Journal of Alloys and Compounds, *207/208* (1994) 237–240
JALCOM 3098

The low temperature behavior of some light lanthanide RRhSb and RPdSb compounds

S.K. Malik*, H. Takeya** and K.A. Gschneidner, Jr.***
Ames Laboratory and Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011 (USA)

Abstract

The low temperature heat capacity and magnetic susceptibilities of LaRhSb, LaPdSb, PrRhSb and PrPdSb have been examined. LaRhSb is a superconductor with a T_c of 2.1 K, while LaPdSb is normal down to 0.6 K. Both Pr compounds order magnetically: PrRhSb at 6 and 18 K, and PrPdSb at 10 K. The upper ordering temperature of PrRhSb is probably antiferromagnetic and the lower one may correspond to a spin glass state. Both Pr compounds have unusually large electronic specific heat constant values of 35 and 75 mJ mol^{-1} K^{-2} for PrRhSb and PrPdSb, respectively.

1. Introduction

During the last few years there has been a great deal of interest in the study of magnetic, electronic and transport properties of equiatomic ternary intermetallic compounds of the type RTX where R is a rare earth metal, T is a transition metal such as Ni, Cu, Pd, Ag, Pt and Au etc., and X is an sp element such as Al, Ga, Sn, Sb and Bi etc. (see, *e.g.* [1–3]). Several families of such compounds are known to form which crystallize in a variety of structure types. Studies on such systems offer the opportunity to examine the effect of structure, the transition and the sp elements on the physical properties of these compounds. This has led to the observation of interesting behaviors in several of these systems, such as mixed valent behavior in cerium [4] and ytterbium [5] based compounds, gap formation in the density of states in CeNiSn [6] and CeRhSb [7], ferromagnetism in cerium based compounds [6] in the possible presence of Kondo interaction, etc.

Recently, an unusual behavior was observed in CeRhSb [7]. In this compound, cerium is in a mixed valent state as inferred from lattice volume anomaly and susceptibility measurements. Its resistivity shows a sharp increase at low temperatures indicative of the opening of a gap in the density of states. Similarly, in the RPdSb series, CePdSb shows ferromagnetism [8] with a fairly high ordering temperature in the possible presence of Kondo type interactions. In the light of these observations, we decided to investigate the magnetic and transport properties of other members of this series, the light RPdSb compounds with R = La and Pr.

2. Experimental details

The RRhSb and RPdSb samples were prepared by arc melting of stoichiometric amounts of the rare earths, Rh, Pd and Sb elements. The high purity lanthanides were prepared by the Materials Preparation Center of the Ames Laboratory while Rh, Pd and Sb were obtained commercially and were claimed by the vendor to be 99.99% pure. The alloy buttons were melted several times to obtain homogeneous mixing. Weight losses were found to be negligible. The alloy buttons were wrapped in tantalum foils and annealed in a vacuum at 950 °C for 2 weeks. Metallographic investigations revealed that the samples are single phase materials with no evidence of impurity phases.

The heat capacity measurements were performed on an adiabatic calorimeter using a standard heat pulse technique with and without the application of a magnetic field. Details of the set up are described elsewhere [9]. Magnetic measurements were carried out using a commercial SQUID magnetometer (Quantum Design) and an ac susceptometer (Lake Shore) in the temperature range of 1.8–300 K and in applied fields of 5.5 T.

---

*Present address: Tata Institute of Fundamental Research, Bombay 400 005, India.

**Present address: National Research Institute for Metals, Sengen 1-2-1, Tsukuba, Ibaraki-ken 305, Japan.

***Author to whom correspondence should be addressed.

0925-8388/94/$07.00
SSDI 0925-8388(94)03098-H

3. Results and discussion

The RRhSb compounds crystallize in the orthorhombic ϵ-TiNiSi type structure while the RPdSb compounds form in the hexagonal $CaIn_2$ (or an ordered variant of this) type structure. The results of magnetic and heat capacity measurements on each of the compounds are described below.

3.1. LaRhSb

This compound is found to be superconducting with a T_c of 2.1 K. Its magnetic susceptibility is weakly paramagnetic in the normal state and shows a sharp change to diamagnetic state (Fig. 1) at about 2.1 K signaling the onset of the superconducting transition. This is confirmed by the heat capacity (C) measurements which show a peak in the C/T versus T^2 curve (Fig. 2) at about the same temperature where a transition from weakly paramagnetic to the diamagnetic state is seen. The magnitude of the jump in the heat capacity at T_c is in conformity with the BCS weak coupling limit and confirms the bulk nature of superconductivity. Application of a field of 0.5 T suppresses the heat capacity peak. The electronic specific heat coefficient γ is found to be 7.7 ± 0.2 mJ mol^{-1} K^{-2} and the Debye temperature θ_D is 252 ± 3 K. Detailed results are presented elsewhere [10].

3.2. LaPdSb

From susceptibility and heat capacity measurements it is found that this compound does not exhibit superconductivity down to 1.8 K. Recently, ac susceptibility measurements down to 0.6 K also show no transition to the superconducting state [11]. Its susceptibility is weakly diamagnetic and becomes paramagnetic at low temperatures; the latter effect could be due to the presence of trace amounts of paramagnetic impurities. From the plot of C/T versus T^2 (Fig. 2), the electronic specific heat coefficient is found to be 4.2 ± 0.1 mJ mol^{-1} K^{-2} and θ_D is 273 ± 3 K.

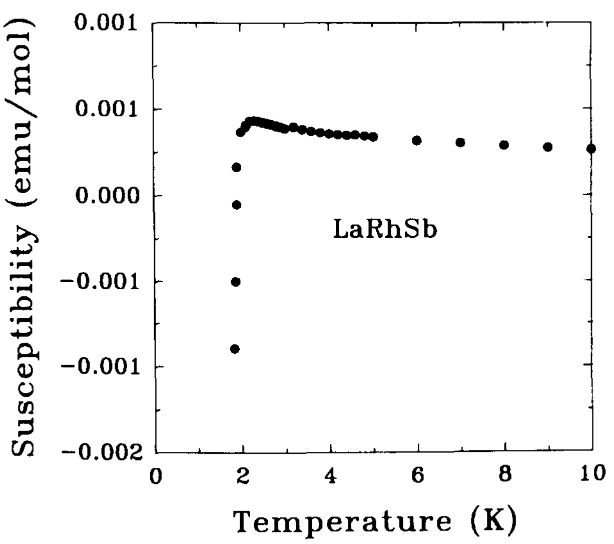

Fig. 1. Magnetic susceptibility versus temperature for LaRhSb showing the transition from normal to the superconducting state.

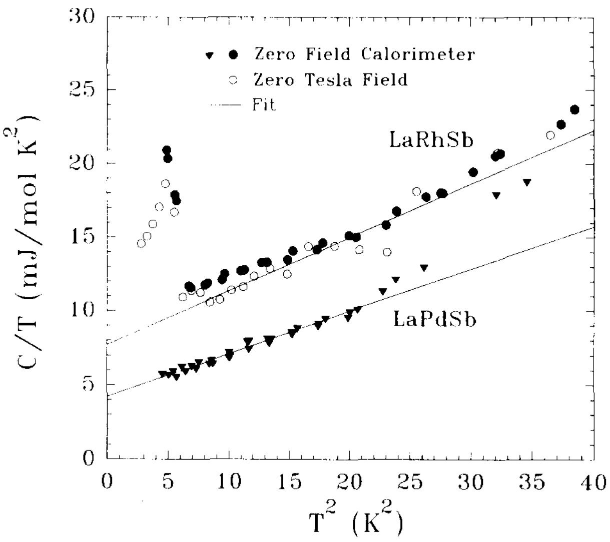

Fig. 2. C/T versus T^2 plots for LaRhSb and LaPdSb. The fitted line for LaPhSb includes data taken at two applied magnetic fields, which are not shown here, but are presented elsewhere [10].

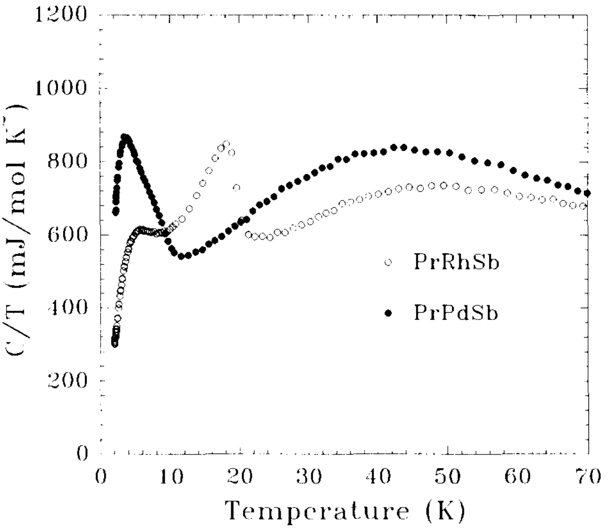

Fig. 3. C/T versus T for PrRhSb and PrPdSb.

3.3. PrRhSb

The zero field heat capacity measurements on this compound are shown in Fig. 3 as a plot of C/T versus T. Heat capacity shows two pronounced anomalies, one at about 18 K and the other around 6 K. Magnetization measurements confirm that the 18 K transition is magnetic in origin. The 6 K transition is difficult to observe in the magnetization data. Magnetic susceptibility (χ), in various applied fields ranging from 100 to 2000 Oe, does not show a peak around 18 K but instead deviates from Curie–Weiss behavior below this temperature. Furthermore, χ is found to be field dependent below 18 K (Fig. 4). The magnetization-field isotherms show a sharp rise at low fields and a small departure from linearity at high fields. Because of the difficulty in observing the lower transition by dc measurements, the ac susceptibility was measured and both magnetic ordering temperatures were clearly evident (Fig. 5). The magnetic behavior suggests a predominantly antiferromagnetic coupling of the Pr moments with a weak ferromagnetic component for the upper transition. The deviation of the dc susceptibility from linearity at high fields could also be due to the usual paramagnetic saturation in the presence of high magnetic fields at low temperatures.

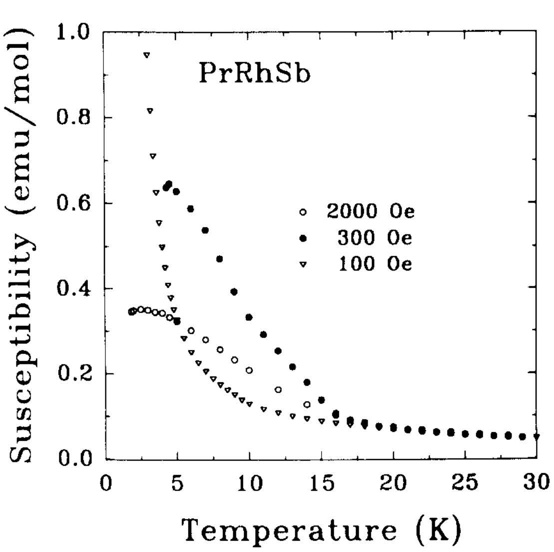

Fig. 4. Magnetic susceptibility of PrRhSb as a function of temperature in various applied fields showing the field dependence of susceptibility below 20 K.

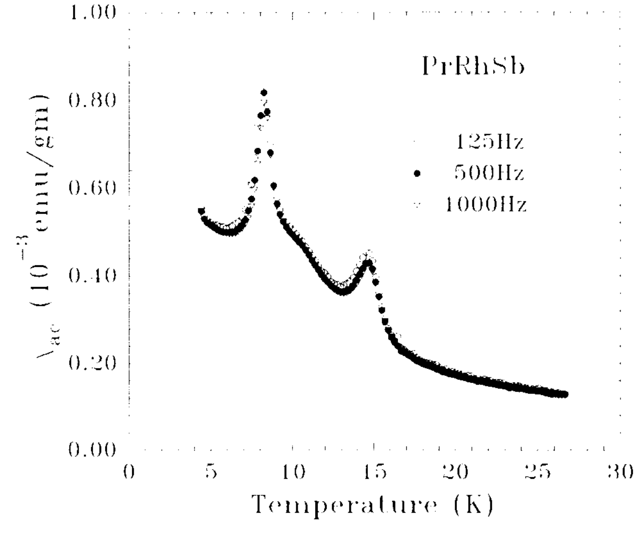

Fig. 5. The ac magnetic susceptibility of PrRhSb at low temperature.

The magnetic entropy associated with the lower (6 K) heat capacity peak is nearly the same as that associated with the higher (18 K) peak. From dc and ac susceptibilities, and the field dependent heat capacity measurements, it is conjectured that the lower transition may be due to a ferromagnetic ordering below 6 K, while the upper transition may be due to the onset of antiferromagnetic ordering. However, further work needs to be done to understand the magnetic and transport behavior of this compound. After subtracting the lattice contribution to the heat capacity, which is assumed to be the same as that in its La analog, LaRhSb, a residual, but constant C/T value was found from 40 to 70 K, which gives an electronic specific heat coefficient, γ, of 35 mJ mol^{-1} K^{-2}. Considering the scatter in the heat capacity data and the subtraction of the LaRhSb results from the PrRhSb values, we estimate an error of ± 20 mJ mol^{-1} K^{-2} for this γ value. It is believed that this γ value is intrinsic and is not associated with the Schottky anomaly due to crystal field effects, which if it exists must be much smaller than 30 K (see below). Furthermore, a Schottky anomaly does not have a linear temperature dependence, and thus it is difficult to see how this could lead to a linear temperature dependence above 40 K. (For Pr metal with a crystal field splitting of 23 K for the first excited state and an overall splitting of 246 K, there is a large Schottky heat capacity peak at 30 K, which is 1/2 times as large as the total heat capacity of PrRhSb at that temperature, and extends over the temperature range of 5–200 K [12].) The total magnetic entropy due to ordering is 12.9 J mol^{-1} Pr K^{-1}, which compares to the theoretical $R\ln(2J+1)$ value of 18.5 J mol^{-1} Pr K^{-1}. The magnetic entropy under the two peaks is about the same, indicating that an equal number of spins are involved in each transition.

In the paramagnetic state between 30 and 300 K, the susceptibility of PrRhSb can be fitted to a Curie–Weiss law with effective paramagnetic moment $\mu_{\text{eff}} = 3.50\ \mu_B$ and the paramagnetic Curie temperature $\theta_p = -1.3$ K. The observed value above 30 K is close to that of the free Pr^{3+} value. The value of θ_p is too small to make any meaningful comparison with the type of ordering observed.

3.4. PrPdSb

To some extent, the behavior of PrPdSb is similar to that of PrRhSb. A peak in the heat capacity was found at about 10 K (Fig. 3). That this corresponds to magnetic ordering is inferred from the field dependence of the susceptibility which starts at about 8 K. Again there is no obvious feature like a peak in the susceptibility at this temperature at least in the magnetic fields used in the present measurements. The paramagnetic susceptibility follows Curie–Weiss behavior above 10 K with $\mu_{\text{eff}} = 3.50\ \mu_B$ and $\theta_p = +0.5$ K.

The γ value in this compound is found to be even larger, namely 75 mJ mol^{-1} K^{-2}, than the 35 mJ mol^{-1} K^{-2} value of PrRhSb. However, in this case the C/T versus T curve is only parallel to the T axis from 30 to ~60 K and above 60 K, C/T begins to increase with increasing temperature suggesting possible contributions from other sources. When properly taken into account, this may lower the γ value. The magnetic entropy of the PrPdSb compound below 40 K is 12.2 J mol^{-1} Pr K^{-1} which is about two-thirds of the theoretical value of 18.5 J mol^{-1} Pr K^{-1}. Part of the missing magnetic entropy (~15% if Pr behaves like Gd) is tied up in spin fluctuations [13] while the rest may be involved in crystal field transitions (Schottky anomalies).

4. Conclusion

In conclusion, we have studied the magnetic and transport behavior of RTSb (R = La and Pr, and T = Rh and Pd). LaRhSb is found to be superconducting with T_c of 2.1 K while LaPdSb is a normal metallic system down to 0.6 K. Both PrRhSb and PrPdSb order magnetically with the former showing two magnetic transitions. In addition, both PrRhSb and PrPdSb show relatively large γ values suggesting a possible origin in terms of the hybridization of the Pr 4f electrons with conduction electrons and/or the 4d electrons of Rh and/or the sp electrons of Sb. This makes sense in view of the recent band structure calculations by Temmerman *et al.* [14] who find that the unoccupied 4f bands in Pr metal strongly hybridize with s, p and d bands, and the same thing could occur in these PrMSb compounds. Thus, the magnetic and transport properties of these Pr compounds appear very intriguing and warrant further studies.

Acknowledgment

The authors wish to thank Dr. S. Ramakrishnan, Tata Institute of Fundamental Research for his assistance in carrying out some aspects of the experimental work of this study. The Ames Laboratory is operated for the US 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.

References

1 W.H. Lee and R.N. Shelton, *Phys. Rev. B, 35* (1987) 5396.
2 S.K. Malik and D.T. Adroja, *J. Magn. Magn. Mater., 100* (1991) 126.
3 T. Fujita, T. Suzuki, S. Nishigori, T. Takabatake, H. Fujii and J. Sakurai, *J. Magn. Magn. Mater., 108* (1992) 35.
4 D.T. Adroja, S.K. Malik, B.D. Padalia and R. Vijayaraghavan, *Phys. Rev. B, 39* (1990) 4831.
5 D.T. Adroja, S.K. Malik, B.D. Padalia, S.N. Bhatia, R. Walia and R. Vijayaraghavan, *Phys. Rev. B, 42* (1990) 2700.
6 T. Takabatake, F. Teshima, H. Fujii, S. Nishigori, T. Suzuki, T. Fujita, Y. Yamaguchi, J. Sakurai and D. Jaccard, *Phys. Rev. B, 41* (1990) 9607.
7 S.K. Malik and D.T. Adroja, *Phys. Rev. B, 43* (1991) 6277.
8 S.K. Malik and D.T. Adroja, *Phys. Rev. B, 43* (1991) 6295.
9 K. Ikeda, K.A. Gschneidner, Jr., B.J. Beaudry and U. Atzmony, *Phys. Rev. B, 25* (1982) 4604.
10 S.K. Malik, H. Takeya and K.A. Gschneidner, Jr., *Phys. Rev. B, 47* (1993) 9858.
11 S. Ramakrishnan, Tata Institute of Fundamental Research, Bombay, India, private communication, May 1993.
12 B. Bleaney, *Proc. R. Soc. A, 276* (1963) 39.
13 M. Bouvier. P. Lethuillier and D. Schmitt, *Phys. Rev. B, 43* (1991) 13137.
14 W.M. Temmerman, Z. Szotek and H. Winter, *Phys. Rev. B, 47* (1993) 1184.