Spin reorientation and structural changes in NdFeO$_3$

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Abstract
The crystal structure and the Fe^{3+} magnetic moment ordering in NdFeO$_3$ have been studied by high-resolution neutron powder diffraction at temperatures ranging from 1.5 to 300 K. Between 100 and 200 K a spin reorientation transition is observed with gradual changes of the directions of the Fe^{3+} ordered magnetic moments. The spin reorientation temperature range is associated with changes of the crystal structure. The b lattice parameter has a broad local minimum in the spin reorientation region. There is also a coherent rotation of the FeO$_6$ octahedra with an increase of the Fe–O–Fe angles with increasing temperature. These structural changes tend to increase the strength of the in-plane (a, b) Fe–Fe interactions and to decrease the strength of Fe–Fe interactions along the c-axis as the temperature increases. The Fe^{3+} magnetic moment ordering above 200 K is close to the antiferromagnetic G_x type. The total Fe^{3+} ordered magnetic moment at room temperature equals 3.87(5) μ_B. Below 100 K the Fe^{3+} magnetic moment ordering is a combination of the antiferromagnetic G_x and G_z type. The ordered Fe^{3+} magnetic moment components at 1.5 K are $M_x = 1.30(15)$ μ_B and $M_z = 3.97(5)$ μ_B. There is a C-type antiferromagnetic ordering of the Nd^{3+} magnetic moments at 1.5 K with the ordered Nd^{3+} moment value of 1.10(7) μ_B.

1. Introduction

The group of rare earth (R) orthoferrites with the general formula RFeO$_3$ belongs to the widely studied family of transition metal oxides with distorted perovskite structure [1]. The magnetic properties of rare earth orthoferrites are interesting because of the magnetic interactions of the two different types of magnetic ions: Fe^{3+} and R^{3+}. The competition of Fe–Fe, R–Fe and R–R interactions leads to a few interesting phenomena in these materials. At high temperatures the magnetic properties of RFeO$_3$ systems depend mostly on the Fe–Fe interactions which lead to an antiferromagnetic type ordering with Néel temperatures ranging from 620 to 740 K [1, 2]. As the temperature is lowered to about 100–200 K the competition of the Fe–Fe and R–Fe interactions [3] leads to a so-called spin-reorientation transition of the ordered Fe^{3+} magnetic moments [1]. Spin reorientation is a more general phenomenon observed in many compounds containing rare earth and iron ions. It is especially important for Nd–Fe compounds in which spin reorientation was observed in intermetallic compounds such as
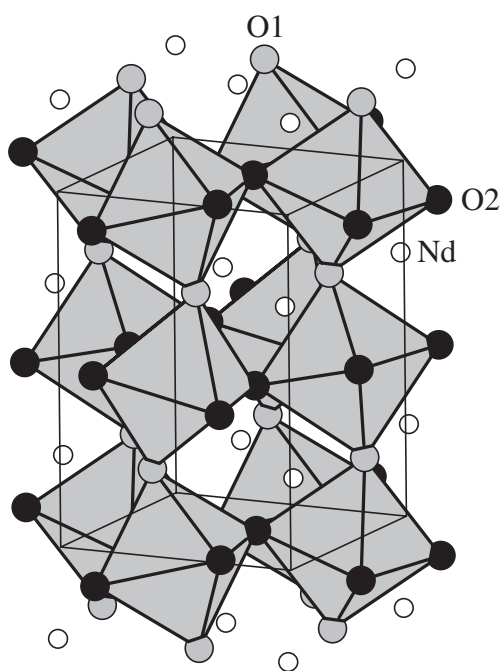
Figure 1. Schematic presentation of the $NdFeO_3$ orthorhombic unit cell. The Nd atoms are shown as small empty circles. The Fe atoms (not shown) are located at the centres of the FeO_6 corner-linked octahedra. The oxygen atoms located in O1 positions are shown as grey circles, while the oxygen atoms at O2 positions are shown as black circles.

$Nd_2Fe_{14}B$ [4], $NdDyFe_{14}B$ [5], $Nd_6Fe_{13}Si$ [6], as well as in oxides $NdFeO_3$ [7], $SrNdFeO_4$ [8], and $CaNdFeO_4$ [9]. The present studies are focused on neodymium orthoferrite $NdFeO_3$. The structural and magnetic properties of $NdFeO_3$ have been widely studied in the past [1], but the present paper describes new results of high-resolution neutron diffraction measurements which provide new information about the spin reorientation process and structural changes associated with it.

1.1. Crystal structure of $NdFeO_3$

The orthorhombic crystal structure of $NdFeO_3$ has been described by several authors [10–16] by using the space group *Pbnm* with the following distribution of ions in crystallographic positions: Nd^{3+} ions in (4c), Fe^{3+} ions in (4b) and O^{2-} ions in (4c) and (8d). The Fe^{3+} ions are surrounded by six O^{2-} ions arranged in FeO_6 octahedra. The orientation of the corner-sharing FeO_6 octahedra in $NdFeO_3$ can be described by using the tilting Glazer system $a^+a^-a^-$ [17–19] with in-phase tilting about the direction of the c-axis (space group *Pbnm*). A schematic presentation of the $NdFeO_3$ orthorhombic unit cell is shown in figure 1.

The orthorhombic distortion from the undistorted cubic perovskite structure of $RFeO_3$ compounds increases with increasing rare earth atomic number. The lattice constant b/a ratio changes monotonically from 1.017 for $PrFeO_3$ up to 1.064 for $LuFeO_3$ with a relatively small value of 1.024 for $NdFeO_3$ [12]. In order to study the spin reorientation transition in $NdFeO_3$ one has to determine the directions of the ordered magnetic moments. This can be done by neutron powder diffraction but very high resolution [20, 21] and sample quality are required.

Table 1. Review of neutron powder diffraction studies of the Fe^{3+} magnetic moment ordering in NdFeO$_3$ published in the literature. The method used was constant wavelength (CW) or time-of-flight (TOF). The ordering symbol $G_x 13° \rightarrow z$ means a $G_x G_z$ ordering in which the magnetic moments are canted from the x-axis by 13° towards the z-axis. $|M|$ in column 3 refers to the value of the total ordered Fe^{3+} magnetic moment observed at RT or 200 K for [7]. $|M|$ in column 5 refers to the value of the total ordered Fe^{3+} magnetic moment observed at the low temperature indicated in column 4.

Method	Ordering at RT	$\|M\|$ (μ_B)	Ordering at LT	$\|M\|$ (μ_B)	Reference
1	2	3	4	5	6
CW	G	—	43 K G	4.5(7)	[22]
CW	G_x	—	—	—	[24]
CW	G_x	—	4 K G_z	—	[25]
TOF	G_x 13° → z	—	80 K G_z	—	[26]
TOF	G_x 15° → y	—	—	—	[27]
CW	G_x	3.82(4)	8 K G_z	4.13(4)	[15]
CW	G_x 12° → z & 7° → y	4.24(24)	50 K G_z 10° → x & 7° → y	4.39(10)	[7]
CW	—	—	1.5 K G_z	4.24(2)	[28]
CW	—	—	1.5 K G_z 10° → x	4.18(5)	[14]
CW	—	—	1.5 K G_z 20° → x	4.12(5)	[29]
CW	G_x up to 13° → z	3.87(5)	1.5 K G_z 20° → x	4.18(5)	This work

1.2. Magnetic ordering of Fe^{3+} magnetic moments in NdFeO$_3$

The first neutron diffraction studies of the magnetic ordering in NdFeO$_3$ [22] have shown an antiferromagnetic ordering of the Fe^{3+} magnetic moments with the Néel temperature $T_N = 760$ K. In this ordering, denoted as G-type [23], each Fe^{3+} magnetic moment is aligned antiparallel to the moments of all six nearest Fe^{3+} neighbours. The ordering is denoted as G_x, G_y or G_z if the ordered magnetic moments are directed along the x, y or z axes, respectively. The directions of the Fe^{3+} magnetic moments could not be determined in [22] because of insufficient instrumental resolution.

The results of several high-resolution neutron powder diffraction studies [7, 14, 15, 22, 24–29] of the Fe^{3+} magnetic moment ordering in NdFeO$_3$ at room temperature (RT) and low temperatures in NdFeO$_3$ are reviewed in table 1. All these studies confirm that the ordering of the Fe^{3+} magnetic moments is close to the G_x type at RT and close to the G_z type below 80 K. The ordered ferromagnetic component of F-type in NdFeO$_3$ is about 120 times smaller that the ordered antiferromagnetic G-type component [30], and it is too small to give a measurable contribution to the neutron powder diffraction patterns.

1.3. Spin reorientation in NdFeO$_3$

The first neutron diffraction evidence of the spin reorientation process in NdFeO$_3$ [25] has shown a gradual change of the ordered Fe^{3+} magnetic moment from G_z type to G_x type between 70 and 160 K. Further high-resolution neutron diffraction measurements [7, 15] have confirmed a continuous spin reorientation process in the range from 105 K up to 180 K and that the ordering below and above the reorientation transition, i.e. at 200 and at 50 K, differs slightly from the pure G_x and G_z modes, as shown in table 1.

The spin reorientation transition in NdFeO$_3$ has been also studied in previous decades by several techniques including NMR [31, 32], Young's modulus [33] and magnetic susceptibility [30, 33, 34]. Other evidence of the spin reorientation in NdFeO$_3$ has been obtained by inelastic neutron scattering measurements [35]. The ground-state doublet of Nd^{3+} ions in NdFeO$_3$ is split by 0.49 meV due to the molecular field. The inelastic neutron scattering

peaks change their shape at temperatures inside the spin reorientation region due to a change of the distribution of molecular fields at Nd^{3+} sites in $NdFeO_3$ [35].

1.4. Magnetic ordering of Nd^{3+} magnetic moments in $NdFeO_3$

Low-temperature powder [14, 28, 36] and single-crystal [37] $NdFeO_3$ neutron diffraction studies performed at 1.5 K and below have shown a long-range C-type [23] antiferromagnetic ordering of the Nd^{3+} magnetic moments. The values of the ordered Nd^{3+} magnetic moments is about 1.14(10) μ_B at 1.5 K [14, 28, 36, 38]. Low-temperature $NdFeO_3$ neutron diffraction [37] and inelastic neutron scattering [36] studies have shown a long-range ordering of the nuclear magnetic moments of Nd nuclei below about 500 mK. The long-range ordering of the Nd^{3+} magnetic moments below 1 K have also been studied by specific heat measurements [39].

1.5. Motivation

The main motivation of this study was to verify to what extent the spin reorientation transition in $NdFeO_3$ is accompanied by changes of the structural parameters. Accurate $NdFeO_3$ single-crystal x-ray [12] and synchrotron radiation (SR) [13] diffraction studies were performed only at RT. Previous neutron diffraction studies of $NdFeO_3$, described in table 1, were focused on magnetic structure determination and gave only limited information about the temperature changes of the crystal structure.

2. Experimental details

Neutron powder diffraction measurements on $NdFeO_3$ were performed using the high-resolution neutron powder diffractometer D2B at ILL Grenoble operating at the neutron wavelength $\lambda = 1.5942$ Å. A polycrystalline sample of $NdFeO_3$ was placed in a thin-walled vanadium container attached to the standard ILL orange cryostat. The measurements were performed at several temperature steps ranging from 1.5 to 290 K. The measurements covered the Q range from 1 to 7.5 Å^{-1}, where Q is the length of the scattering vector $Q = (4\pi/\lambda)\sin\theta$ (2θ being the scattering angle).

3. Results

3.1. Crystal structure of $NdFeO_3$ at room temperature and 1.5 K

The observed neutron diffraction patterns of $NdFeO_3$ show no traces of any impurity phases. The observed Bragg peaks were narrow with an FWHM corresponding to $\Delta d/d \simeq 1.3 \times 10^{-3}$ for Q-values around 6 Å^{-1}. The parameters describing the crystal and magnetic ordering in $NdFeO_3$ were refined by the Rietveld method using the program FullProf [40]. The starting structural parameters were taken from earlier $NdFeO_3$ neutron diffraction studies [14]. Individual isotropic Debye–Waller factors were fitted for Nd, Fe and O atoms. The neutron diffraction patterns were also analysed by assuming refinable oxygen occupancies. The resulting occupancies varied from 0.993 to 1.000 oxygen atom per site, which indicates that the number of oxygen vacancies is small, and that the nominal composition of $NdFeO_3$ is correct. The magnetic contribution was calculated by assuming a G-type antiferromagnetic ordering of the Fe^{3+} magnetic moments [22]. The refinement of the 1.5 K patterns needed to include an antiferromagnetic ordering of the Nd^{3+} magnetic moments of C-type [23] as already discussed in [14, 27, 37]. In order to illustrate the refinement quality, the measured and refined neutron diffraction patterns of $NdFeO_3$ obtained at 1.5 K are shown in figure 2.
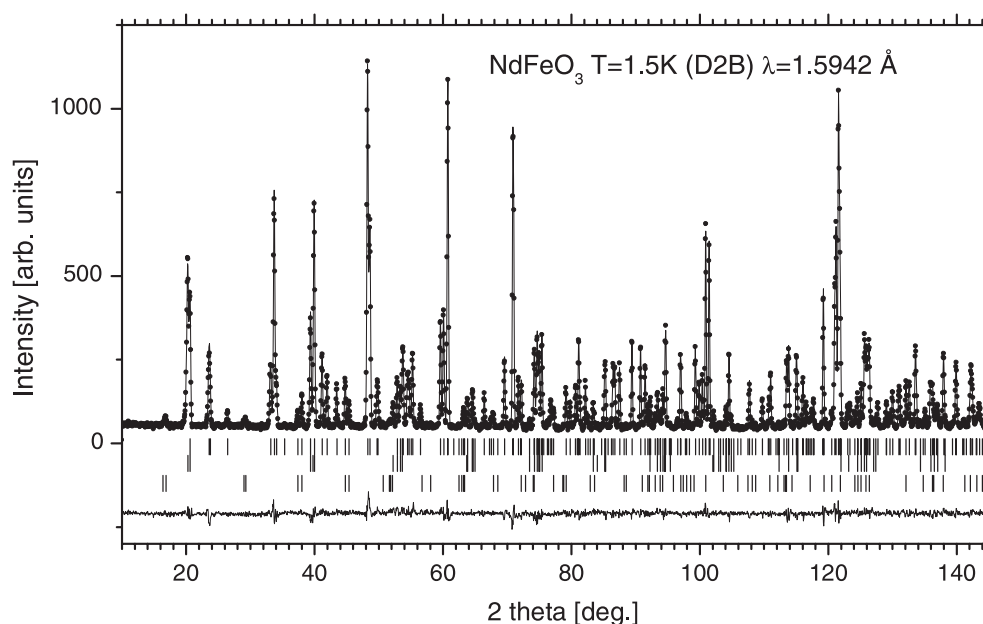
Figure 2. Results of the Rietveld refinement of the neutron powder diffraction pattern of NdFeO$_3$ at $T = 1.5$ K. The solid circles present the measured data while the solid line presents the calculated diffraction pattern. Below the plot a difference curve is given. Ticks indicating the positions for the Bragg peaks due to the crystal structure of NdFeO$_3$, the antiferromagnetic G-type ordering of the Fe^{3+} magnetic moments and the C-type antiferromagnetic ordering of Nd^{3+} magnetic moments are shown from top to bottom, respectively.

The structural parameters refined from the neutron diffraction patterns at 290 and 1.5 K are shown in table 2. The values of the a, b, c lattice parameters at RT determined in this paper differ from earlier results of single-crystal x-ray [12] and SR [13] NdFeO$_3$ diffraction studies. It is however important to point that our present a, b, c values determined at RT are between those of [12] and [13]. The present values of a, b, c refined at 1.5 K are in satisfactory agreement with those from [14]. The main goal of this paper is not a determination of the absolute values but rather the temperature changes of the lattice parameters a, b, c. Another important point is that the atomic position parameters refined at 290 and 1.5 K agree within 2σ error with the results of RT single-crystal NdFeO$_3$ studies [12, 13] and low-temperature studies [14], respectively. It should be noted that due to the high resolution of the present neutron diffraction measurements the estimated errors are much smaller than those in the earlier work [14]. The Debye–Waller values shown in table 2 differ from those obtained in earlier NdFeO$_3$ studies [12–14].

3.2. Temperature dependence of lattice parameters

The temperature dependence of the refined values of the lattice parameters a, b, c and of the unit cell volume V is shown in figures 3(a)–(d), respectively. The refined values are compared with the reference results of earlier RT studies [12, 13], as well as with the results of neutron studies at 1.5 K [14]. The reference values of the b lattice parameter at RT from [12, 13] have been omitted because it would be difficult to present them in the same scale (figure 3(b)).

One can see that a and c parameters increase with temperature but the b lattice parameter has a local minimum near 150 K. It is important to note that the fairly broad minimum of

Table 2. Parameters of the crystal and magnetic structure of $NdFeO_3$ obtained from Rietveld refinement of neutron diffraction patterns at 290 and 1.5 K. The space group is *Pbnm*. The quality of fit indicators R_p, R_{wp}, R_{wp} and R_{mag} are defined in [40].

Parameter	290 K	1.5 K
a (Å)	5.451 02(10)	5.441 04(10)
b (Å)	5.588 08(10)	5.587 17(10)
c (Å)	7.761 65(12)	7.746 07(13)
x_{Nd} (4c)	0.9887(3)	0.9878(3)
y_{Nd} (4c)	0.0487(2)	0.0504(2)
x_{O1} (4c)	0.0862(3)	0.0859(3)
y_{O1} (4c)	0.4756(3)	0.4747(3)
x_{O2} (8d)	0.7048(2)	0.7038(2)
y_{O2} (8d)	0.2950(2)	0.2957(2)
z_{O2} (8d)	0.0460(2)	0.0462(2)
B_{Nd} (Å^2)	0.270(23)	0.013(20)
B_{Fe} (Å^2)	0.217(18)	0.051(15)
B_{O} (Å^2)	0.438(23)	0.133(20)
$M_x^{Fe^{3+}}$ (μ_B)	3.84(5)	1.24(15)
$M_z^{Fe^{3+}}$ (μ_B)	0.46(48)	3.96(5)
$M_y^{Nd^{3+}}$ (μ_B)	—	1.10(7)
R_p (%)	4.88	4.99
R_{wp} (%)	6.30	6.53
R_{wp} (%)	4.17	3.86
R_{mag}^{Fe} (%)	2.88	4.91
R_{mag}^{Nd} (%)	—	31.0
χ^2	1.58	1.76

the *b* lattice parameter extends from 100 to 200 K, i.e. it coincides with the Fe^{3+} magnetic moment reorientation temperature range in $NdFeO_3$ [7]. A similar minimum of one of the lattice parameters in the vicinity of a magnetic transition temperature has been observed in β-MnO_2 [41, 42].

3.3. Temperature changes of the FeO_6 octahedra network arrangement

Knowledge of the structural arrangement of the FeO_6 octahedra network is very important for the understanding of the magnetic properties of rare earth orthoferrites. An inspection of crystallographic [12] and magnetic [2] data on the orthoferrites shows that the magnetic interactions are mainly due to the superexchange via Fe–O–Fe bonds [1]. The Fe–O bondlengths in the whole $RFeO_3$ family vary by less than 1% [12], while the average Fe–O–Fe angle (α) decreases continuously from 153.3° in Pr down to 140.7° in Lu [12]. The observed Néel temperatures also decrease from 740 K in Pr down to 623 K in Lu in agreement with the superexchange model scaling: $T_N = T_N(0)\cos\alpha$ [1, 2].

In the $NdFeO_3$ structure there are two different nearest neighbour Fe–Fe distances. The Fe–Fe distance between atoms in the same horizontal plane, e.g. between $(\frac{1}{2}, 0, 0)$ and $(0, \frac{1}{2}, 0)$, will be denoted as t_{ab}, while between $(\frac{1}{2}, 0, 0)$ and $(\frac{1}{2}, 0, \frac{1}{2})$, it will be denoted as t_c. The values of t_{ab}, and t_c are calculated as:

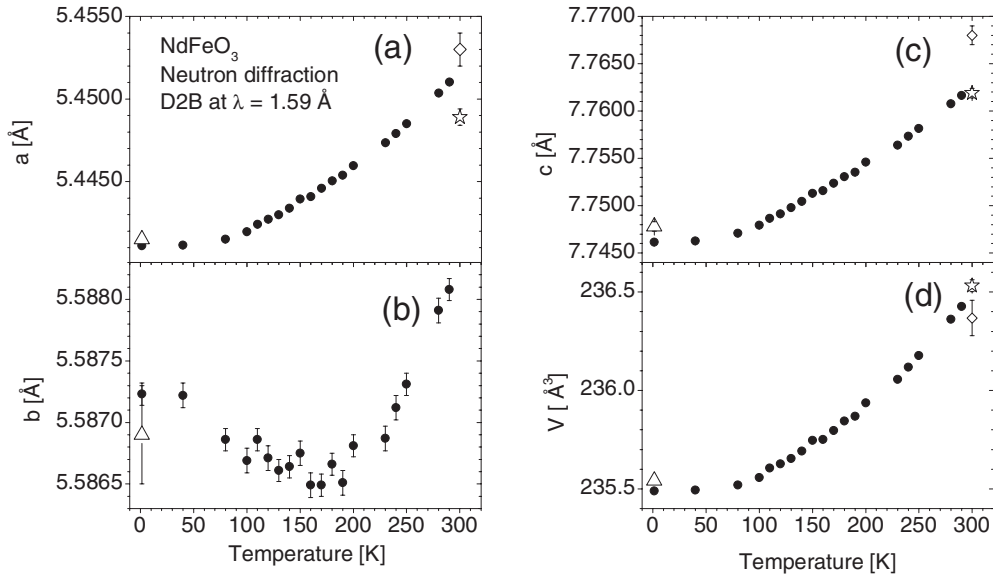$$t_{ab} = \sqrt{\frac{a^2}{4} + \frac{b^2}{4}} \qquad t_c = \frac{c}{2}.$$

Figure 3. Temperature dependence of the lattice parameters (a) a, (b) b, (c) c and (d) unit cell volume, V of NdFeO₃ determined from Rietveld refinement of neutron powder diffraction data. The present results are compared with reference RT x-ray results from [12] (◇), [13] (✩) and low-temperature neutron results [14] (△) (except for the b parameter at RT where the discrepancies with the [12] and [13] data would be difficult to present in this scale). Note the different vertical axis scales on the plots of the a, c lattice parameters and the b lattice parameter. The statistical errors of a, c and V are smaller than the plot symbols.

The temperature dependence of the lattice parameters shown in figure 3 gives a decrease of the t_{ab}/t_c ratio from 1.0068 at 1.5 K down to 1.0058 at 290 K.

As is shown in figure 1, each FeO₆ octahedron is composed of two pairs of Fe–O2 bonds which are slightly out of the (a, b) plane and one pair of Fe–O1 bonds which are nearly parallel to the c-axis (inclination about 14°).

The temperature dependence of the different Fe–O bondlengths and Fe–O–Fe angles observed in NdFeO₃ are shown in figure 4 (left-hand and right-hand panels, respectively). The present data are compared with the reference data [12–14]. The 'nearly vertical' Fe–O1 bondlength shows an increasing trend with temperature while the Fe–O1–Fe angle do not vary in a systematic way with temperature. The long and short 'nearly in-plane' Fe–O2 bondlengths (see figure 4) vary within ±0.002 Å without any evident correlation with temperature changes, while the Fe–O2–Fe angle increases with temperature.

One can conclude that the Fe–O2 bonds do not expand with temperature increase and the FeO₆ octahedra perform a coherent rotation around the (nearly vertical) Fe–O1 bonds. A similar behaviour was observed in another distorted perovskite type material, Sr₂LaFe₃O₉₋δ [43], in which the Fe–O distances measured at RT and 50 K retain the same value within experimental error while the Fe–O–Fe angle decreases from 174° to 171°.

3.4. Magnetic ordering of Fe³⁺ and Nd³⁺ magnetic moments at 1.5 K

The refined Fe³⁺ ordered magnetic moment components at 1.5 K are $M_x = 1.30(15)$ μ_B and $M_z = 3.97(5)$ μ_B, which gives a total moment of 4.14(9) μ_B canted from the c-axis by about 19(3)° towards the a-axis in agreement with earlier low-temperature NdFeO₃
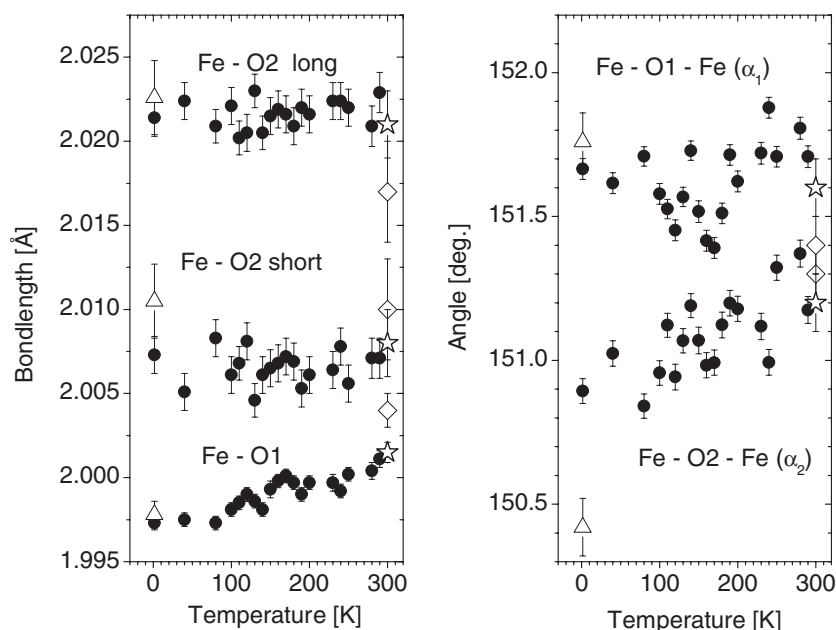
Figure 4. Values of the Fe–O1, Fe–O2 bondlengths (left panel) and Fe–O1–Fe, Fe–O2–Fe angles (right panel) in NdFeO$_3$ obtained from Rietveld refinement of neutron powder diffraction patterns are shown as solid circles. The present results are compared with RT x-ray results [12] ($\diamondsuit$), [13] ($\star$) and low-temperature neutron results [14] ($\triangle$).

neutron diffraction studies [29]. Due to the relatively small intensity of the magnetic Bragg peaks corresponding to the C-type ordering, (010) + (100) and (102) + (012), it was not possible to determine precisely the direction of the Nd^{3+} magnetic moments. By following the conclusions of our earlier NdFeO$_3$ single-crystal neutron diffraction studies it was assumed that the magnetic ordering is of C$_y$ type only. The resulting value of the ordered Nd^{3+} magnetic moment is 1.10(7) μ_B also in agreement with earlier values [14, 37].

3.5. Reorientation of the ordered Fe^{3+} magnetic moments

The Rietveld refinement of the ordered Fe^{3+} magnetic moments was performed assuming a $G_x G_z$ antiferromagnetic ordering. The resulting values of the total ordered Fe^{3+} magnetic moment is shown in figure 5 (upper panel) while the M_x and M_z components are shown in figure 5 (lower panel). The total magnetic moment at RT and 1.5 K is shown to be similar to the results of earlier neutron diffraction [15] and Mössbauer studies [44]. Earlier studies [7] were interpreted by assuming a three-component ordering, $G_x G_y G_z$. The values of M_y determined in [7] varied in the range between 0.2 and 1.0 μ_B with a statistical error of about 0.3 μ_B and they did not show any clear temperature trend, so they have not been plotted in figure 5. The analysis of the present data assuming a $G_x G_y G_z$ type ordering gave M_y values of the same order as their statistical errors, so it was assumed that there is no G_y ordering. One can compare the present values of M_x and M_z with the values from [7] as shown in figure 5 (lower panel) only qualitatively because of the different assumptions regarding the G_y ordering.

The refined values of M_x start to increase at the expense of M_z at 100 K, and these changes proceed gradually up to 190 K. In the temperature range from 190 to 290 K we compare the results of refinements assuming a single G_x ordering and mixed $G_x G_z$ orderings. The results
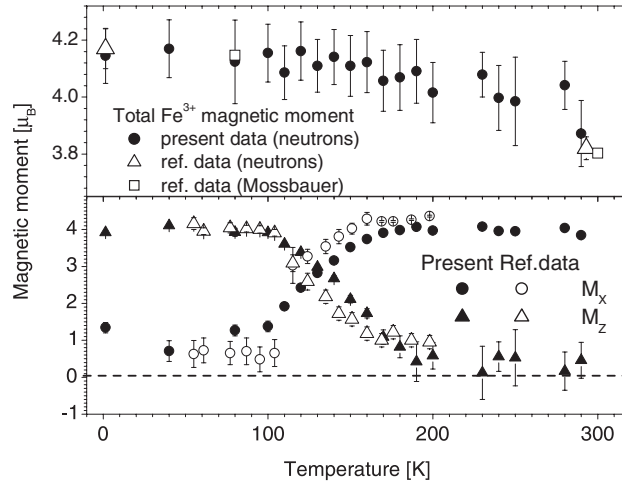
Figure 5. Temperature dependence of the total ordered Fe^{3+} magnetic moment (upper panel) and its M_x and M_z components (lower panel) in NdFeO₃ obtained from Rietveld refinement of neutron powder diffraction patterns. The present data are given by solid symbols while the reference data are given by empty symbols. The upper panel shows reference values of the magnetic moment obtained from Mössbauer data [44] (□) and neutron diffraction [15] data (△). The lower panel shows reference data from [7].

give similar values of the fit quality indicator R_{mag} [40]. However, the relative statistical errors of the M_z values of about 0.5–0.8 μ_B obtained in the mixed $G_x G_z$ refinement are of the order of 100%, so it is concluded that the most probable interpretation is a G_x-type ordering with a possible deviation from the a-axis by no more than 13° above 190 K. Due to resolution limitations of the present measurements at the (101) + (011) magnetic Bragg peaks it is not possible to determine the directions of the ordered Fe^{3+} magnetic moments more precisely and to remove the ambiguities of the earlier NdFeO₃ magnetic structure determinations reviewed in table 1. It is important to note the temperature dependence of the ordered magnetic moments components M_x, M_z is smooth and that the spin reorientation transition is not associated with any sudden changes of the total magnetic moment, as shown in figure 5.

4. Conclusions

The present neutron powder diffraction studies on NdFeO₃ confirm that there is a gradual spin reorientation of the ordered Fe^{3+} magnetic moments between 100 and 190 K. The most important conclusions are related to structural changes of NdFeO₃ in the spin reorientation region. First of all, the thermal lattice expansion in the b direction is much smaller as compared with the expansion along the a and c directions. It is important to note that the spin reorientation occurs in the (a, c) plane, i.e. the plane perpendicular to the b-axis. Secondly, the temperature changes of the FeO₆ octahedra network arrangement above 100 K may influence the magnetic Fe–Fe interactions in the system. As the temperature increases the interactions within the (a, b) plane become stronger as compared with the interactions along the c-axis. This is due to several factors: (i) the increase of the 'in-plane' Fe–O2–Fe angle, (ii) an increase of the 'vertical' Fe–O1 bondlengths without changes of the Fe–O1–Fe angles, and (iii) decrease of the ratio of the in-plane to vertical Fe–Fe distances t_{ab}/t_c with increasing temperature. All these structural changes tend to favour a change from the G_z-type ordering at low temperatures to the G_x-type ordering at high temperatures. The present results show clearly that realistic

models of magnetic interaction in NdFeO$_3$ should take into account the spin–lattice coupling which leads to the above-described effects.

Acknowledgment

References

[1] Landolt-Börnstein 1994 *Numerical Data and Functional Relationships in Science and Technology* Group III, vol 27f3, ed H P J Wijn (Berlin: Springer)
[2] White R L 1969 *J. Appl. Phys.* **40** 1061
[3] Yamaguchi T 1974 *J. Phys. Chem. Solids* **35** 479
[4] Abache C and Oesterreicher H 1985 *J. Appl. Phys.* **57** 4112
[5] Yelon W B, Foley B, Abache C and Oesterreicher H 1986 *J. Appl. Phys.* **60** 2982
[6] Isnard O, Long G J, Hautot D, Buschow K H J and Grandjean F 2002 *J. Phys.: Condens. Matter* **14** 12391
[7] Sosnowska I, Steichele E and Hewat A 1986 *Physica* B **136** 394
[8] Oyama S, Wakeshima M, Hinatsu Y and Ohoyama K 2004 *J. Phys.: Condens. Matter* **16** 1823
[9] Oyama S, Wakeshima M, Hinatsu Y and Ohoyama K 2004 *J. Phys.: Condens. Matter* **16** 8429
[10] Geller S and Wood E 1956 *Acta Crystallogr.* **9** 563
[11] Bertaut E F and Forrat F 1956 *J. Phys. Radium* **17** 129
[12] Marezio M, Remeika J P and Dernier P D 1970 *Acta Crystallogr.* B **26** 2008
[13] Streltsov V A and Ishizawa N 1999 *Acta Crystallogr.* B **55** 1
[14] Przeniosło R, Sosnowska I and Fischer P 1995 *J. Magn. Magn. Mater.* **140–144** 2153
[15] Sosnowska I and Fischer P 1982 *Neutron Scattering 1981* ed J Faber Jr (New York: AIP) p 346
[16] Blasco J and Garcia J 1994 *J. Phys. Chem. Solids* **55** 843
[17] Glazer A M 1972 *Acta Crystallogr.* B **28** 3384
[18] Woodward P M 1997 *Acta Crystallogr.* B **53** 32
[19] Woodward P M 1997 *Acta Crystallogr.* B **53** 44
[20] Shirane G 1959 *Acta Crystallogr.* **12** 282
[21] Shaked H 2004 *Physica* B **353** 310
[22] Koehler W C, Wollan E O and Wilkinson M K 1960 *Phys. Rev.* **118** 58
[23] Bertaut E F 1963 *Magnetism III* ed G T Rado and H Suhl (New York: Academic) p 149
[24] Epstein A and Shaked H 1969 *Phys. Lett.* A **29** 659
[25] Pinto H and Shaked H 1972 *Solid State Commun.* **10** 663
[26] Kaun L P *et al* 1976 *Sov. Phys.—Crystallogr.* **21** 212
[27] Sosnowska I and Steichele E 1982 *Neutron Scattering 1981* ed J Faber Jr (New York: AIP) p 309
[28] Sosnowska I and Fischer P 1987 *Phase Transit.* **8** 319
[29] Przeniosło R, Sosnowska I, Fischer P, Marti W, Bartolomé F, Bartolomé J, Palacois E and Sonntag R 1996 *J. Magn. Magn. Mater.* **160** 370
[30] Hornreich R M and Yaeger I 1973 *Int. J. Magn.* **4** 71
[31] Karnachev A S, Kovtun N M, Luikina M M and Solovev E E 1977 *Sov. Phys.—Solid State* **9** 950
[32] Barilo S N *et al* 1991 *Sov. Phys.—Solid State* **33** 354
[33] Belov K P, Kadomtseva A M, Ovchinnikova T L, Timofeeva V A and Uskov V V 1971 *Sov. Phys.—Solid State* **13** 518
[34] Chmielowski M and Sosnowska I 1983 *Solid State Commun.* **48** 1007
[35] Sosnowska I, Loewenhaupt M and Frick B 1988 *J. Physique Coll.* **49** C8 921
[36] Przeniosło R, Sosnowska I and Frick B 2005 in preparation
[37] Bartolomé J, Palacois E, Kuźmin M D, Bartolomé F, Sosnowska I, Przeniosło R, Sonntag R and Łukina M M 1997 *Phys. Rev.* B **55** 11432
[38] Przeniosło R 1992 *PhD Thesis* Warsaw University
[39] Bartolomé F, Kuźmin M D, Bartolomé J, Blasco J, Garcia J and Sapiña J 1994 *Solid State Commun.* **91** 177
[40] Rodriguez-Carvajal J 1992 *Physica* B **192** 55
[41] Regulski M, Przeniosło R, Sosnowska I and Hoffmann J-U 2003 *Phys. Rev.* B **68** 172401
[42] Regulski M, Przeniosło R, Sosnowska I and Hoffmann J-U 2004 *J. Phys. Soc. Japan* **73** 3444
[43] Battle P D, Gibb T C and Lightfoot P 1990 *J. Solid State Chem.* **84** 271
[44] Eibschütz M, Shtrikman S and Treves D 1967 *Phys. Rev.* **156** 562