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Specific heat of $PrNi_5$

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Abstract

Specific-heat measurements have been performed on single-crystalline $PrNi_5$ from 1.3 to 250 K, in order to evaluate the contribution of the Pr subsystem. $PrNi_5$ does not order magnetically down to the lowest temperatures as crystalline-electric-field (CEF) interactions, producing the non-magnetic singlet ground state Γ_4, dominate the exchange interactions. Analysis of the specific heat unambiguously establishes the position of the two lowest excited levels at 33.7 K (Γ_1) and 45.7 K (Γ_6) which levels cannot be observed in inelastic-neutron-scattering experiments. A set of CEF parameters of the Pr^{3+} ion in the f^2 configuration has been evaluated that gives the best account for all known experimental results of this compound.

The hexagonal compound $PrNi_5$ does not order magnetically down to the lowest temperatures. The absence of magnetic order between the Pr 4f spins is due to the non-magnetic singlet ground state Γ_4 produced by the crystalline-electric-field (CEF) interactions that dominate the weak spin-dependent interactions between the Pr ions. The electronic and magnetic properties of this compound are quite well explained in terms of CEF parameters [1–3]. The energy level scheme (ELS) obtained by point contact spectroscopy allowed for a further refinement of the CEF parameters [4]. However, despite of the long-lasting analysis of the properties of this compound, the ELS is still not fully established. Recent inelastic-neutron-scattering (INS) experiments on a single crystalline sample [5] largely enlightened the overall structure of ELS of the Pr^{3+} ion, but the positions of two lowest excited states were not yet clear since these excitations are forbidden.

In this paper, we present results of specific-heat measurements on single crystalline $PrNi_5$. Analysis of the specific heat unambiguously establishes the position of the two lowest excited levels.

The specific heat of $PrNi_5$ has been measured from 1.3 to 250 K. Two small pieces of a single crystalline batch, grown at the Material Centre ALMOS (University of Amsterdam), have been used. Details of the specific-heat measurements have been described elsewhere [6].

The specific heat of $PrNi_5$ is considered to contain electronic (C_{el}), phonon (C_{ph}) and f-subsystem (C_f) contributions. Information about the C_{el} and C_{ph} contributions is provided by the specific heat of the Pauli paramagnetic $LaNi_5$ compound, which results in a value for the Sommerfeld coefficient γ^c of 36 mJ/K^{2}mol and a Debye temperature θ_D of 322 K [7]. The C_f contribution, shown in Fig. 1, is obtained by direct subtraction of the measured molar specific heat of $PrNi_5$ and $LaNi_5$, since the correction for the difference in the molar mass is expected to be negligible. No anomaly connected with a magnetic phase transition was found, whereas a pronounced bump centered at 16–20 K is visible. The entropy involved in the specific heat C_f reaches at 250 K the value of 17.2 J/Kmol, close to that expected for the $(2J+1)$-fold degeneracy of the ground multiplet of the Pr^{3+} ion (= 18.3 J/Kmol).

The f specific heat is calculated by considering the following Hamiltonian of the Pr^{3+} ion:

$$H_R = \sum \sum B_n^m O_n^m + ng^2\mu_B^2\left(-J\langle J\rangle + \tfrac{1}{2}\langle J\rangle^2\right). \quad (1)$$

The first term is the CEF Hamiltonian written for the lowest multiplet $^3H_4$ given by Hund's rules with $J = 4$,

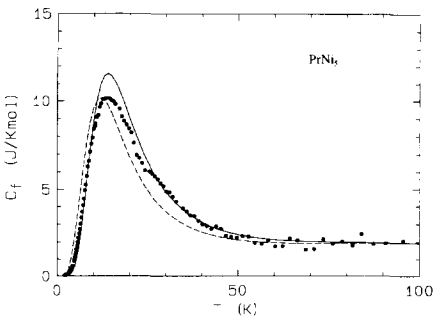

Fig. 1. Temperature variation of the f specific heat, C_f, of $PrNi_5$ (●). The solid line presents a calculated curve resulting from the CEF parameters of this work, listed in Table 1; the dotted line refers to those of Ref. [5].

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Table 1
Various sets of CEF parameters B_n^m, the molecular-field coefficient n, and the susceptibility of the Ni sublattice χ_{Ni} for $PrNi_5$. The position of three lowest excited levels (Γ_1, Γ_6 and Γ_5, respectively) are reported. The ground state is Γ_4

	[1]	[2]	[3]	[4]	[5]	Here
B_2^0 (K)	5.82	5.68	5.84	5.8	5.92	5.75
B_4^0 (mK)	49.4	44.3	45.3	52	46.4	50
B_6^0 (mK)	0.88	0.65	0.89	0.8	0.91	0.82
B_6^6 (mK)	31	36.1	31.4	31	30.2	29.8
n (T f.u./μ_B)	2.8	3.2	2.1	3.5	2.6	3.5
χ_{Ni} ($10^{-3}\mu_B$/T f.u)	–	3.7	3.7	3.7	–	4.0
Γ_1 (K)	22.9	38.9	22.2	38.2	22.9	33.7
Γ_6 (K)	39.4	49.2	38.9	49.0	39	45.7
Γ_5 (K)	48.2	47.9	48.1	48.3	47.7	47.4

$S = 1$, $L = 5$ and the Landé factor $g = 4/5$. It contains 4 parameters B_n^m for the hexagonal symmetry. The second term represents the exchange interactions between the Pr ions written in the mean-field approximation. Different experiments lead to slightly different sets of CEF parameters, as listed in Table 1. They all provide the singlet Γ_4 as the ground state, but give a large discrepancy in the positions of the first and the second excited states. Analysis of the specific heat at low temperatures leads to the adjustment of these states. For the best fit, the set of CEF parameters: $B_2^0 = 5.75$ K, $B_4^0 = 50$ mK, $B_6^0 = 0.82$ mK, $B_6^6 = 29.8$ mK has been used. The calculated contribution of the Pr^{3+} ion to the specific heat of $PrNi_5$ is in very good agreement with the experimental results (see Fig. 1). The ELS of the Pr^{3+} ion in the f^2 configuration and the appropriate eigenfunctions are shown in Fig. 2. The third, fourth and fifth excited levels are located at 47.4 K (doublet-Γ_5^1), 150 K (singlet-Γ_3) and 334 K (doublet-Γ_5^2), respectively, in agreement with the observed INS excitations [5]. On the basis of our specific-heat results, the first (singlet-Γ_1) and the second (doublet-Γ_6) excited levels were established to lie at 33.7 and 45.7 K, respectively,

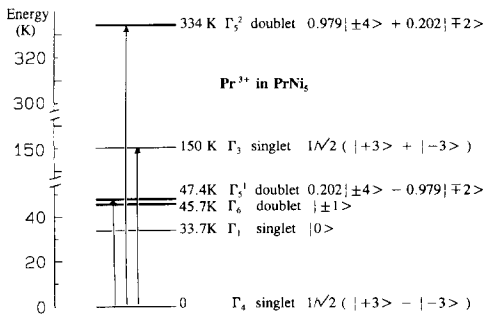

Fig. 2. The energy level scheme of the Pr^{3+} ion in $PrNi_5$ and the appropriate eigen-functions. Arrows show excitations observed in INS experiments [5].

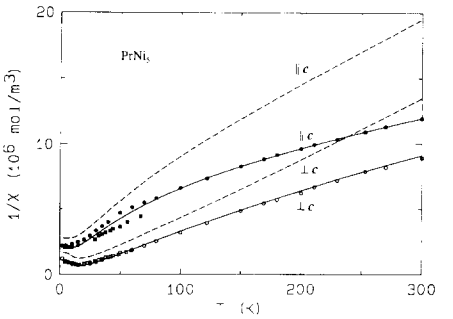

Fig. 3. Calculated thermal variation of the reciprocal susceptibilities of $PrNi_5$ parallel and perpendicular to the c-axis (solid lines). The experimental data are taken from [2] (●, ○) and [5] (■, □). Dashed lines show the bare f-ion susceptibility without taking into account the Ni-contribution χ_{Ni} of $4 \cdot 10^{-3}$ T f.u./μ_B.

whereas in Ref. [5] they were put much lower (22.9 and 39 K, respectively). Note that the $\Gamma_4 \rightarrow \Gamma_1$ and $\Gamma_4 \rightarrow \Gamma_6$ excitations *cannot* be observed in INS experiments. The lower position of these states clearly contradicts the specific-heat results at low temperatures (see Fig. 1). For further checking of our CEF parameters, we calculated the paramagnetic susceptibility χ of the Pr subsystem which is very anisotropic. The exchange enhanced susceptibility has been determined by taking the value 3.5 T f.u./μ_B for the molecular-field coefficient n. The temperature dependence of the reciprocal susceptibility parallel and perpendicular to the c-axis is shown in Fig. 3. The contribution to the susceptibility arising from the Ni-sublattice was taken into account with $\chi_{Ni} = 4 \times 10^{-3}\mu_B$/T f.u., a value obtained in $LaNi_5$. Note in Fig. 3 that neclecting this small contribution brings a large discrepancy at high temperatures.

In conclusion, an improved set of CEF parameters has been evaluated. The ELS of the Pr^{3+} ion has been constructed taking into account all known experimental results of the $PrNi_5$ compound.

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