



Incommensurate Magnetic Order in PrNiAl₄

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Neutron diffraction experiments on PrNiAl₄ have revealed the presence of a second magnetic phase, in addition to the previously known commensurate magnetic structure. The second phase orders at 8.1 K, is incommensurate with the crystal lattice with propagation vector $\mathbf{k} = (0.07(1), 1, 0)$ and has the magnetic moments aligned along the *a*-axis. The moments also vary sinusoidally along this same direction.

1. Introduction

Subject to a number of investigations over the past few years, the RNiAl₄ series (where $R = \text{Ln}^{3+}$) has revealed itself to be host to a number of interesting magnetic compounds. Many of these compounds display complex magnetic behaviour, with multiple metamagnetic phase transitions and incommensurate phases. The $R = \text{Tb}$, Er and Nd compounds in this series have all been observed to have incommensurate magnetic phases [1-3] with the Tb structure being an elliptical helix [4] and the Er structure being a transverse sine wave [5]. Initial studies on PrNiAl₄ found hints that it too could possess an incommensurate magnetic phase, with the magnetic peaks in powder diffraction patterns showing positions dependent on the temperature [6]. Further evidence was found while examining Pr/Nd mixed compounds, with specific heat measurements on pure PrNiAl₄ revealing two distinct transitions at 8.1 K and 6.9 K [7]. With these clues in mind, a neutron diffraction experiment on PrNiAl₄ was undertaken in order to identify and characterise the unknown magnetic phase in the 8.1-6.9 K range.

2. Experimental

PrNiAl₄ was prepared using stoichiometric amounts of the component metals which were melted in an argon arc furnace. After this initial melting, the ingots were wrapped in tantalum foil and placed in an evacuated quartz glass tube, where they were annealed for approximately seven days at 1030 °C. Upon removal the ingots were crushed and phase purity was checked using a Panalytical Empyrean X-ray diffractometer. Neutron powder diffraction was carried out on the *ECHIDNA* [8] instrument located at the OPAL Reactor, Lucas Heights with neutron wavelength 2.44 Å at a number of temperatures (3.0 K, 7.0 K, 7.5 K and 30 K). Diffraction data was analysed using the *Fullprof* suite of programs [9], with the *Basireps* tool used to evaluate the irreducible representations associated with the propagation vector and *Cmcm* space group.

3. Results and Discussion

The diffraction pattern at 3.0 K revealed a magnetic structure identical to that found in the earlier study by Mizushima et al [6] with the magnetic moments being aligned with the *a*-

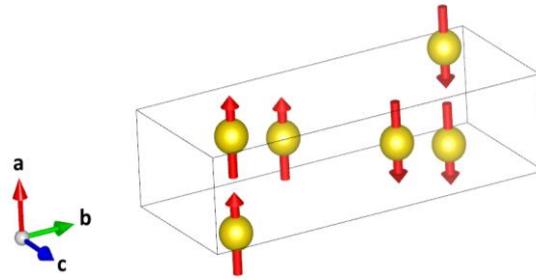


Figure 1: The commensurate magnetic structure of PrNiAl₄ with propagation vector $k = (0,1,0)$. Atoms other than Pr have been excluded for clarity.

axis in a simple antiferromagnetic configuration with propagation vector $k = (0,1,0)$. This is shown in Figure 1.

At 7.0 K, a significant difference in peak positions can be seen when compared to the 3.0 K pattern, with the lowest two theta magnetic reflection having shifted to higher angle and also with decreased intensity (Figure 2 and Figure 3). The same is also true of other magnetic peaks indicating that there has been a change in the magnetic structure of the material. In order to refine the magnetic phase in *Fullprof* using irreducible representations obtained from *Basireps*, a propagation vector describing the magnetic structure was needed. A ‘best guess’ was used initially based on the propagation vectors of the incommensurate phases in TbNiAl₄ and ErNiAl₄ and also by indexing the first magnetic peak in such a way as to contain an *a* or *c* component so that it was shifted to higher angle. It was found that the most reliable refinement was achieved using a propagation vector of $k = (0.071(1), 1, 0)$ and although it is possible to have a very small *c*-component, its effect on the overall refinement

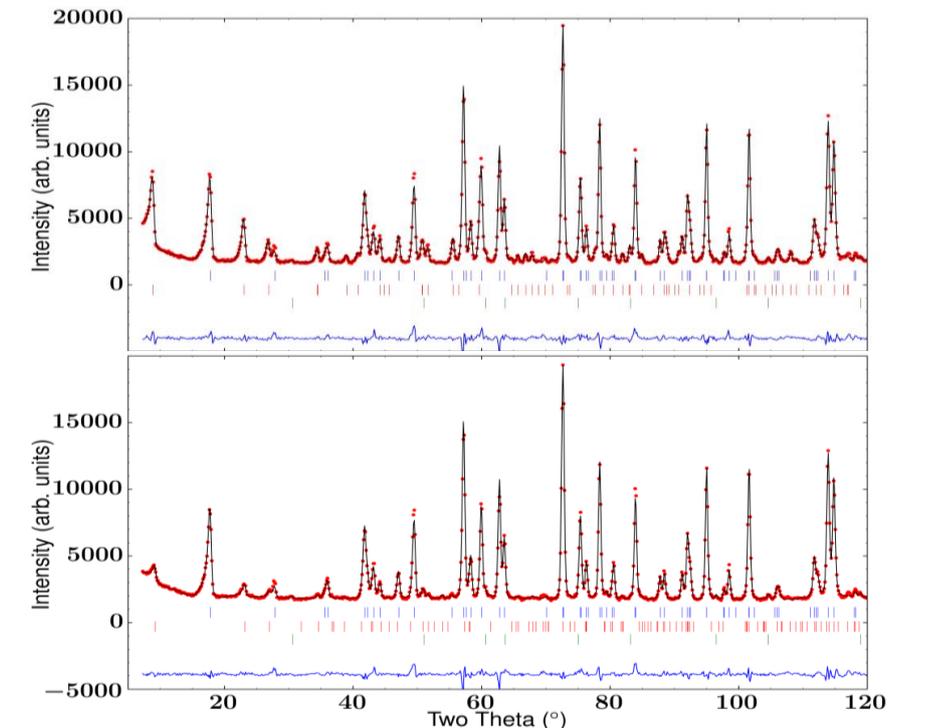


Figure 2: Neutron diffraction patterns from PrNiAl₄ at 3 K (upper) and 7 K (lower) taken on the *ECHIDNA* instrument. There is a significant change in the intensity of the magnetic peaks across this range, and also a slight change in their position indicating a change in the magnetic structure. The green ticks in each case represent a small amount of PrAl₂ as an impurity phase.

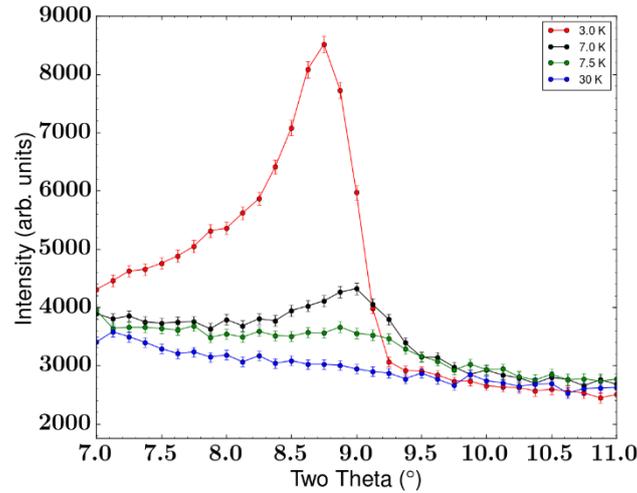


Figure 3: Evolution of the lowest two theta magnetic reflection across the four temperatures in this experiment. The peak shifts to the right and becomes much less intense as the temperature increases. The change in the position (3.0 K to 7.0K) corresponds to the addition of a small (0.07) a component to the propagation vector.

is minimal and the uncertainty is large.

The magnetic moments in a magnetic structure can be expressed as the Fourier series:

$$m_j = \sum_k S_{k,j} \exp(-2\pi \cdot i \cdot k \cdot t)$$

Where $S_{k,j}$ is a Fourier coefficient associated with the j^{th} atom expressed as the product of refinable coefficients and basis vectors obtained from the irreducible representations of the propagation vector and space group (see Table 1 for the basis vectors used in this analysis), k is the propagation vector itself and t is the unit cell translations from the 0th cell. Because the propagation vector is incommensurate, to ensure real moments $-k$, the negative of the propagation vector, must be included in the sum and requires $S_{-k,j} = S_{k^*,j}$. This reduces the above to a (co)sinusoidal term only. (Full details may be found in [10]). A purely sinusoidal modulation of the moments is consistent with the data as no reflections corresponding to higher order harmonics of the propagation vector are observable. The best result from refinement was obtained when the moments are aligned parallel to the a -axis with the modulation in the magnitude occurring along this same direction (i.e. longitudinally). This is an unusual structure when viewed in light of the other magnetic structures seen so far within

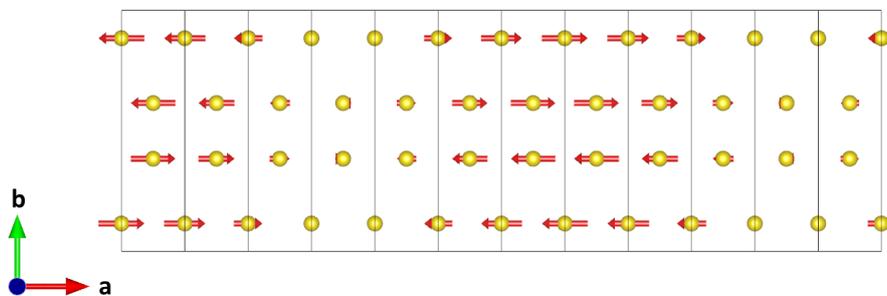


Figure 4: The incommensurate magnetic structure of PrNiAl₄ at 7.0 K. As can be seen, the magnetic moments vary sinusoidally in size along the a -axis which is also the axis of easy magnetisation.



this series, as the sinusoidal components in those cases were perpendicular to the propagation direction. This is likely the result of crystalline electric field and anisotropy effects which are dependent on the particular rare earth ion that is present. Statistics for the refinement at 7 K are shown in Table 1.

The incommensurate structure of PrNiAl₄ persists up to at least 7.5 K, though it is clear that the magnetic intensity has been significantly diminished at this point. It is also interesting to note that the peaks at 7.5 K lie exactly under the peaks at 7.0 K, indicating the no further evolution of the magnetic unit cell has taken place, other than the magnetic moments reducing in magnitude. At 30 K, the magnetic peaks have completely vanished, leaving only the structural peaks as expected given the 8.1 K transition temperature.

Table 1: Refinement statistics for PrNiAl₄ at 7 K

Atom	x	y	z		
Pr	0	0.1154(5)	0.25		
Ni	0	0.7752(2)	0.25		
Al1	0	0.5	0		
Al2	0	0.9215(6)	0.25		
Al3	0	0.3079(4)	0.0520(9)		
<i>a,b,c</i> (Å)	4.1205(1)	15.746(4)	6.619(2)		
	Pr Site 1 (x,y,z)		Pr Site 2 (x, -y, z+1/2)		
<i>Irreducible Rep: Γ₄</i>	(u 0 0)		(-u 0 0)		
	(0 v 0)		(0 v 0)		
<i>Peak Magnetic Moment</i>	1.9(1) μ _B				
R_p	R_{wp}	R_{exp}	R_{Bragg}	R_{Mag}	χ²
9.75	9.74	6.42	3.77	13.3	2.30

4. Conclusion

The magnetic structure of the incommensurate phase in PrNiAl₄ has been determined using neutron powder diffraction and was found to be present at 7.0 K and 7.5 K. The structure consists of a longitudinal sine wave, with the moments varying along the *a*-axis, which is also the easy axis. This is markedly different to the other structures in this series, for which the modulation is perpendicular to the propagation direction. A full description of the magnetic structure of the related NdNiAl₄ may be enlightening with regards to trends, as it appears that compound also has a complex incommensurate magnetic phase based on its propagation vector of $\mathbf{k} = (0.076, 0.352, 0.478)$ [3].

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