ELSEVIER

Journal of Alloys and Compounds 460 (2008) 26–30

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Magnetism in PrRhSn studied on a single crystal

M. Mihalik [a,b], H. Kitazawa [b], M. Diviš [a], V. Sechovský [a,*]

[a] *Charles University, Faculty of Mathematics and Physics, Department of Condensed Matter, Ke Karlovu 5, 121 16 Prague 2, Czech Republic*
[b] *National Institute for Material Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*

Received 18 May 2007; received in revised form 24 May 2007; accepted 25 May 2007
Available online 31 May 2007

Abstract

We have grown a single crystal of PrRhSn, analyzed the structure by X-ray diffraction methods and measured the specific heat, ac susceptibility, magnetization, and electrical resistivity as functions of temperature and magnetic field. Also we have calculated the electronic structure of this compound by *ab initio* methods. Ferromagnetism below $T_C = 2.9$ K characterized by strong uniaxial anisotropy (an anisotropy field ~65 T) has been confirmed. Pronounced crystal field (CF) effects were observed on the temperature dependences of the magnetic susceptibility, electrical resistivity and specific heat. The calculations revealed that besides the stable Pr magnetic moment owing to the localized 4f-electrons a small magnetic moment of at most $0.2\mu_B$ is induced at the Rh site (and $0.1\mu_B$ at the Sn site) due to the polarized Rh 4d-electron states (Sn 5p-states) hybridizing with the Pr 5d-electron states, i.e. the Rh and Sn moments play some role in the total balance of the magnetic moments in this compound. This result is in agreement with the experimentally determined saturated magnetic moment of PrRhSn, which is about $0.3\mu_B$ larger than the ordered moment value expected for the Pr^{3+} free ion.

Keywords: Intermetallics; Magnetically ordered materials; Anisotropy; Heat capacity; Magnetic measurements

1. Introduction

In recent years, there has been a great deal of interest paid to studies of the rare-earth (R) containing intermetallic compounds of the type RTX, where T is a d-metal and X is a p-metal. PrRhSn crystallizes in the hexagonal ZrNiAl-type crystal structure (space group $P\bar{6}2m$). The lattice parameters of PrRhSn are reported to be $a = 742.49(7)$ pm, $c = 415.05(5)$, $x_{Pr} = 0.41460(15)$ and $x_{Sn} = 0.75196(16)$ [1]. Routsi et al. [2] studied magnetic properties of PrRhSn polycrystals and reported absence of magnetic ordering above 4.2 K and the paramagnetic susceptibility obeying Curie–Weiss law for temperatures higher than 40 K with the parameters $\theta_p = 10$ K and $\mu_{eff} = 3.83\mu_B$. Łątka et al. [1] claimed, that the compound orders ferromagnetically at $T_C = 3(0)$ K and exhibits a hysteresis loop with a small coercive field of 2 mT. The same authors [1] presented very broad field distribution functions obtained at the Sn sites by ^{119}Sn Mössbauer spectroscopy, which were considered as an argument against the ferromagnetic ordering. The magnetization curve measured on a polycrystal does not saturate in fields up to 5 T, which was attributed to possible high magnetic anisotropy.

Since all the so far published, sometimes contradictory, results have been obtained only on polycrystalline samples we decided to grow a PrRhSn single crystal, which was then studied by measuring the specific heat, ac susceptibility, magnetization, and electrical resistivity as functions of temperature and external magnetic field oriented along the main crystallographic directions. Some preliminary data were reported in [3]. To understand experimental findings better, especially to study the role of the Rh and Sn atoms in the magnetism of PrRhSn, we performed first principles calculations of electronic structure focused on the magnetic ground state characteristics.

2. Sample preparation and experimental details

The single crystal of PrRhSn has been grown by a modified Czochralski pulling technique in a tri-arc furnace with purified argon atmosphere. The growth was performed using about 6 g of a melt consisting of the stoichiometric composition of the elemental constituents with the nominal purity: Pr-2N8, Rh-3N and Sn-3N. A tungsten rod was used as a seed. Using the random necking procedure and pulling speed between 6 and 10 mm/h we

* Corresponding author.
E-mail address: sech@mag.mff.cuni.cz (V. Sechovský).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.05.095

succeeded to grow a single crystalline ingot about 20 mm long with the maximum diameter of 3.5 mm.

The X-ray Laue analysis has confirmed good quality of the single-crystalline ingot. Part of the ingot was pulverized and used for an X-ray powder diffraction experiment to find out whether the compound is single phase and to determine the lattice parameters. The Rietveld analysis of the powder pattern confirmed that the sample contains only the PrRhSn phase (no trace of spurious phases was detected within the sensitivity of the method—3%) that crystallizes in the hexagonal ZrNiAl-type crystal structure with the lattice parameters $a = 741.5(3)$ pm, $c = 415.1(2)$ pm. These values are in a reasonable agreement with previously published data [1,2].

The reported measurements of the ac susceptibility, magnetization, specific heat and electrical resistivity were performed in the temperature range 2–300 K and in magnetic fields up to 9 T (except for the ac susceptibility) using a PPMS (Quantum Design) apparatus. The ac susceptibility was measured with the sampling ac field of the amplitude of 1 mT and the frequency of 1 kHz.

For the specific heat (of sample mass of 11.76 mg) measurements the fitting of the whole temperature response of a heat-pulse calorimeter technique [4] was applied. The resistivity was measured using a standard ac four-probe method. The samples for resistivity measurements were too small to allow reliable determination of the geometrical factor of the samples. Therefore, we present only relative data.

3. Results and discussion

The specific heat of PrRhSn as a function of temperature exhibits a sharp peak at 2.9 K (Fig. 1), which we associate with a magnetic ordering transition. Since the majority of available experimental data show evidences of ferromagnetism below 2.9 we denote this transition temperature as Curie temperature T_C. Just above T_C, there is a bump in the specific heat, which shifts to higher temperatures and broadens (Fig. 1) with applying a magnetic field along the c-axis. We attribute this feature to a Schottky contribution to the specific heat. In order to determine the magnetic contribution C_{mag} to the specific heat of PrRhSn we have grown a single crystal of a non-magnetic analogue LaRhSn, and measured the temperature dependence of the specific heat C_{LaRhSn} of this crystal. The magnetic contribution to the specific heat of PrRhSn, has been calculated as $C_{mag} = C_{PrRhSn} - C_{LaRhSn}$. The C_{mag} versus T plot is displayed in Fig. 2. The crystal field at the Pr site is orthorhombic and it splits the ground state multiplet into nine singlets. The error in determining C_{mag} increases with temperature (see Fig. 2) and becomes too large at temperatures higher than 20 K, which allowed us to determine only the six lowest levels of ground state multiplet. According to the fit in the temperature region 2–2.38 together with 3.11–80 K we have found levels at the energies of 0 K (fixed level); 2.4 ± 0.05 K; 12 ± 1 K; 12 ± 1 K; 31 ± 0.7 K and 54 ± 2 K. One can see that our fit suggests a doublet or a quasidoublet at 12 K. Also we should note that the magnetic entropy calculated from the C_{mag} reaches a value of $\sim R \ln 4$ (see the inset of Fig. 2), which is consistent with the discussed CF-level scheme.

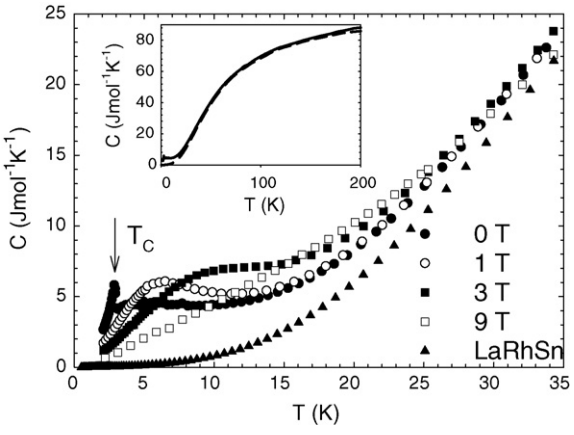

Fig. 1. Temperature dependence of the specific heat of PrRhSn below 35 K in various magnetic fields applied along the c-axis. The triangles represent the specific heat of a nonmagnetic analogue—LaRhSn (in zero field). The inset shows the temperature dependence of the specific heat of PrRhSn (full line) and LaRhSn (dashed line) in zero field in a wide temperature interval up to 200 K.

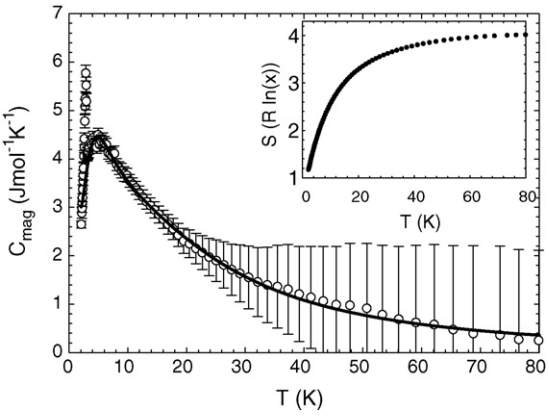

Fig. 2. Temperature dependence of the magnetic contribution to the specific heat of PrRhSn up to 80 K obtained from the comparative analysis together with the best fit due to Schottky contribution. Evolution of experimental error is also displayed. Inset: Temperature dependence of the magnetic entropy determined up to 80 K.

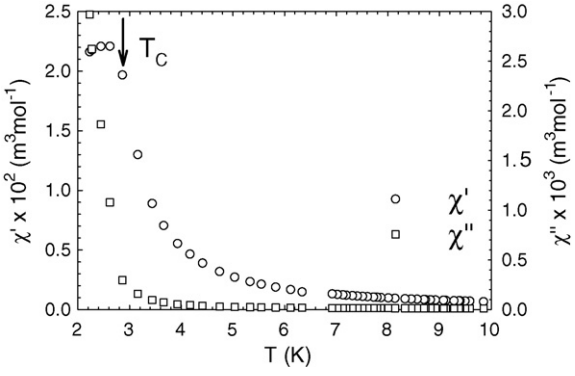

Fig. 3. Temperature dependence of the real (χ') and imaginary (χ'') component of the ac susceptibility of PrRhSn below 10 K measured in the ac sampling field oriented along the c-axis. The arrow denotes the Curie temperature T_C determined from the specific heat data (see Fig. 1).