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# Neutron diffraction investigation of the magnetic structure and magnetoelastic effects in NdMnO<sub>3</sub>

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## Abstract

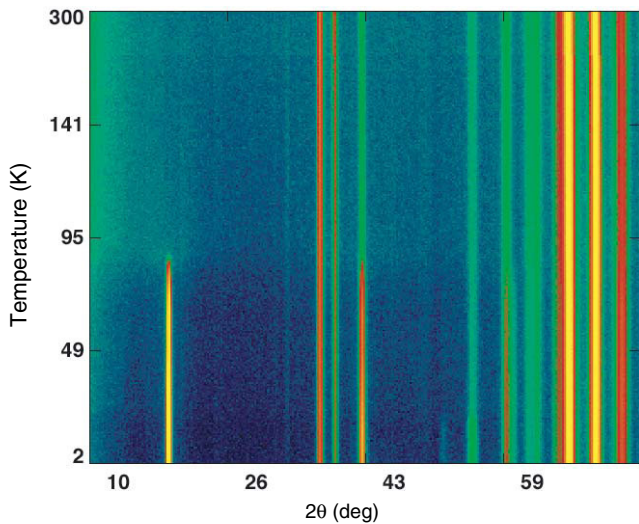
We investigated the evolution of the magnetic structure and magnetoelastic effects of NdMnO<sub>3</sub> by neutron powder diffraction. We confirmed the A-type antiferromagnetic (AF) structure of NdMnO<sub>3</sub> below  $T_N \approx 82$  K with magnetic moments parallel to the  $b$  axis of the orthorhombic crystal structure (space group  $Pbnm$ ). We found that the magnetic moments of Nd order below about  $T_N(\text{Nd}) \approx 20$  K in a ferromagnetic structure with moments parallel to the  $c$  axis. At the same temperature the magnetic moments of Mn develop a ferromagnetic component parallel to the  $c$  axis. We found strong magnetoelastic effects associated with the AF transition at  $T_N \approx 82$  K. The effect is very prominent for the  $b$  lattice parameter. All three lattice parameters and therefore the unit cell volume contracts at  $T_N \approx 82$  K. We treated quantitatively the magnetoelastic effect of the  $b$  lattice parameter and found that the extra change in the lattice parameter  $\Delta b$  due to the magnetoelastic effect is proportional to the magnetic moment of the Mn ion. We also determined the critical exponent of the AF phase transition to be  $\beta = 0.296 \pm 0.008$ .

(Some figures in this article are in colour only in the electronic version)

Although the optimally hole-doped PrMnO<sub>3</sub> and NdMnO<sub>3</sub> show very large magnetoresistive effects their parent compounds have attracted much less theoretical, as well as experimental, investigations compared to LaMnO<sub>3</sub> [1–14]. This is certainly due to the presence of the second rare-earth magnetic sublattices that makes them more complex than LaMnO<sub>3</sub>, which has a single magnetic Mn sublattice. These compounds crystallize with the GdFeO<sub>3</sub> type crystal structure with the  $Pbnm$  space group. The MnO<sub>6</sub> octahedra are distorted due to the Jahn–Teller effect. Cooperative Jahn–Teller distortion removes the degeneracy of the  $e_g$  orbitals in the  $t_{2g}^3 e_g^1$  electron configuration of the Mn<sup>3+</sup> ions and stabilizes  $d_{3x^2-r^2}/d_{3y^2-r^2}$  orbitals, which are ordered. The orbital order consists of the ordering of the  $d_{3x^2-r^2}$  and  $d_{3y^2-r^2}$  orbitals in an alternate staggered pattern in the  $a$ – $b$  plane. The orbital ordering pattern repeats itself along the  $c$  axis. This type of orbital order induces A-type antiferromagnetic (AF) ordering [3, 4] below the Néel temperature  $T_N$ . In the A-type AF phase the spins in the  $a$ – $b$  plane are ferromagnetically ordered. The

ferromagnetic planes are stacked antiferromagnetically along the  $c$  axis. The most significant effect on the crystal structure by decreasing ionic radius  $r_R$  of the rare-earth ion R as one moves along the lanthanide series (lanthanide contraction) is an enhancement of the cooperative rotation of the MnO<sub>6</sub> octahedra (the GdFeO<sub>3</sub> type distortion) characterized by the decrease of the Mn–O–Mn bond angle  $\phi$ . This causes a profound effect on the orbital ordering temperature  $T_{OO}$  and also the magnetic ordering temperature  $T_N$ . The orbital ordering temperature  $T_{OO}$  increases monotonically whereas the  $T_N$  decreases significantly. Also the A-type AF phase goes to an E-type phase through the intermediate incommensurate structure that induces multiferroic behaviour [15]. Thus the lighter PrMnO<sub>3</sub>, and especially NdMnO<sub>3</sub> which is the parent compound of both colossal magnetoresistive and multiferroic materials, obviously deserves more experimental and theoretical investigations.

Neutron diffraction [16–18] investigations have established that NdMnO<sub>3</sub> undergoes an antiferromagnetic transition



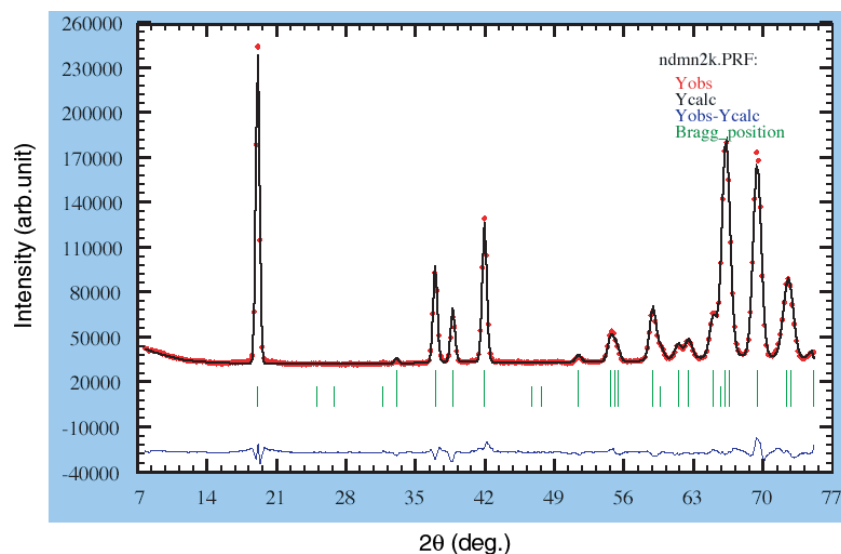
**Figure 1.** Temperature variation of the diffraction intensities of NdMnO<sub>3</sub> measured with a neutron wavelength of  $\lambda = 2.52 \text{ \AA}$ .

at  $T_N \approx 78 \text{ K}$ . The ferromagnetic (001) layers are stacked antiferromagnetically along the [001] axis. The magnetic moments in the ferromagnetic  $a$ - $b$  planes are parallel to the  $b$  axis. At a temperature below  $T = 70 \text{ K}$  a ferromagnetic component along the  $c$  axis develops [17]. At  $T_{Nd} \approx 13 \text{ K}$  the Nd magnetic moments get ordered with a ferromagnetic arrangement [17] parallel to the  $c$  axis. However, the ordering of the Nd atoms has not been observed by Quezel-Ambrunaz [16] nor by Wu *et al* [18]. We recently measured the hyperfine splitting of the Nd nucleus by inelastic neutron scattering on high resolution backscattering neutron spectrometers and showed directly that the Nd magnetic moments do indeed order at low temperature [19]. Here we reinvestigated the magnetic ordering of NdMnO<sub>3</sub> at low temperature by neutron powder diffraction and confirmed the results of Munoz *et al* [17]. In addition we investigated the magnetoelastic effects near the

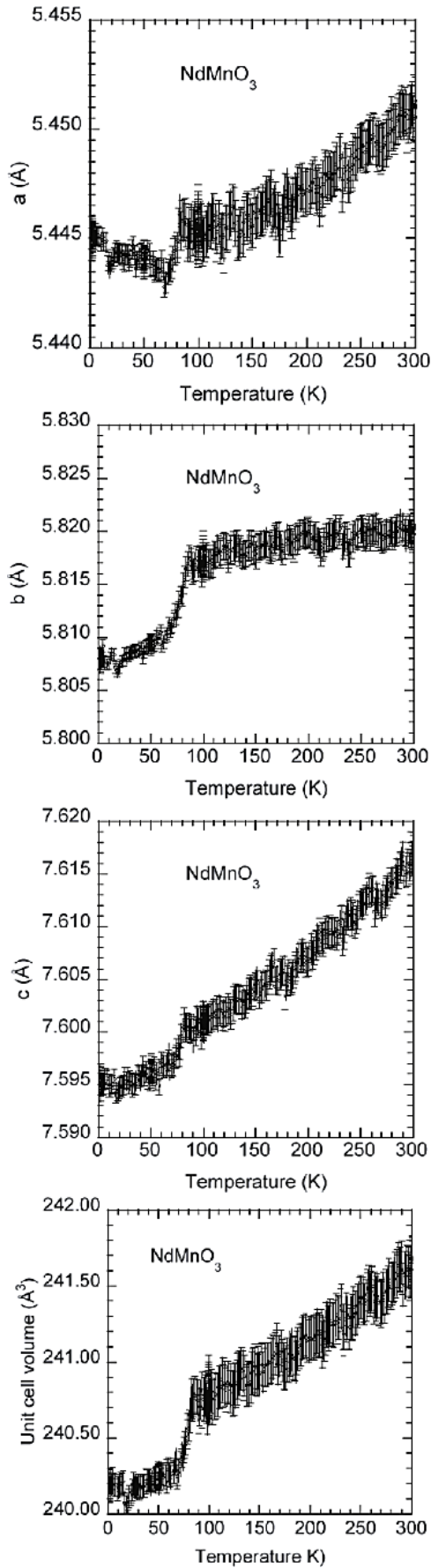
magnetic ordering temperature of NdMnO<sub>3</sub> by determining the temperature variation of the lattice parameters in small temperature steps. It is remarkable that, although the orbital ordering and high temperature magnetic structure of NdMnO<sub>3</sub> are identical to those of LaMnO<sub>3</sub>, the magnetoelastic effects determined during the present investigation differ considerably from those reported by Chatterji *et al* [6] in LaMnO<sub>3</sub>. The presence of a second magnetic Nd sublattice in NdMnO<sub>3</sub> and its complex magnetic ordering at low temperature may be the reason for this difference.

The neutron powder diffraction study of NdMnO<sub>3</sub> was performed on the powder diffractometer D1B of the Institute Laue-Langevin in Grenoble. The powder NdMnO<sub>3</sub> samples were prepared by the method described by Bhattacharya *et al* [13]. About 3 g of the powder NdMnO<sub>3</sub> sample was placed inside a vanadium can fixed to the cold tip of a standard He cryostat capable of generating sample temperatures in the temperature range from 1.5 to 300 K. The neutron wavelength was  $\lambda = 2.52 \text{ \AA}$ . We measured diffraction intensities from NdMnO<sub>3</sub> in the temperature range 1.5–300 K with a very fine temperature step. Figure 1 shows the diffraction pattern as a function of temperature. We did Rietveld [20] profile refinement of the data by using the FULLPROF program [21]. We used the same structure and magnetic models of Munoz *et al* [17], albeit using the space group setting  $Pbnm$  rather than  $Pnma$  used by them. The refinement at temperatures above  $T_N \approx 82 \text{ K}$  showed that the sample did not have any detectable impurity phase. All the Bragg peaks could be indexed and accounted for from the distorted orthorhombic perovskite GdFeO<sub>3</sub> type crystal structure model. The magnetic peaks appear below  $T_N \approx 82 \text{ K}$  and grow in intensities with decreasing temperature. Figure 2 shows the result of the refinement at  $T = 1.5 \text{ K}$ . The agreement factor for the crystal structure refinement was 3.60% and that for the magnetic structure refinement was 4.7%.

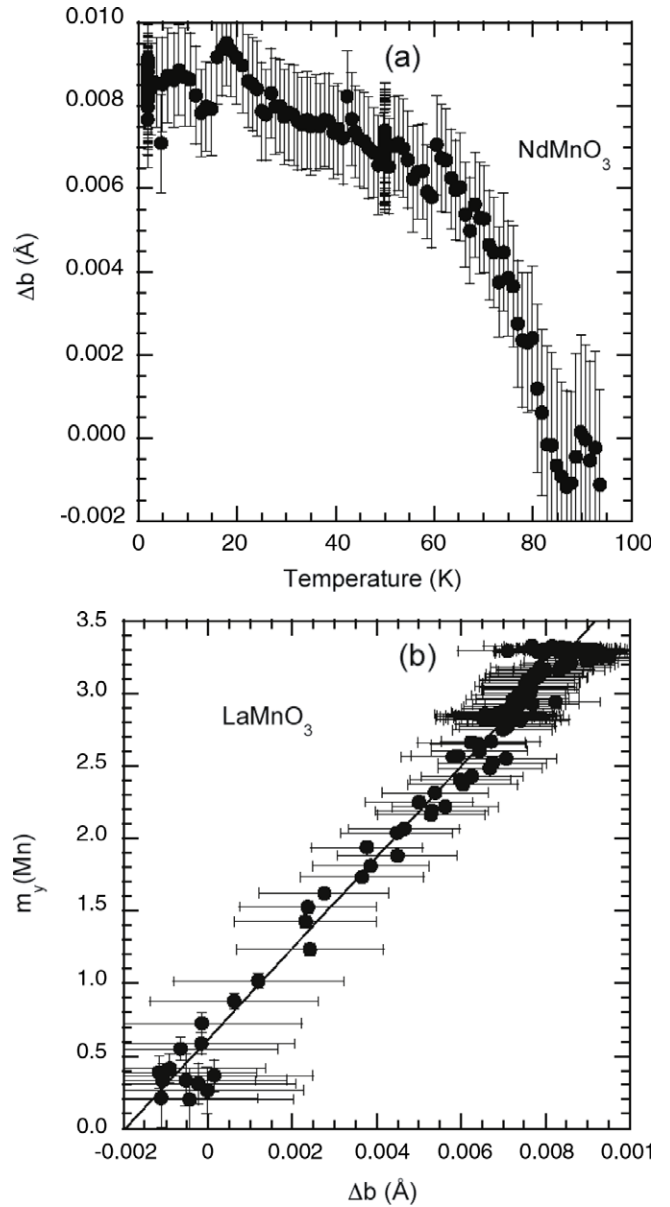
Figure 3 shows the temperature variation of the lattice parameters and the unit cell volume. All three lattice



**Figure 2.** Rietveld profile refinement of the crystal and magnetic structures of NdMnO<sub>3</sub> at  $T = 1.5 \text{ K}$ .

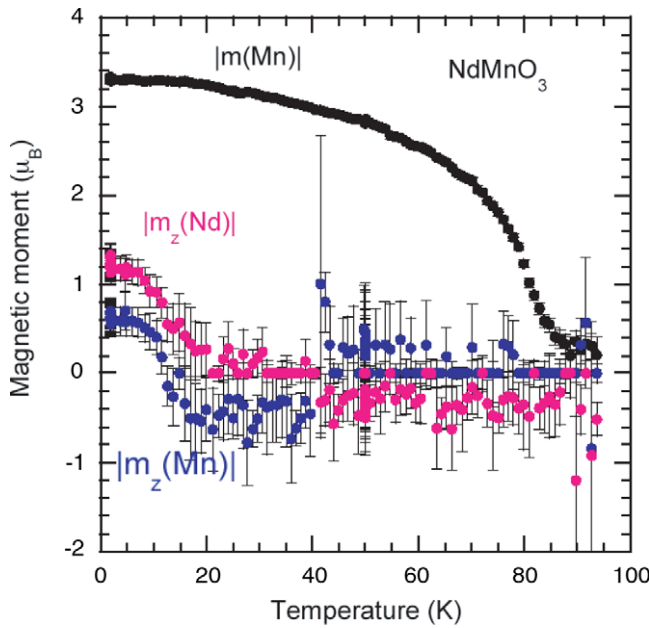


**Figure 3.** Temperature variation of the lattice parameters of NdMnO<sub>3</sub> showing magnetoelastic effects.

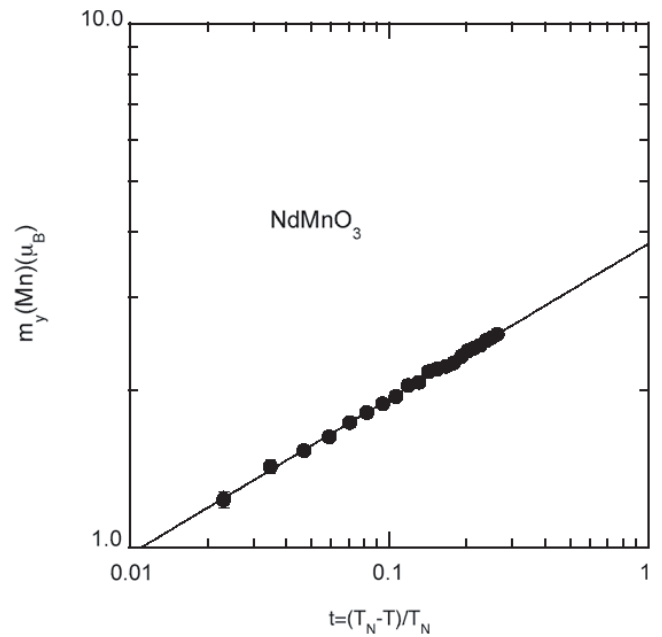


**Figure 4.** (a) Temperature variation of the lattice strain  $\Delta b$  of NdMnO<sub>3</sub>, which is obtained from the lattice parameter  $b$  by subtracting the background by the method described in the text. (b) Plot of the  $y$  component of the magnetic moment of the Mn ion of NdMnO<sub>3</sub> along the  $b$  axis as a function of the lattice strain  $\Delta b$ .

parameters decrease abruptly at  $T_N \approx 82$  K as the temperature was decreased. The unit cell volume therefore also decreases abruptly at  $T_N$ . However, the magnitude of this effect is different along the three axial directions. It is strongest along the  $b$  axis along which the magnetic moments of the Mn ions are oriented below  $T_N$ . There exist smaller magnetoelastic effects along all the other axes at which the magnetic moments of the Nd ions become oriented ferromagnetically along the  $c$  axis and also the ferromagnetic component of the Mn ions develops along the  $c$  axis. However, the error bars of the lattice parameters are too large for doing quantitative analysis. We have, however, succeeded in analysing the magnetoelastic data along the  $b$  axis for which the effect is very prominent and



**Figure 5.** Temperature variation of the ordered magnetic moments of Mn and Nd ions.



**Figure 6.** Log–log plot of ordered magnetic moment versus the reduced temperature.

has been measured with reasonable accuracy. We fitted the lattice parameter in the paramagnetic region by a polynomial and determined the lattice parameter  $b$  below  $T_N$  expected in the absence of the magnetoelastic effect. The change in lattice parameter  $\Delta b$  has been plotted as a function of temperature in figure 4(a). One expects the lattice strain  $\Delta b$  due to the magnetoelastic effect (exchange striction) to be proportional to the order parameter or the ordered magnetic moment [22] along  $b$ . The  $y$  component of the ordered magnetic moment of the Mn atom below  $T_N$  has been plotted as a function of the lattice strain  $\Delta b$  shown in figure 4(b). The linear relationship is quite evident from the figure despite the large error bars of the measured lattice strain  $\Delta b$ . The magnetic moment determined from the refinement of magnetic intensities described in the following paragraph is of much greater accuracy than that of  $\Delta b$ .

Surprisingly the magnetoelastic effect determined in  $\text{NdMnO}_3$  differs considerably from that reported by Chatterji *et al* [6] in  $\text{LaMnO}_3$  although the orbital ordering and the high temperature magnetic structure of  $\text{NdMnO}_3$  are identical to those of  $\text{LaMnO}_3$ . This is probably because  $\text{NdMnO}_3$  has an additional Nd magnetic sublattice leading to complex magnetic ordering at low temperature. Contrary to the case of  $\text{LaMnO}_3$  which has just Mn–Mn exchange interaction,  $\text{NdMnO}_3$  has in addition the Nd–Mn and Nd–Nd exchange interactions and their coupling with the lattice.

The magnetic structure of  $\text{NdMnO}_3$  was analysed starting from the model of Munoz *et al* [17]. Figure 5 shows the temperature variation of the magnetic moment of Mn ions along the  $b$  axis as well as that of the ferromagnetic components of the magnetic moments of both Mn and Nd ions along the  $c$  axis. These ferromagnetic components of Mn and Nd ions appear below about 20 K. However, determination of these components of the ferromagnetic moments of Mn and Nd

ions is difficult because the moments are strongly correlated. The temperature variation of the magnetic moment of Mn ions along the  $b$  axis, however, is well determined and could be analysed quantitatively. We therefore attempted to extract the critical exponent  $\beta$  from these data. At first we fitted the data in the temperature range of 60–80 K by

$$m(T) = m_0((T_N - T)/T_N)^\beta. \quad (1)$$

The least-squares fit gave  $m_0 = 3.80 \pm 0.04 \mu_B$ ,  $T_N = 81.7 \pm 0.2 \text{ K}$  and  $\beta = 0.296 \pm 0.008$ . Using the fitted value  $T_N = 81.7 \text{ K}$  we calculated the reduced temperature  $t = (T_N - T)/T_N$  and plotted the magnetic moment versus the reduced temperature in a log–log plot shown in figure 6. From the slope of the fitted straight line we get  $\beta = 0.296$ . The critical exponent  $\beta$  thus determined is closer to the three-dimensional Ising value  $\beta = 0.326$  than to the corresponding Heisenberg value  $\beta = 0.367$ . The present experimental determination of  $\beta$  is not done with enough temperature resolution close to the critical region and therefore should not be taken too seriously. We already commented that the ferromagnetic components of the magnetic moments of Mn and Nd ions are strongly correlated. Looking at figure 5 we note that these moments are essentially zero or at least very small down to about  $T_{\text{Nd}} \approx 20 \text{ K}$ . Below  $T_{\text{Nd}} \approx 20 \text{ K}$  the ferromagnetic components of both Mn and Nd ions increase substantially and their determination is more accurate. We find the ordering temperatures of these moments are about the same, namely  $T_{\text{Nd}} \approx 20 \text{ K}$ . This result is consistent with our recent element-specific investigation by inelastic neutron scattering [19] of the hyperfine field of the Nd electronic magnetic moment at the Nd nucleus. The present results are only in qualitative agreement with those of Munoz *et al* [17]. The important difference is that our results show that the ferromagnetic ordering of both

Mn and Nd ions sets in below the same temperature which we call  $T_{Nd} \approx 20$  K. Munoz *et al* [17] found that Mn ions develop a ferromagnetic component at a much higher temperature just below  $T_N$ . We believe on the contrary that the ferromagnetic ordering of the Nd ions induces the ferromagnetic component in the Mn sublattice.

In summary we investigated the evolution of the magnetic structure and magnetoelastic effects of NdMnO<sub>3</sub> by neutron powder diffraction. We confirmed the A-type antiferromagnetic (AF) structure of the Mn magnetic sublattice of NdMnO<sub>3</sub> below  $T_N \approx 81.7$  K and found that the magnetic moments of Nd order below at about  $T_N(Nd) \approx 20$  K in a ferromagnetic structure with moments parallel to the *c* axis. At the same temperature the magnetic moments of Mn develop a ferromagnetic component parallel to the *c* axis. We found strong magnetoelastic effects associated with the AF transition below  $T_N \approx 81.7$  K and established a linear relationship between the ordered magnetic moment of the Mn ion and the extra lattice parameter contraction  $\Delta b$  due to the magnetoelastic effect.

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