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Specific heat studies of PrCoAl₄ single crystal

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Abstract

We have studied the heat capacity of a single crystal PrCoAl₄. The data indicate that Pr³⁺ in this compound has a non-magnetic singlet ground state. The compound becomes antiferromagnetically ordered below the Néel temperature of 17 K. The magnetocrystalline anisotropy in PrCoAl₄ is relatively strong. Up to 300 K, the entropy contained in the specific heat is 15.2 J/Kmol, which is only 83% of 18.3 J/Kmol expected for the 2J+1-fold degeneracy of the ground multiplet of the Pr³⁺ ion.

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1. Introduction

The RCoAl₄ compounds (R = La, Ce and Pr) crystallize in the orthorhombic LaCoAl₄ type of structure [1]. Structural investigations on CeCoAl₄ [2] and PrCoAl₄ [3] have shown that there is no site-disorder and the rare earth atom is primarily surrounded by the Al atoms. Previous neutron diffraction studies on powder samples [3] have

revealed a longitudinal amplitude modulated structure of the PrCoAl₄ compound with the wave vector $q = (0, 0, 0.437)$ below $T_N = 17$ K and that this magnetic structure remains stable down to 1.5 K.

The magnetic properties of the PrCoAl₄ compound are strongly anisotropic [4]. In the magnetisation isotherm measured at 4.2 K a spin-flip transition was observed only when a magnetic field of about 0.7 T is applied along the *c*-axis after which the forced ferromagnetic state is attained. Along the *a*- and *b*-axes, up to 20 T, the magnetisation is still far from saturation. The

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behaviour of the magnetisation curves of PrCoAl_4 is more or less similar to that observed in the isostructural compound CeCoAl_4 [5]. It is noted that, both Ce and Pr are trivalent in these compounds [4,5]. Ce^{3+} is a Kramer's ion with $J = 5/2$ whereas, Pr^{3+} is non-Kramer's ion with $J = 4$. In orthorhombic symmetry, under the effect of the crystal field, one would expect that the J ground state multiplet splits into 3 doublets for Ce^{3+} , whereas it will be 9 singlets for Pr^{3+} [6]. The ground state of Pr^{3+} , in the absence of an exchange field, therefore should be a non-magnetic singlet state. In this case, a large enough exchange energy as compared with the energy separation Δ between the ground and the first excited state is necessary to make the magnetic state a pseudo-doublet.

In order to obtain information on the crystalline electric field (CEF), in this present paper, we have extended our study of the heat capacity to a PrCoAl_4 single crystal and compared the results with those of CeCoAl_4 .

2. Experimental

A single crystal of PrCoAl_4 was grown by means of a modified tri-arc Czochralski technique [7] from a stoichiometric composition using 3N Pr, 3N Co and 5N Al in a Ti-gettered argon atmosphere. The sample was then cut into a cube with each dimension of about 1.7 mm along the crystallographic axes. The heat capacity measurements were made in the temperature range from 0.45 to 300 K using a Quantum Design Physical Property Measurement System (PPMS) with a heat capacity option.

3. Results and discussion

In Fig. 1, we present the ratio C/T vs. T for PrCoAl_4 in zero field. Similar data for a CeCoAl_4 crystal and for polycrystalline LaCoAl_4 are also added in this figure for comparison. In contrast to CeCoAl_4 , in which typical λ -like peak behaviour occurred at the ordering temperature T_N , in PrCoAl_4 we just observed a Schottky like anomaly

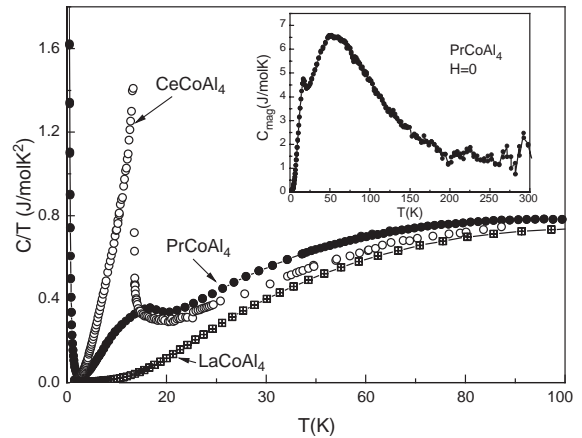


Fig. 1. The ratio C/T vs. T for RCoAl_4 ($R = \text{Ce}, \text{Pr}, \text{La}$). The inset shows the magnetic contribution to the heat capacity C_m vs. T of PrCoAl_4 .

centred at around 15 K. At temperatures below 2.5 K, the heat capacity of the sample strongly increases with decreasing temperature. In CeCoAl_4 , we also observed an upturn at very low temperature (< 1 K), which was attributed to a nuclear contribution (presumably from Co and Al atoms) because the upturn strongly increases and shifts towards higher temperature with increasing magnetic field [5]. However, the fact that the upturn in PrCoAl_4 occurs at higher temperature and is some order of magnitude stronger than that of CeCoAl_4 rules out the possibility of a nuclear contribution of the same nature. In PrCoAl_4 it is mainly the strong contribution from the Pr nucleus, a contribution which is frequently observed in Pr materials and which is absent for Ce. This upturn, together with the tail of magnetic peak make it difficult to obtain the exact value of γ from the fitting $C/T = \gamma + \beta T^2$ at low temperature (where the coefficients γ and β represent for the electronic and phonon contributions to the heat capacity, respectively). We estimate that the value of γ should be smaller than 17 mJ/molK^2 . At room temperature, we obtained only 83% of $R \ln 9$, a value expected for the $2J+1$ -fold degeneracy of the ground multiplet of Pr^{3+} ion.

In inset of Fig. 1, we plotted the magnetic contribution to the specific heat of PrCoAl_4 as a function of the temperature. This data was

obtained by subtracting the phonon and electronic contributions as derived from the isostructural non-magnetic LaCoAl_4 compound. In this figure, we observe a peak related to the magnetic ordering at around 17 K followed by a broad Schottky-typed peak at T_s of about 51 K. The value of the ordering temperature $T_N = 17$ K obtained in our specific heat results is consistent with value of T_N found from the neutron diffraction measurements on powder sample [3] and measurements on the Laue diffractometer, LADI, and the D10 four-circles single-crystal diffractometer at ILL, Grenoble with the same batch of crystals [8].

As mentioned earlier, in orthorhombic symmetry, under the effect of crystal field, one would expect that the J ground state multiplet splits into 9 singlets for Pr^{3+} [6]. In our case, the maximum value of the heat capacity obtained at the Schottky peak is $C_s(\text{max}) = 6.55$ J/mol K with the entropy of $S_{\text{mag}} = 8.44$ J/mol K. This value, however, is close to $C_s(\text{max}) = 6.31$ J/mol K with entropy $R \ln 3 = 9.13$ J/mol K expected for the simple case of a system which involves a singlet ground state and an excited doublet state [9]. Therefore, we assume that, in PrCoAl_4 the first excited state involves two energy levels very close to each other, and separated from the (singlet) ground state by a gap of about $T_s/0.377$ (≈ 135 K).

The magnetic entropy S_m vs. T is presented in Fig. 2 for PrCoAl_4 and CeCoAl_4 . In this figure, the

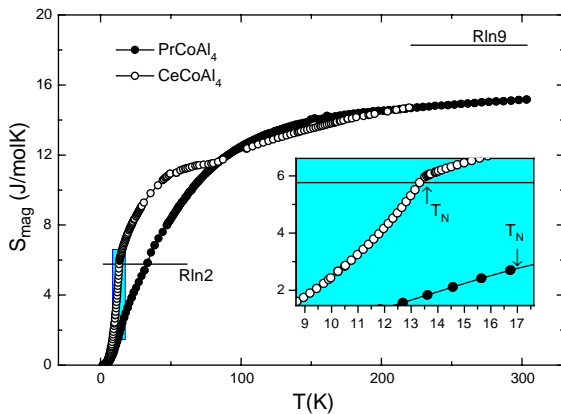


Fig. 2. Temperature dependence of the magnetic entropy S_m of PrCoAl_4 and CeCoAl_4 . The shaded area is an extended view of S_m around the ordering temperature.

shaded region on the right is an extended view of the magnetic entropy around the ordering temperature. In this figure, it can be seen that for CeCoAl_4 at T_N the magnetic entropy is close to $R \ln 2$ and therefore just confirming the doublet ground state of this compound. On the other hand, at the ordering temperature of PrCoAl_4 (17 K), the magnetic entropy reaches only 47% of $R \ln 2$.

In Fig. 3, we present the heat capacity C/T as function of temperature T for PrCoAl_4 measured in different magnetic fields applied along the c -axis. In this direction, we observed a spin–flop transition in the magnetisation isotherm at a critical field $H_c = 0.7$ T at 4.2 K [4]. With lowering temperature, H_c slightly decreases to 0.6 T at 2 K. As can be seen in this figure, the peak observed at T_N begins gradually to broaden with increasing applied magnetic fields up to 1 T at which the material is in the forced ferromagnetic state, indeed. In inset of Fig. 3, we also plotted the number of available states W (which is derived from the magnetic anisotropy by the relation $W = \exp(S_m/R)$) as a function of magnetic field at 2 K. The value of W increases with increasing magnetic field and thus indicating the approach of the excited state to the ground state. However, since the values of W are very close to 1, we can conclude that there is no level crossing involved at the spin–flop transition of 0.6 T for the compound.

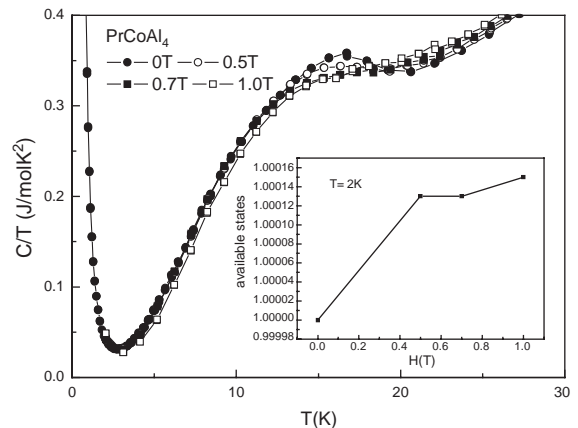


Fig. 3. The ratio C/T vs. T of PrCoAl_4 measured along the c -axis. Inset shows the calculated number of available states as function of magnetic field at temperature of 2 K.

In summary, we have studied the heat capacity of a single crystal PrCoAl_4 . The data indicate the presence of strong CEF effect in the compounds. The ground state in PrCoAl_4 is a singlet and well separated by a gap of about 135 K from the next excited state. Such CEF level scheme obviously supports the stability of sinusoidal magnetic structure as observed by neutron diffraction studies [3] at low temperature.

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References

- [1] R.M. Rykhal, O.S. Zarechnyuk, Ya.P. Yarmolyuk, *Dopov. Akad. Nauk. Ukr. RSR. Ser. A* (1977) 265.
- [2] O. Moze, L.D. Tung, J.J.M. Franse, K.H.J. Buschow, *J. Alloys Compounds* 256 (1997) 45.
- [3] P. Schobinger-Papamantellos, G. André, J. Rodriguez-Carvajal, O. Moze, W. Kockelmann, L.D. Tung, K.H.J. Buschow, *J. Magn. Magn. Mater.* 231 (2001) 162.
- [4] L.D. Tung, K.H.J. Buschow, *J. Alloys Compounds* 291 (1999) 37.
- [5] L.D. Tung, Ph.D Thesis, University of Amsterdam, 1998.
- [6] M. Loewenhaupt, *Physica B* 163 (1990) 479.
- [7] A.A. Menovsky, J.J.M. Franse, *J. Cryst. Growth* 65 (1983) 286.
- [8] P. Schobinger-Papamantellos, C. Wilkinson, L.D. Tung, K.H.J. Buschow, G.J. McIntyre. *J. Magn. Magn. Mater.*, submitted.
- [9] E.S.R. Gopal, *Specific heats at low temperature*, 1965.