Investigation of the magnetic structure in NaFeGe$_2$O$_6$ using neutron powder diffraction

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Abstract. NaFeGe$_2$O$_6$ is a one of the representatives of the pyroxene family with the general formula $\text{Me}^{1+}\text{Me}^{3+}\text{Si(Ge)}_{2}\text{O}_6$ ($\text{Me}^{1+}$ - monovalent metal cation, $\text{Me}^{3+}$ - 3-d transition metal cation), which regained strong interest in spintronics as a new class of multiferroic materials and in solid-state physics as a quasi-low-dimensional insulating system. The sodium iron germanate NaFeGe$_2$O$_6$ powder was synthesized at 800$^\circ$, 900$^\circ$ C for 4 days from the stoichiometric mixture of Na$_2$CO$_3$, Fe$_2$O$_3$, GeO$_2$ by solid state reaction after several cycles of regrinding. Using neutron powder diffraction the magnetic order below $T_N \approx 13$ K was found and the magnetic structure has been determined. It is incommensurate and consists of antiferromagnetically coupled $\text{Fe}^{3+}$ pairs with helical modulation within the $a$-$c$ plane of the crystal lattice.

1. Introduction

The sodium iron germanate NaFeGe$_2$O$_6$ is a one of the representatives of the pyroxene family with the general formula $\text{Me}^{1+}\text{Me}^{3+}\text{Si(Ge)}_{2}\text{O}_6$ ($\text{Me}^{1+}$ - monovalent metal cation, $\text{Me}^{3+}$ - 3-d transition metal cation). These systems as a new class of multiferroic materials, which are simultaneously magnetic, ferroelectric and ferroelastic, have interesting physical properties and promise important applications [1].

The room temperature crystallographic NaFeGe$_2$O$_6$ structure was first determined by L. Solovyova et al. (1967) [2]. This compound belongs to the monoclinic type of pyroxene structures that crystallize in the space group C 2/c. The structure of this dielectric material contains GeO$_4$ tetrahedra that are connected into infinite chains extended along the c axis. The oxygen polyhedra around the Fe atoms are octahedra. They are bound through shared edges into continuous zigzag ribbons running along the c axis. The two types of ribbons alternate along the b axis.

The structure of the magnetic subsystem in pyroxenes is quasi-one-dimensional [3, 4]. The theoretical and experimental peculiarities of low-dimensional insulating systems with a low magnetic transition temperature were discussed that emphasized the importance of the investigation of the magnetic ordering in such systems [3]. The general topology of exchange interactions is such that the magnetic

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system may be frustrated [3]. It may lead to nontrivial magnetic structures and properties of pyroxenes, which depend both on intrachain and interchain magnetic exchange interactions. The SQUID magnetic measurement of Fe-based pyroxenes was carried out in a magnetic field of 100 Oe on a sample cooled to 4.2 K in zero magnetic field [4]. This magnetic measurement showed that the inverse susceptibility above \( T = 100 \) K in NaFeGe\(_2\)O\(_6\), can be approximated by a Curie-Weiss law.

The negative asymptotic temperature (\( \Theta_p \approx -135 \) K) shows the prevailing presence of the antiferromagnetic exchange interactions in NaFeGe\(_2\)O\(_6\). Below 100 K the susceptibility deviates from the Curie–Weiss behavior and exhibits a maximum at the temperature \( T_m=25 \) K. The magnetic transition temperature is defined as the inflection point at \( T_N=15 \) K. The value of the effective magnetic moment (molar value) \( \mu_{\text{eff}} = 5.89 \mu_B \) (\( \mu_B \) is the Bohr magneton) close to the theoretically expected value of the Fe\(^{3+}\) (s=5/2) magnetic moments 5.91 \( \mu_B \).

The NaFeGe\(_2\)O\(_6\) Mössbauer studies were carried out at room temperature on powder samples 5–10 mg/cm\(^2\) in thickness in the natural iron content using a \(^{57}\)Co(Cr) source [4]. In paramagnetic phase the \(^{57}\)Fe Mössbauer spectrum (300 K) is a doublet with the isomer shift \( \Theta = 0.40 \) mm/s relatively to \( \alpha \) - Fe, the quadrupole splitting 0.34 mm/s. This spectrum is attributed to Fe\(^{3+}\) ions with oxygen octahedral surroundings.

The aim of this study was to investigate the magnetic structure in the NaFe\(^{3+}\)Ge\(_2\)O\(_6\).

2. Sample preparation

The NaFeGe\(_2\)O\(_6\) powder (2 cm\(^3\)) was synthesized at 800°- 900° C in air for 4 days using reagents: 16% Na\(_2\)CO\(_3\), 23% Fe\(_2\)O\(_3\), 61% GeO\(_2\) by the solid state reaction after several cycles of regrinding. The product contained some value of Na\(_4\)Ge\(_9\)O\(_{20}\) as an impurity phase. The unit cell parameters of our specimen, which were found by X-ray powder diffraction method at 300 K, are \( a=10.008 \) Å, \( b = 8.948 \) Å, \( c=5.523 \) Å, \( \beta = 107.59^\circ \) [4]. This structure coincides with that of a mineral diopside [2].

3. Experiment

The neutron scattering experiments in the temperature range of 1.6-100 K were performed on the cold neutron powder diffractometer DMC [5] at Swiss spallation neutron source SINQ [6]. The sample was enclosed in a cylindrical vanadium container under helium atmosphere and mounted in a helium cryostat. The neutron wavelength used was \( \lambda = 2.4576 \) Å. The data has been corrected for absorption and was refined using the FULLPROF program package [7]. For the refinement of the magnetic structure at 1.6 K the paramagnetic data at 30 K was subtracted to obtain the pure magnetic diffraction pattern.

4. Results

Neutron diffraction is the method of choice for the determination of magnetic structures. In the paramagnetic state the experiment confirmed the monoclinic crystallographic structure. Below the critical temperature for magnetic order we find a large number of additional Bragg peaks due to long-range order of the magnetic moments (figure 2). The temperature dependence of the strongest magnetic peak is shown in figure 3, revealing the onset of magnetic order near 13 K. This is in accordance with the results of SQUID magnetic measurements [4]. The integrated neutron intensity increases with decreasing temperature as the square of the ordered moment and at the lowest temperature \( T \approx 1.6 \) K saturation is not yet reached.

A careful analysis of the experimental peak positions showed that the magnetic reflections cannot be described with a commensurate magnetic unit cell and immediately revealed the incommensurate nature of the magnetic order. We succeeded to refine the magnetic periodicity and the magnetic peaks can be indexed by the incommensurate propagation vector \( \mathbf{k} = (0.3357(4), 0, 0.0814(3)) \) at 1.6 K.

We performed a systematic refinement of the arrangement of the magnetic moments at 1.6 K and it turned out that just two models are able to describe the incommensurate peak positions as well as the
observed magnetic intensities. Both models consist of antiferromagnetically coupled pairs of iron moments with incommensurate modulation along the propagation vector \( k \). One model describes a sine-modulation of the moments, the other describes a helical modulation. The R-factor and \( \chi^2 \) of the refinement clearly favor the second model which shows an overall better agreement with the data (figure1). Neutron powder diffraction experiments results are listed in table 1.

**Figure 1.** Difference (1.6 K – 30 K) neutron diffraction pattern measured on DMC at SINQ, showing the pure magnetic scattering only (○). The lines denote the model calculation and the deviation of experiment and refinement as described in the text.

**Figure 2.** Integrated intensity of the strongest magnetic peak \((0, 1, 0) \pm k\) of \( \text{NaFeGe}_2\text{O}_6 \) determined by neutron diffraction as a function of temperature, Néel temperature \( T_N \approx 13 \text{ K} \).

**Figure 3.** (Color online) Fe moments in one crystallographic unit cell, view along \( c \) (ab in plane). The magnetic structure of \( \text{NaFeGe}_2\text{O}_6 \) is built up by antiferromagnetically coupled pairs.

**Figure 4.** (Color online) Incommensurate modulation of the magnetic structure of \( \text{NaFeGe}_2\text{O}_6 \) (ac in plane).

Therefore we conclude that \( \text{NaFeGe}_2\text{O}_6 \) orders with an incommensurate helical modulation of the iron magnetic moments along \( k = (0.3357(4), 0, 0.0814(3)) \). At \( T = 1.6 \text{ K} \) the ordered moment per \( \text{Fe}^{3+} \) ion is refined to be 2.55(1) \( \mu_B \). The refinement of the difference pattern (1.6 K – 30 K) with the helical model described above is shown in figure 1. In the difference pattern all peaks are due to magnetic order and our magnetic model nicely reproduces the experimental data with a large number of magnetic peaks for the full scattering angle range. The resulting pair arrangement of the moments in one chemical unit cell is shown in figure 3. The magnetic moments mainly lie in the ac plane and the
refinement only shows a small component along b due to a canting of ~10 degrees in respect to the ac-plane. The modulation over several chemical unit cells is shown in figure 4, displaying the incommensurate nature of the order in the ac plane. The errors in the refinement of the incommensurate vector in figure 5 as well as the magnetic moment do not include systematic errors and are therefore underestimated in the Rietveld refinement.

**Figure 5.** (color online) Temperature dependence of the propagation vector $k_x$ (left axis, red) and $k_z$ (right axis, blue)

| Temperature [K] | $k_x$ | $k_z$ |
|-----------------|------|------|
| 0.0             | 0.060| 0.090|
| 0.275           | 0.065| 0.075|
| 0.300           | 0.070| 0.080|
| 0.325           | 0.085| 0.085|
| 0.3375          | 0.3375| 0.3375|
| 0.3500          | 0.3500| 0.3500|

**TABLE I.** Results for a helical spin arrangement at 1.6K

| Propagation vector | Moment arrangement: |
|--------------------|---------------------|
| $k = (0.3357(4), 0, 0.0814(3))$ | helical modulation of antiferromagnetically coupled pairs |

| ordered moment per Fe$^{3+}$ ion | Plane of moments |
|----------------------------------|------------------|
| $M = 2.55(1)$ $\mu_B$ | close to a-c plane (small component along b) |

| Reliability factors of refinement | $R_p = 4.5$, $\chi^2 = 4.43$ |

**Conclusions**

The magnetic structure of the sodium iron germanate NaFeGe$_2$O$_6$ was determined by neutron diffraction. Below $T_N \approx 13$ K NaFeGe$_2$O$_6$ undergoes a phase transition to an incommensurate magnetic structure. Antiferromagnetically coupled pairs of Fe$^{3+}$ moments show an incommensurate modulation according to the magnetic propagation vector $k = (0.3357(4), 0, 0.0814(3))$ at 1.6 K within the ac plane and no modulation along b. The k vector is slightly temperature dependent (c.f. figure 5).

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