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Published in: Journal of Magnetism and Magnetic Materials

DOI: 10.1016/0304-8853(94)01494-9

Citation for published version (APA):

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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 $^7F_0$, dominate the exchange interactions. Analysis of the specific heat unambiguously establishes the position of the two lowest excited levels at 33.7 K ($^1F_0$) and 45.7 K ($^3D_1$) 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 $^7F_0$ 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 ($C_e$), phonon ($C_p$) and f-subsystem ($C_f$) contributions. Information about the $C_e$ and $C_p$ contributions is provided by the specific heat of the Pauli paramagnetic LaNi$_5$ compound, which results in a value for the Sommerfeld coefficient $\gamma$ of 36 mJ/K$^2$mol and a Debye temperature $\theta_D$ 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:

$$H_f = \sum \sum B_{nm}^* Q_n^{*} + C_\mu \nu (\mu, \nu) \left(-J(\mu) + \frac{1}{2} J(\nu)^2\right).$$

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].](image-url)
Table 1
Various sets of CEF parameters $B^\mu_n$, the molecular-field coefficient $n$, and the susceptibility of the Ni sublattice $\chi_{Ni}$ for PrNi$_5$. The position of three lowest excited levels ($\Gamma_1$, $\Gamma_6$, and $\Gamma_5$, respectively) are reported. The ground state is $\Gamma_4$.

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<tbody>
<tr>
<td>$B^0_1$ (K)</td>
<td>5.82</td>
<td>5.68</td>
<td>5.84</td>
<td>5.8</td>
<td>5.92</td>
<td>5.75</td>
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<tr>
<td>$B^0_2$ (mK)</td>
<td>49.4</td>
<td>44.3</td>
<td>45.3</td>
<td>52</td>
<td>46.4</td>
<td>50</td>
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<tr>
<td>$B^0_3$ (mK)</td>
<td>0.88</td>
<td>0.65</td>
<td>0.89</td>
<td>0.8</td>
<td>0.91</td>
<td>0.82</td>
</tr>
<tr>
<td>$B^0_4$ (mK)</td>
<td>31</td>
<td>36.1</td>
<td>31.4</td>
<td>31</td>
<td>30.2</td>
<td>29.8</td>
</tr>
<tr>
<td>$B^0_6$ (mK)</td>
<td>0.88</td>
<td>0.65</td>
<td>0.89</td>
<td>0.8</td>
<td>0.91</td>
<td>0.82</td>
</tr>
<tr>
<td>$B^0_6$ (inK)</td>
<td>31</td>
<td>36.1</td>
<td>31.4</td>
<td>31</td>
<td>30.2</td>
<td>29.8</td>
</tr>
<tr>
<td>$n (T f.u./\mu_B)$</td>
<td>2.8</td>
<td>3.2</td>
<td>2.1</td>
<td>2.5</td>
<td>2.6</td>
<td>3.5</td>
</tr>
<tr>
<td>$\chi_{Ni} (10^{-3} \mu_0 B^3/T f.u.)$</td>
<td>-</td>
<td>3.7</td>
<td>3.7</td>
<td>3.7</td>
<td>-</td>
<td>4.0</td>
</tr>
</tbody>
</table>

$S = 1$, $L = 5$ and the Landé factor $g = 4/5$. It contains 4 parameters $B^\mu_n$ 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 $\Gamma_4$ 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: $B^0_1 = 5.75$ K, $B^0_2 = 50$ mK, $B^0_3 = 0.82$ mK, $B^0_6 = 29.8$ 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 of Ref. [5].

Fig. 2. The energy level scheme of the Pr$^{3+}$ ion in PrNi$_5$ and the appropriate eigenfunctions. Arrows show excitations observed in INS experiments [5].

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 $\chi$ of the Pr subsystem which is very anisotropic. The exchange enhanced susceptibility has been determined by taking the value $3.5$ T f.u./$\mu_B$ 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 $\chi_{Ni} = 4 \times 10^{-3} \mu_0 B^3/T f.u.$, a value obtained in LaNi$_5$. Note in Fig. 3 that neglecting 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.

References