formation of a gap in the density of states of CeRhSb at low temperatures reveals that the magnetic, electronic, and transport properties of these RRhSb compounds are quite fascinating, and further studies are required on these systems.

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