

Magnetic structure of the spin-1/2 layer compound NaNiO_2

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Abstract. We have carried out high resolution neutron powder diffraction experiments aiming at a determination of the magnetic structure of the $S = 1/2$ layer compound NaNiO_2 . The magnetic moments are ferromagnetically aligned in the NiO_2 layers and antiparallel between layers. The direction of the magnetic moment has a small component along the a -direction.

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1 Introduction

Triangular lattice antiferromagnets have triggered a great deal of interest due largely to the likely physical realization of a long-sought resonating valence bond (RVB) phase of frustrated magnets. This idea, firstly proposed by Pauling [1], was greatly developed in the context of high T_C superconductivity at the end of the eighties and early nineties [2]. Unfortunately, very soon it turned out that RVB ideas were inappropriate in the context of square lattices as the dimer models exhibit crystalline order in a wide variety of the phase space [3]. The search for this exotic magnetic ground state has been pursued in triangular lattices where the occurrence of RVB liquids has been theoretically predicted [4].

Among the triangular lattice antiferromagnet class of compounds the charge transfer insulators LiNiO_2 and NaNiO_2 have raised quite a lot of expectations because of their different physical properties. In these compounds the electronic state of the transition metal ion is found to be Ni^{3+} ($3d^7$) in the low spin configuration ($t_{2g}^6 e_g^1$) [5] with the e_g electron located in a doubly degenerate orbital configuration. NaNiO_2 undergoes a cooperative Jahn-Teller ordering at 480 K that removes this orbital degeneracy by reducing the lattice symmetry from rhombohedral to monoclinic. Finally an antiferromagnetic ordering has been observed to develop at around $T_N = 20$ K [6]. The structurally identical compound, LiNiO_2 , shows neither orbital nor spin orderings, a situation that puzzles the scientific community since long ago. The absence of electronic ordering has led to think that LiNiO_2 may be a good candidate for the realization of a RVB state due to presence of

orbital as well as spin frustration. However quite a number of experimental studies have shown that in addition to a quantum spin-liquid, LiNiO_2 may be considered as 2D frustrated antiferromagnet, or a weakly coupled 2D Ising ferromagnet, or a 2D Heisenberg ferromagnet, or a spin-glass or even possessing ferromagnetic clusters embedded in a frustrated antiferromagnetic matrix. These apparently contradictory interpretations seem to be sample dependent and are very likely originated from the presence of a non-negligible amount of Ni^{2+} sitting in the Li-planes. Indeed, it turns out that the pure compound is very difficult to synthesize and often it is in a non-stoichiometric form $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$. This aspect has been recently revisited in [7].

Despite this controversy regarding the actual magnetic state in LiNiO_2 (or rather $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$), this is still quite different from the *classical* Néel magnet in NaNiO_2 . In order to accommodate both compounds under similar footings two different theoretical views have been recently proposed [9,10], assuming an *intrinsic* ground state, i.e., with no impurities. On the one hand it has been proposed that in systems with 90° -exchange spins and orbital states are essentially decoupled [9]. This view is questioned by Vernay and coworkers [10] in that the decoupling might hold true for NaNiO_2 , but it is not applicable to LiNiO_2 . They, instead, have proposed a four-state model where the orbital degeneracy (2) times the spin degeneracy (2) constitutes the ensemble of states of the phase space where the distinct physics found in both compounds can be reunited. This controversy has been recently fueled by the results of Holzapfel et al. [11] where they have clearly found a separation between orbital and spin degrees of freedom, even in the undistorted, stoichiometric $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$. The role of orbital ordering (OO) is to introduce a

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magnetic anisotropy field but magnetic long range order can be achieved even in the absence of OO. The determination of the magnetic order in $\text{Li}_{1-x}\text{Na}_x\text{NiO}_2$ is therefore of crucial importance if one seeks to understand the type of ground state that occurs in the small- x compounds.

Since the pioneering work of Bongers and Enz [12] there has been quite a lot of speculation on the actual magnetic ordering occurring in the layer compound NaNiO_2 below T_N . The inverse magnetic susceptibility shows a Curie-Weiss law with a positive T_{CW} , a signature of prevailing ferromagnetic interactions. The occurrence of *near* 90° Ni-O-Ni interactions (already discussed in [6,8]) suggests that a ferromagnetic ordering is expected between the Ni^{3+} ions in the same layer. High magnetic field experiments have been interpreted along this scheme supposing, in addition, an antiferromagnetic stacking of the ferromagnetic layers along the c -axes (an A -type antiferromagnetic ordering) [6]. This relatively simple structure should hold true to a good extent but it has never been validated by adequate crystallographic studies. In particular, the relatively low symmetry of the unit cell allows for components of the magnetic moment within the layers that display the same symmetry features as the originally proposed A -type antiferromagnetic structure. The goal of this paper is to completely determine the antiferromagnetic structure of NaNiO_2 by high resolution neutron powder diffraction.

2 Experiment

The preparation of NaNiO_2 powder is a very critical aspect of the success of this experiment and indeed previous attempts by neutron diffraction had failed due to the lack of appropriate sample quality. The starting materials (Na_2O_2 (97% pellets, Aldrich) and NiO (prepared shortly before use by thermal decomposition of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98% Aldrich) were intimately mixed in an argon-filled glove-box with 5% excess of Na to account for volatilization losses. The mixture was heated under flowing oxygen at 500°C for 1h, and at 680°C for 24 h after grinding under argon. The resulting NaNiO_2 product was kept in dry atmosphere until the transfer into the container for the neutron scattering experiment. These precautions are necessary because of the hygroscopic character of the product as well as by the presence of residual Na_2O_2 detected in some preparations [13].

High resolution neutron powder diffraction experiments were carried out at the D2B diffractometer of the Institut Laue-Langevin in Grenoble, operated at a wavelength of 1.594 \AA selected by the (335) reflection of a vertically focusing Ge monochromator. The sample (about 5 g) was placed in a cylindrical vanadium can inside a close-cycle refrigerator. The diffraction patterns were recorded between 3 and 160° (in 2θ) with a step of 0.05° . The detector consists on an array of 128 ^3He high pressure cells and collimators. Further technical details can be checked in [14]. Two data collections were made at $T = 4\text{ K}$ and $T = 50\text{ K}$. Figure 1 shows the diffraction pattern at $T = 4\text{ K}$ and the refinement of the atomic and the magnetic structures. Due to the weakness of the magnetic

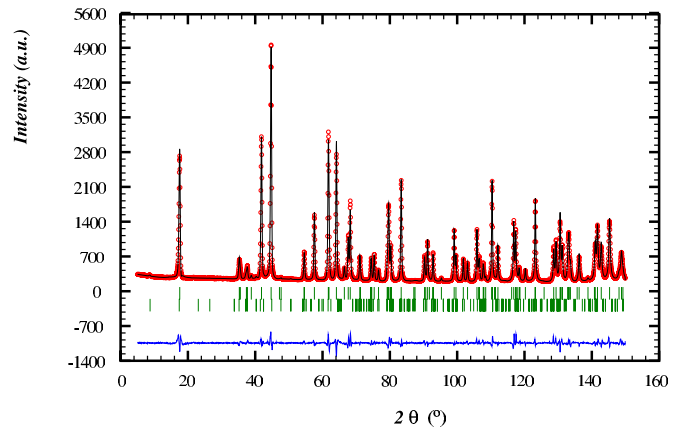


Fig. 1. High resolution neutron powder diffractometer taken at $T = 4\text{ K}$. The first row of ticked marks correspond to the Bragg reflection of the monoclinic space group $C2/m$ and the second row of marks are the positions of the magnetic peaks generated within a primitive magnetic cell with a $\mathbf{q} = (0, 0, \frac{1}{2})$ magnetic modulation wavevector. Magnetic reflections having $h + k = 2n$ are extinct within the experimental accuracy.

signal for this compound, data were accumulated during about 8 hours for each scan. In order to keep the highest instrumental resolution, only the pixels from the center part of the D2B 2D-detector were used. A close examination of the diffraction pattern taken at $T = 4\text{ K}$ has revealed the presence of 6 additional weak peaks, the two more intense being at 8.6° , and 40.3° , that we display in Figure 2. All of them can be indexed by using a magnetic supercell with double c -axis parameter, indicating antiferromagnetic ordering.

3 Results

3.1 Structure refinement

The refinements were carried out by the Rietveld technique with the WinPlotR and FullProf programs [16]. The background was described by linear interpolation between 51 points. A pseudo-Voigt lineshape was used to describe the observed peaks. For the 4 K data, the parameters describing the widths of the nuclear and magnetic Bragg peaks were constrained to be equal. Thanks to the simplicity of the nuclear structure, the refinement of the anisotropic atomic displacement parameters for all atoms, in addition to the x and z positional parameter of oxygen, has been possible. A summary of the results is given in Table 1. The given agreement factors correspond to the definition given in [17]. All nuclear structure and profile parameters change by less than one standard deviation between the refinements at both temperatures, except for the cell parameters which decreased from $a = 5.30874(3)\text{ \AA}$, $b = 2.84142(1)\text{ \AA}$, $c = 5.56708(3)\text{ \AA}$ and $\beta = 110.4530(4)^\circ$ at $T = 50\text{ K}$ to $a = 5.30811(3)\text{ \AA}$, $b = 2.84193(1)\text{ \AA}$, $c = 5.56671(3)\text{ \AA}$ and $\beta = 110.4504(3)^\circ$ at $T = 4\text{ K}$. The Debye-Waller parameter U_{11} is roughly 2 (for the O)

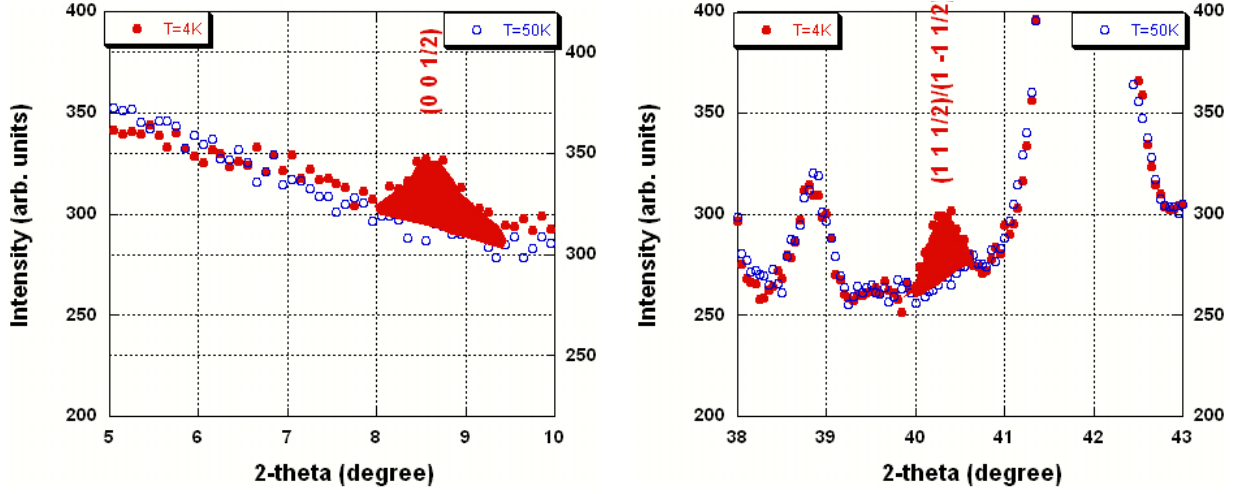


Fig. 2. Comparison between diffraction scans at $T = 4$ K and $T = 50$ K, i.e., above and below T_N , respectively, in two different angular regions. The shadowed peaks are two magnetic peaks that appear clearly in the low temperature diffraction pattern. The magnetic modulation wavevector is $\mathbf{q} = (0, 0, \frac{1}{2})$. The magnetic scattering cross-section for neutrons is directly proportional to transverse-to- \mathbf{Q} component of the magnetization, m_x : this explains the small signal detected at $\mathbf{Q} = (0, 0, \frac{1}{2})$. Note that this reflection should be 30 times more intense for the magnetic moments pointing towards the b -direction.

Table 1. Structural and magnetic parameters after the Rietveld refinement of the neutron powder diffraction pattern of NaNiO₂ at $T = 4$ K. Space group $C2/m$ with atomic positions: Na at $2d (0, \frac{1}{2}, \frac{1}{2})$, Ni at $2a (0, 0, 0)$ and O at $4i (x, 0, z)$. Unit cell dimensions are $a = 5.30811(3)$ Å, $b = 2.84193(1)$ Å, $c = 5.56671(3)$ Å and $\beta = 110.4504(3)^\circ$. Reliability factors are: $R_p = 3.49\%$, $R_{wp} = 4.82\%$, $R_{exp} = 1.24\%$, R_B (nuclear) = 2.08%, R_B (magnetic) = 8.71% and $\chi^2 = 15.2$.

Atom	x	y	z	
O	0.2836(2)	0	0.8040(2)	
	U_{11}	U_{22}	U_{33}	
Na	0.013(1)	0.0039(8)	0.004(1)	0.005(1)
Ni	0.0021(4)	0.0037(5)	0.0039(4)	-0.0004(4)
O	0.0084(6)	0.0045(6)	0.0037(5)	0.0022(5)
	m_x	m_y	m_z	$ m $
Ni (μ_B)	0.18(3)	0	1.02(5)	0.97(5)

and 3 (for the Na atoms) times larger than their corresponding values for U_{22} and U_{33} . This is the signature of the anisotropy along the a -direction of the O and Na environments.

3.2 Determination of the magnetic structure

There is no substantial change in the structural refinement between 4 and 50 K. The determination of the magnetic structure is based on the analysis of the intensities of 6 magnetic reflections that appear clearly in the neutron powder diffraction data, all of them indexed with a $\mathbf{q} = (0, 0, \frac{1}{2})$ modulation wavevector and $h + k = 2n$. In view of this rule we can assume, to a very good approximation, that the magnetic structure satisfies a C -

centering that connects Ni ions within the same layer. Note that at this point we can already establish that spins are parallel within each layer and antiparallel between adjacent layers. The direction of the spins remains to be determined. Ni atoms are located at $2/m$ site symmetry positions and is straightforward to realize that m_y has different symmetry than m_x and m_z , and thus 2 possible magnetic structures are to be tested. The first structure will yield a rather large scattering amplitude at the $\mathbf{Q} = (0, 0, \frac{1}{2})$ reflection (see Fig. 2, left), approximately thirty times larger than experimentally observed. This spin arrangement along b -direction can be therefore safely ruled out. The refinement with a pure antiferromagnetic model with m_x and m_z as fitted parameters leads to a satisfactory agreement ($R_B^{mag} = 8.71\%$) despite the small number of magnetic reflections that can be singled out of the diffraction pattern. The magnetic structure is depicted in Figure 3. The Ni³⁺ moments lie in the ac -plane, with a major component along the c -axis. The angle between the magnetic moment direction and the a -axis is $100(2)^\circ$ and the refined magnetic moment value of $0.97(5)\mu_B$ is in good agreement with the magnetic measurement data and the value of $1 \mu_B$ expected for a $S = 1/2$ Ni³⁺ cation.

4 Discussion and conclusions

The magnetic structure, ferromagnetic in the NiO₂ layers with a doubling of the unit cell along c , is relatively simple despite the complexity of interactions as raised in theoretical papers [9, 10]. The magnetic moments lie in the ac -plane and the spins at consecutive layers are *exactly* antiparallel. The magnetic moment does not point towards the apical oxygen atom. This would be the case for spins in $d_{3x^2-z^2}$ orbitals, with an anisotropy exclusively dominated by the spin-orbit which is otherwise expected to

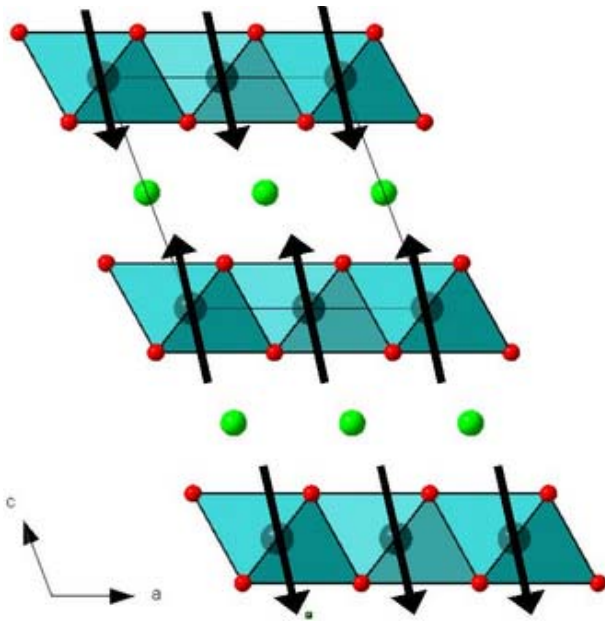


Fig. 3. The magnetic structure projected in the ac -plane. Magnetic moments lie in this plane. Within a layer the Ni-atoms are arranged in rows parallel to the b -direction, and the y -coordinate is shifted by $\frac{1}{2}$ from one row to the next. The angle of the magnetic moment direction with respect to the a -axis is $100(2)^\circ$. The magnetic moment points toward the center of the oxygen triangles above and below the Ni-layer.

be small for $S = \frac{1}{2}$. Rather it points towards the center of the triangle formed by the oxygens. This magnetic alignment was not evident beforehand and implies that another source of anisotropy is present in NaNiO_2 that determines the values of m_x and m_z . It is well known that the leading magnetic (super)exchange interaction is small in almost 90° -exchange systems and thus high-order perturbation processes have a significant contribution. Along this line, next-nearest Ni-Ni couplings are expected to be non-negligible. This aspect has been treated in the context of Cu-O *near* 90° chains [18] where they have shown that a certain number of interactions, that scales with the magnitude of the angle corresponding to the deviation to the perfect 90° geometry, may conspire to give different sources of anisotropy. Either a planar anisotropy or a more complex one resulting from high-order terms, this point needs further clarification and studies on Li-doped compounds are presently under way. The magnitude of the spin moment, $0.97(5) \mu_B$, is in agreement with the magnetic moment extracted from the Curie-Weiss law and from the saturation value at high magnetic fields [6].

In conclusion we have uncovered the magnetic structure developing below T_N in the $S = \frac{1}{2}$ triangular lattice layer compound NaNiO_2 . The magnetic unit cell is indexed as $\mathbf{q} = (0, 0, \frac{1}{2})$ with respect to the $C2/m$ unit cell. The magnetic moment is found to be

$0.97(5) \mu_B$ and lies in the plane perpendicular to the 2-fold axis, b -axis. This structure turns out to be a slight modification of the already predicted A -type antiferromagnetic structure (antiparallel stack from layer to layer along c -direction) and the magnetic moment direction seemingly results from different sources, among which is the spin-orbit. Our study can not exclude other very small components of the magnetization in the form of long period Fourier components which may remain difficult to observe in the neutron powder diffraction experiments. The presence of this extra component is necessary to account for the results of ESR experiments [19].

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