Neutron powder diffraction determination of the magnetic structure of Nd$_2$Al

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Abstract. We have determined the magnetic structure of Nd$_2$Al by neutron powder diffraction. This orthorhombic intermetallic compound orders ferromagnetically below 36 K with the Nd moments aligned along the b-axis. Even at 1.7 K, the larger of the two Nd moments is only 2.3(2) $\mu_B$, about 70% of the ‘free-ion’ value of 3.27 $\mu_B$. This reduction is a consequence of the substantial crystal-field effects at the Nd$^{3+}$ sites.

1. Introduction
The R$_2$Al intermetallic compounds (R = rare earth) crystallize in the orthorhombic Co$_2$Si-type structure (space group Pnma, #62) in which the R atoms occupy two crystallographic sites (both 4c) and the Al occupies a third 4c site. In 1978, Sill and Biggers [1] showed that Nd$_2$Al is a ferromagnet with a Curie temperature of 36 K and they quoted a “fully-stretched” Nd magnetic moment of 3.27 $\mu_B$. More recent work [2, 3, 4] suggested that the Nd magnetic moment at low temperatures is actually quite strongly reduced from the free-ion value of 3.27 $\mu_B$ and it was proposed that this reduction in moment may be due to either strong crystal-field quenching or antiferromagnetic components in the magnetic order, either intrinsic or as clusters. In this paper we present neutron powder diffraction measurements we recently made on Nd$_2$Al. In particular, we confirm that Nd$_2$Al is ferromagnetic with a strongly quenched Nd moment. No antiferromagnetic components in the magnetic order were observed.

2. Experimental Methods
The Nd$_2$Al sample was prepared by arc melting stoichiometric amounts of the pure elements (Nd 99.9 wt.%, Al 99.99 wt.%). The sample was turned and remelted several times in order to ensure homogeneity. The alloyed button was then sealed under vacuum in a quartz tube, annealed for 3 weeks at 700 °C and quenched in water. Cu-K$_\alpha$ x-ray powder diffraction and EDAX analysis confirmed the majority phase to be the intended orthorhombic Nd$_2$Al phase. It proved impossible to prepare a single-phase sample. Refinement of the x-ray diffraction pattern using the GSAS/EXPGUI package [5, 6] showed the presence of impurities of about 5 wt% each...
of NdAl (orthorhombic $Pbcm$ [7]) and Nd$_3$Al (cubic $Pm\overline{3}m$ [8]), with a trace of unreacted Al (cubic $Fm\overline{3}m$) also present. Basic magnetic characterization was carried out on a Quantum Design PPMS susceptometer/magnetometer operated down to 1.8 K.

Neutron diffraction experiments were carried out on the Echidna high-resolution powder diffractometer at the OPAL reactor in Sydney, Australia [9]. The neutron wavelength was 2.44160(2) Å, calibrated against a standard Al$_2$O$_3$ sample (NIST SRM676). All refinements of the neutron diffraction patterns employed the GSAS/EXPGUI package [5, 6]. The neutron diffraction data were corrected for absorption effects.

3. Results and Discussion

In figure 1 we show the refined neutron diffraction pattern of Nd$_2$Al obtained at 106 K, at which temperature Nd$_2$Al is paramagnetic and the neutron diffraction pattern exhibits only nuclear scattering.

![Neutron diffraction pattern of Nd$_2$Al obtained at 106 K.](image)

Figure 1. Neutron diffraction pattern of Nd$_2$Al obtained at 106 K (λ = 2.44160(2) Å). The Bragg markers (bottom to top) represent Nd$_2$Al, Al, NdAl and Nd$_3$Al.

The refined lattice parameters at 106 K are $a = 6.6825(4)$ Å, $b = 5.2342(3)$ Å and $c = 9.7321(7)$ Å. In table 1 we give the refined atomic position parameters of Nd$_2$Al, deduced from the refinement of the 106 K neutron powder diffraction pattern. The conventional refinement R-factors (%) are $R(p) = 3.4$ and $R(F^2) = 3.0$.

Table 1. Crystallographic data for Nd$_2$Al obtained by refinement of the 106 K neutron powder diffraction pattern.

| Atom | Site | x     | y     | z     |
|------|------|-------|-------|-------|
| Nd   | 4c   | 0.0184(5) | 0.7040(3) |
| Nd   | 4c   | 0.1929(5) | 0.0724(4) |
| Al   | 4c   | 0.2045(12) | 0.4026(6) |
Figure 2. Neutron diffraction pattern of Nd$_2$Al obtained at 1.7 K ($\lambda = 2.44160(2)$ Å). The Bragg markers (bottom to top) represent Nd$_2$Al, Al, NdAl and Nd$_3$Al.

In figure 2 we show the refinement to the neutron diffraction pattern obtained at 1.7 K. The magnetic contributions to the 1.7 K Nd$_2$Al diffraction pattern occur only at the nuclear peak positions and correspond to the propagation vector $k = [0 0 0]$. We find no evidence for additional magnetic-only peaks from the Nd$_2$Al phase. In order to consider all possible magnetic structures allowed for Nd$_2$Al, we carried out Representational Analysis for the Nd site using the SARA $h$ program [10]. The decomposition of the magnetic representation comprises eight one-dimensional representations:

$$\Gamma_{M_{4g}}^{4c} = 1\Gamma_1^{(1)} + 2\Gamma_2^{(1)} + 2\Gamma_3^{(1)} + 1\Gamma_4^{(1)} + 1\Gamma_5^{(1)} + 2\Gamma_6^{(1)} + 2\Gamma_7^{(1)} + 1\Gamma_8^{(1)}$$

and the basis vectors of these irreducible representations are given in table 2.

**Table 2.** Representational Analysis for the Nd(4c) site in Nd$_2$Al with a propagation vector [0 0 0]. The respective atomic positions are $(x, y, z)$, $(\frac{1}{2} + x, y, \frac{1}{2} - z)$, $(-x, -y, -z)$ and $(\frac{1}{2} - x, -y, z + \frac{1}{2})$.

| Representation | Ordering Mode | First component | Second component |
|----------------|---------------|-----------------|------------------|
| $\Gamma_1$     | $G_Y$         | + - - -         | 0                |
| $\Gamma_2$     | $C_X A_Z$     | + - - -         | - - - -          |
| $\Gamma_3$     | $F_X G_Z$     | + + + +         | - - - -          |
| $\Gamma_4$     | $A_Y$         | + - - +         | 0                |
| $\Gamma_5$     | $F_Y$         | + + + +         | 0                |
| $\Gamma_6$     | $A_X C_Z$     | + - - -         | + + - -          |
| $\Gamma_7$     | $G_X F_Z$     | + - - -         | + + + +          |
| $\Gamma_8$     | $C_Y$         | + - - +         | 0                |

We can immediately rule out the purely antiferromagnetic representations $\Gamma_1$, $\Gamma_2$, $\Gamma_4$, $\Gamma_6$ and $\Gamma_8$ because magnetometry measurements make it clear that Nd$_2$Al is at least “predominantly
ferromagnetic” [4]. This leaves three possible magnetic structures, namely $\Gamma_3$, $\Gamma_5$ and $\Gamma_7$. The only allowed ordering directions for the Nd(4c) magnetic sublattices with $\mathbf{k} = [0 0 0]$ are either along the b-axis ($\Gamma_5$) or in the ac-plane ($\Gamma_3$ and $\Gamma_7$). The best refinement to the measured diffraction pattern is with the Nd(4c) sites ordered ferromagnetically in the $F \bar{V}$ mode, along the crystal b-axis, corresponding to the $\Gamma_5$ representation. Of particular note are the Nd$^{3+}$ magnetic moments, $1.2(2) \mu_B$ and $2.3(2) \mu_B$, both of which are substantially smaller than the ‘free-ion’ value of $3.27 \mu_B$ for the Nd$^{3+}$ ion.

Our refinements show that there are no antiferromagnetic components associated with the magnetic order of the Nd sublattices, either as an intrinsic canting or as clusters. The reduction in the Nd magnetic moments in Nd$_2$Al is therefore most likely the result of crystal-field quenching. It is known that the crystal-field acting on the R$^{3+}$ sites in the orthorhombic R$_2$Al compounds is quite large and this, coupled with the fact that the magnetic exchange interaction is relatively weak ($T_C = 36$ K for Nd$_2$Al), leads to the observed quenching. In a $^{169}$Tm Mössbauer study of Tm$_2$Al, for example, one of us showed that the strong effect of the crystal-field leads to unusually slow electronic relaxation of the Tm$^{3+}$ ion [11].

4. Conclusions
We have determined the magnetic structure of Nd$_2$Al by neutron powder diffraction. The magnetic ordering temperature is $36(2)$ K. At $1.7$ K, the magnetic order of the Nd(4c) sublattices is ferromagnetic along the orthorhombic b-axis. Significant crystal-field quenching of the Nd$^{3+}$ magnetic moments is present.

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