

Crystalline electric field effects in PrNiGe₂

J L Snyman and A M Strydom

Physics Department, University of Johannesburg, P.O. Box 524 Auckland Park, 2006, South Africa

E-mail: jlsnyman@uj.ac.za

Abstract. Within the confines of the standard model of rare earth magnetism, the high temperature magnetic properties of rare earth ions in a crystalline environment are identical to the magnetic behaviour of free tri-positive rare earth ions. At low temperatures deviations from free-ion behaviour occur due to the action of an anisotropic crystalline electric field (CEF). For Pr³⁺-ions occupying sites with orthorhombic point symmetry it is expected that the 9-fold degeneracy of the spin orbit coupled ground state multiplet associated with the free tri-positive ion should be completely uplifted by the CEF yielding a non-magnetic singlet ground state for the Pr³⁺ 4f-electrons. PrNiGe₂ is known to order ferromagnetically despite the fact that the Pr³⁺ ions occupy the low-symmetry $m2m$ sites in the CeNiSi₂-type structure. This has prompted the current study into the ground state properties of PrNiGe₂. We determined the structure of the CEF-split energy levels in this system from specific heat measurements. The analyses points to the formation of a pseudo-doublet ground state and we forward a conceptual explanation of the observed magnetic order in PrNiGe₂ in terms a fortuitous merging of electronic singlet levels into a local level dispensation of higher degeneracy.

1. Introduction

The 4f-electron ground state of free rare earth ions are determined by the spin-orbit interaction, which yields for the 4f-electrons degenerate multiplets, well separated in energy, and characterised by the total angular momentum J . The ground state multiplet of free Pr³⁺ is nine fold degenerate, characterised by the total angular momentum number $J = 4$ and is separated from the first excited multiplet by an energy (in temperature units) of $\Delta/k = 3100$ K [1]. However, the ground state of the rare earth 4f-electrons is subject to additional interactions, one of which is the crystalline electric field (CEF) which adds non-spherically symmetric contributions to the 4f-electron Hamiltonian [2], and which acts to uplift (either fully or partially) the degeneracy of the free-ion multiplet. The nature of this splitting depends crucially on the point symmetry of the rare-earth ion crystallographic site and on the orbital contribution to the free-ion 4f-electron ground state.

PrNiGe₂ crystallises in a CeNiSi₂-type structure (space group $Cmcm$) [3, 4]. Within this structure the Pr³⁺-ions occupy the 4c site (with orthorhombic $m2m$ site symmetry). For such a low symmetry site it is expected that the CEF should completely uplift the degeneracy of the free-ion ground state multiplet [5, 6]. However, a previous study has shown that PrNiGe₂ orders ferromagnetically at a Curie point of $T_C = 15$ K [4]. Thus far very little is known about the ground state of this compound, the nature of the CEF-splitting, or the type of ferromagnetic order exhibited. Here we present a first investigation into these properties. We attempt to determine the CEF-levels and their degeneracies from heat capacity measurements

on a polycrystalline sample of PrNiGe_2 and show that the $4f$ -electron ground state in this compound is a doublet.

2. Experimental Procedure

A polycrystalline sample of PrNiGe_2 was prepared by melting together stoichiometric amounts of the constituent elements in an arc furnace under a purified argon atmosphere. The sample was prepared from 99.9 wt.% purity Pr, 99.99 wt.% Ni and 99.999 wt.% Ge. During the melt the button was flipped over and remelted several times to ensure homogeneity.

Powder X-ray diffraction was carried out on a Philips Analytical X'Pert Pro instrument at room temperature. The sample stage is equipped with a sample spinner rotating the sample around the scattering vector to negate possible effects of preferred orientation in the powder. Cu radiation ($K\alpha$, $\lambda = 1.542 \text{ \AA}$) was used for the incident beam.

The specific heat of PrNiGe_2 was measured by utilizing the Heat Capacity option on a Physical Properties Measurement System [7]. For details regarding the method used, see Refs. [8, 9].

3. Results and Discussion

Figure 1 shows the X-ray diffractogram obtained for PrNiGe_2 together with a simulated diffractogram obtained from the orthorhombic $Cmcm$ CeNiSi_2 -type structure. The simulated diffractogram was obtained by using the lattice parameters and unit cell data reported in [4] as input to a full profile Rietveld refinement program, and refining the lattice parameters in order to obtain the best fit between the observed and calculated diffractograms. The Rietveld refinement was done by utilising the General Structure Analyses System (GSAS) [10, 11]. The lattice parameters used as input for the simulated data are $a = 4.23119 \text{ \AA}$, $b = 16.7813 \text{ \AA}$ and $c = 4.18974 \text{ \AA}$. A comparison between the calculated and observed diffractograms in figure 1 shows that the sample formed in the desired structure.

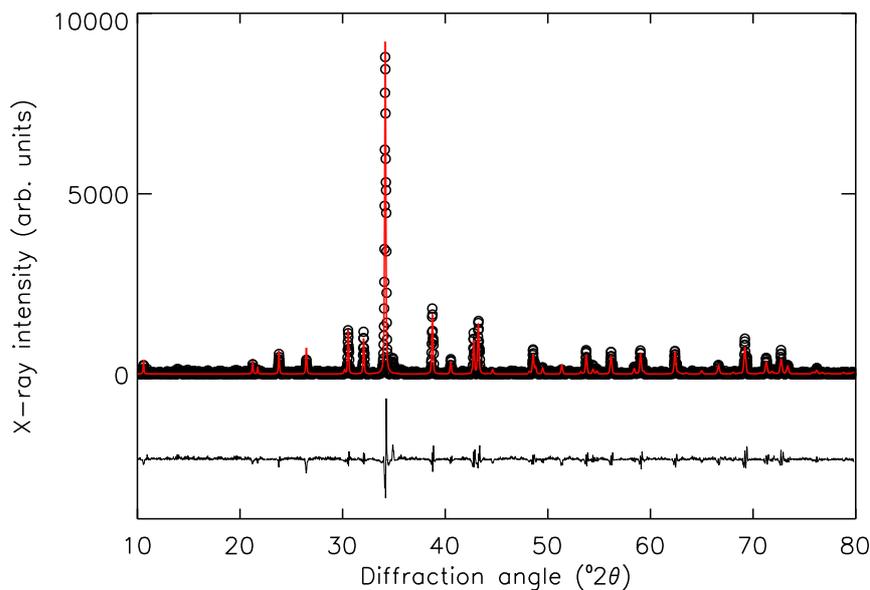


Figure 1. The powder X-ray diffraction spectrum for PrNiGe_2 (open circles) together with the spectrum calculated from a full profile least squares Rietveld refinement fit (solid red line). The difference between the simulated and observed data is shown below the diffractogram.

The specific heat of PrNiGe₂ is shown in figure 2. The low temperature anomaly (reaching a maximum of 17.90 J.mol⁻¹.K⁻¹ at 12.33 K) is associated with the onset of magnetic order. Magnetisation measurements classified the ordering as ferromagnetic [4]. At temperatures well in excess of 12 K the specific heat of PrNiGe₂ resembles that of the well known Debye-model, implying that the specific heat is dominated by a phononic contribution at these temperatures. In order to isolate this contribution the Debye model specific heat (for acoustic modes only) was fitted to the high temperature data in figure 2. Subtraction of the phonon contribution yielded the 4*f*-electron contribution to the specific heat similar to the data shown in the inset of figure 2.

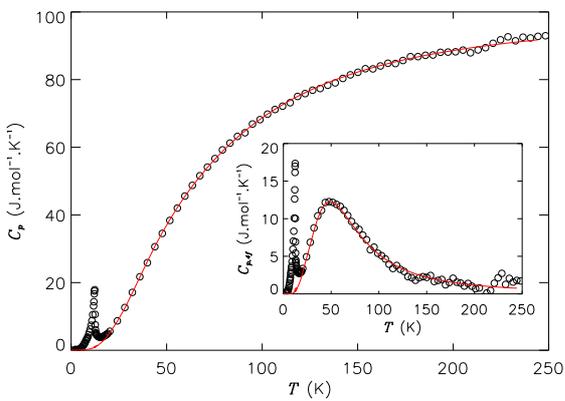


Figure 2. Total measured specific heat of PrNiGe₂ (open symbols). The solid line is a fit of the combined effect of the Schottky, Debye and Sommerfeld contributions to the specific heat of the compound calculated for $n = 7$ as is described in the text. Inset: 4*f*-electron contribution to the specific heat of PrNiGe₂.

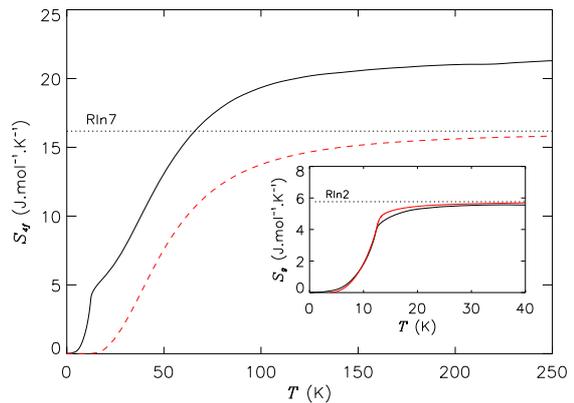


Figure 3. 4*f*-electron contribution (solid line) to the entropy of PrNiGe₂ as calculated from the inset of figure 2. The dashed line corresponds to the entropy of the system due to thermal population of the energy levels listed for $n = 7$ in table 1. Inset: Magnetic configurational entropy, calculated by subtracting the Schottky-contribution from the total 4*f*-entropy. Also shown is the magnetic configurational entropy of an isotropic three dimensional Ising-ferromagnet (red line).

After subtracting the phonon contribution the specific heat showed a clearly defined Schottky-anomaly (with a peak at ~ 50 K), indicating the thermal population of CEF-split energy levels. The Schottky anomaly could not be accurately described using the well known two- or three level descriptions often found in literature (see for example Ref.[12]). In order to adequately parameterise the anomaly a first principles calculation involving up to the full set of nine CEF-levels for Pr³⁺ had to be done. As is discussed below this procedure not only accurately parameterised the Schottky-anomaly but also constrained the CEF-parameters to some extent.

Theoretically the Schottky contribution arises from the thermal population of a number of discrete energy levels. This contribution can readily be calculated from a partition function of the form

$$\mathcal{Z} = \sum_{i=0}^n g_i e^{-E_i/kT} \quad (1)$$

where E_i is the energy of the i 'th level with degeneracy g_i , k is Boltzmann's constant and T is the temperature of the system. The Schottky contribution to the specific heat was found to extend up to the highest measured temperatures (250 K). Therefore it was not deemed sufficient to fit a Debye and Sommerfeld contribution to the specific heat independently from the Schottky contribution (as was indeed done in the first analyses, mentioned above), and hence in order to parameterise the phononic (Debye), electronic (Sommerfeld) and Schottky contributions to the specific heat a Monte-Carlo algorithm was used to optimize all parameters involved simultaneously.

Initially the algorithm generated random instances of the Debye temperature (between 250 K and 350 K), Sommerfeld coefficients (between 0 and $0.1 \text{ J.mol}^{-1}.\text{K}^{-2}$) and nine values of E_i ($E_i/k \in [0 \text{ K}, 1000 \text{ K}]$), subject to the constraint that $E_0/k = 0 \text{ K}$. It was assumed that $g_i = 1$ for all i in Eq.1. This was done in order to find the most general description of the CEF-split levels in the compound. For example, if the CEF-split levels are one doublet and seven singlets, then the algorithm should yield two values of E_i which overlap within the error margins, while the other E_i values should show no overlap. Lastly, the large range for the E_i , $i = 1, 2, 3, \dots, 8$ was used to compensate for the possibility that the total CEF splitting is much larger than the experimental temperature range considered. For example, if the Schottky contribution to the specific heat can be described by six singlets alone, then it is expected that the parameter set that yields the best fit should contain three levels at energies which are sufficiently high to negate any contribution at 250 K.

The algorithm was executed by generating 200000 random instances of each parameter (Debye temperature θ_D , Sommerfeld coefficient γ and nine energy level values E_i). After each instance the average difference $\langle \sqrt{(C_e - C_m)^2} \rangle$ between the experimental specific heat C_e and the modelled specific heat C_m was calculated over the range $17 \leq T \leq 250 \text{ K}$. The lower limit of 17 K was chosen to ensure that the magnetic contribution to the specific heat does not affect the calculation. For every 200000 guesses the parameter set that gave the best fit was chosen. The whole procedure was repeated 30 times, yielding the 30 best parameter sets given the constraints mentioned above.

The data obtained from this simultaneous optimization immediately showed that the Debye temperature lies between 290 K and 320 K, irrespective of how many energy levels were considered in the calculation. Therefore, the procedure noted above was repeated by constraining the instances of θ_D to lie between 290 K and 320 K. The data thus obtained is summarised in table 1, where n denotes the number of discrete energy levels assumed to contribute to the partition function in Eq.1.

The data in table 1 requires careful analyses. For $n = 6, 7, 8$ and 9 the Schottky contribution to the specific heat could be accurately parameterised (within $\sim 0.45 \text{ J.mol}^{-1}.\text{K}^{-1}$). However using fewer than six energy levels to calculate the Schottky contribution yields significantly poorer fits. Therefore it can be concluded that the Schottky anomaly seen in the measured specific heat data arises from the thermal population of at least six CEF-split singlets. While the data in table 1 does constrain the number of levels to some extent it does not adequately constrain the degeneracies of these levels. For example, for $n = 8$ E_5 and E_6 lie close enough together (given the uncertainties implied by the average deviation) to be either two close lying singlets, or a single doublet. However the data in table 1 allows the accurate *parameterisation* of the Schottky, Debye and Sommerfeld contributions to the $4f$ -electron entropy as is shown next.

In general the entropy of a system can be calculated from its specific heat through

$$S(T')_H = \int_0^{T'} \frac{C_{P,H}(T)}{T} dT + S_0(H) \quad (2)$$

where $C_{P,H}(T)$ is the specific heat in constant pressure P and applied field H at temperature

Table 1. The data obtained by simultaneously fitting the Debye temperature Θ_D , Sommerfeld coefficient γ and n energy levels E_i , $i = 0, 1, 2, \dots, n$ to the total measured specific heat of PrNiGe₂. For every value of n the values in the left column denote the average taken over all 30 parameter sets noted above (with average deviations from the mean shown in brackets). $\langle\delta C\rangle = \langle\sqrt{(C_e - C_m)^2}\rangle$ is calculated as mentioned in the text and has units of J.mol⁻¹.K⁻¹. Θ_D and the E_i/k values are all quoted in Kelvin. The γ values shown in the table have units of mJ.mol⁻¹.K⁻².

Param.	$n = 9$	$n = 8$	$n = 7$	$n = 6$	$n = 5$
Θ_D	315 (2)	313 (2)	309 (1)	304 (2)	298 (2)
γ	5 (1)	5 (1)	5 (1)	4 (1)	3 (1)
E_0/k	0	0	0	0	0
E_1/k	99 (10)	105 (13)	111 (10)	112 (10)	115 (6)
E_2/k	130 (9)	134 (8)	130 (7)	134 (8)	125 (6)
E_3/k	156 (12)	148 (9)	147 (9)	146 (7)	141 (6)
E_4/k	172 (8)	170 (7)	166 (12)	162 (9)	159 (9)
E_5/k	187 (8)	187 (11)	187 (12)	181 (10)	-
E_6/k	208 (11)	208 (12)	225 (24)	-	-
E_7/k	227 (11)	249 (27)	-	-	-
E_8/k	296 (42)	-	-	-	-
$\langle\delta C\rangle$	0.431 (0.015)	0.441 (0.017)	0.456 (0.013)	0.471 (0.014)	0.531 (0.014)

T and $S_0(H)$ is the entropy at absolute zero [13]. In calculating the entropy it has been assumed that $S_0(H) = 0$ for all H and that

$$S(T')_H = \int_0^{T'} \frac{C_{P,H}(T)}{T} dT = 0 \text{ for } T' < T_0 \quad (3)$$

where T_0 is the lowest temperature at which experimental data is available. Shown in figure 3 is the total $4f$ -contribution to the entropy for the case where $n = 7$. The inset shows the entropy after the Schottky, Debye and Sommerfeld contributions have been subtracted. Given the magnetic phase transition at ~ 12 K, the entropy in the inset of figure 3 is taken to represent the magnetic configurational entropy associated with the onset of ferromagnetic order as is indeed suggested by the similarity with the magnetic configurational entropy of a three dimensional isotropic Ising-ferromagnet which is also shown. Clearly the magnetic configurational entropy saturates above T_C at a value close to $R \ln 2$ J.mol⁻¹.K⁻¹, which suggest a magnetic doublet ($J = 1/2$) dispensation in the ground state.

It is noted that a similar ground state is found for all parameter sets $n = 6, 7, 8$ and 9 in table 1 as is summarised in table 2. Therefore it can be safely concluded that the magnetic ground state of PrNiGe₂ is a doublet. The usual mechanism by which magnetic order is established in low symmetry Pr-based compounds is through the admixture of two low-lying singlets, given that the exchange energy exceeds a critical value [14]. For example, such a mechanism has been shown to produce an Ising-like doublet ground state in TmNi [15].

4. Conclusion

A Monte Carlo algorithm permitted the parameterization of the Schottky, Debye and Sommerfeld contributions respectively, weighed against experimental data of the specific heat of PrNiGe₂. A subsequent calculation of the magnetic configurational entropy revealed that

Table 2. The saturation entropy S_{sat} calculated for each parameter set in table 1 and the percentage of the theoretical saturation value (equal to $R \ln 2$) S_{sat} represents.

n	S_{sat} (J.mol ⁻¹ .K ⁻¹)	% of $R \ln 2$
9	5.43	94.2
8	5.54	96.2
7	5.56	96.4
6	5.52	95.8
5	5.44	94.5

the magnetic ground state is a doublet. The parameterisation of the Schottky contribution to the specific heat enabled us to constrain the CEF-level scheme as is shown in table 1. The parameterisation suggests that at least six energy levels are responsible for the Schottky contribution observed in the specific heat up to 250 K.

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