
**MAGNETISM
AND FERROELECTRICITY**

Synthesis and Properties of NaFeGe₂O₆ Polycrystals

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Abstract—NaFeGe₂O₆ polycrystals were synthesized and their x-ray diffraction, magnetic, electrical, and Mössbauer characteristics were measured. It is established that this monoclinic compound is a dielectric with a temperature of antiferromagnetic ordering of 15 K. The Mössbauer spectrum at 300 K is a quadrupole doublet. The isomer shift is 0.40 mm/s, which is characteristic of the high-spin Fe³⁺ ion in the octahedral coordination. The quadrupole splitting is 0.34 mm/s, which indicates that the oxygen octahedron around the iron cation is distorted. The exchange interactions are estimated, and the crystal magnetic structure is discussed.

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1. INTRODUCTION

Low-dimensional magnets are of interest because a fairly exact theoretical analysis of the spin state can be carried out for them and because these systems exhibit quantum effects. To date, the main experimental data on low-dimensional magnets have been accumulated for oxide compounds. For example, in oxide cuprates, one- and two-dimensional systems can easily be created. The problem of obtaining and analyzing the properties of low-dimensional materials with high-spin cations is less well studied. In principle, a transition from one dimensionality to another can be realized by synthesizing crystals whose lattices are formed by chains of magnetically active cations with different degree of interchain bonding.

Metagermanate NaFeGe₂O₆ is such a system. The x-ray diffraction study shows that it is isostructural to diopside CaMgSi₂O₆ with Ca, Mg, and Si being replaced by Na, Fe, and Ge, respectively [1]. The NaFeGe₂O₆ compound exhibits a monoclinic structure, space group *C2/c*, and the following unit cell parameters: $a = 10.0100 \text{ \AA}$, $b = 8.9400 \text{ \AA}$, $c = 5.5200 \text{ \AA}$, and $\beta = 108.0000^\circ$ [1]. In common with all pyroxenes, NaFeGe₂O₆ is a chain germanate, in which the GeO₄ tetrahedra are connected into infinite chains extended along the *c* axis. The polyhedra around the Fe atoms are octahedra. They are bound through shared edges into continuous zigzag ribbons running along the *c* axis. Along the *b* axis, the two types of ribbons alternate.

2. EXPERIMENTAL

The polycrystalline NaFe germanate was synthesized using the solid-phase reaction method at normal pressure. The samples were prepared from a charge containing 16% Na₂CO₃, 23% Fe₂O₃, and 61% GeO₂, which was subjected to grinding, followed by molding and pressing of the polydisperse powder. Pellets with a diameter $d = 12 \text{ mm}$ and a thickness $h = 4 \text{ mm}$ compacted under a pressure of $\sim 10 \text{ kbar}$ were subjected to a high-temperature treatment. A preliminary annealing was carried out at a temperature $T_a = 800^\circ\text{C}$ for 25 h. To increase the sample homogeneity, the pellets were again ground, molded, and then sintered at $T_a = 820^\circ\text{C}$ for 24 h.

The x-ray diffraction study of the polycrystals synthesized was performed using a DRON-2.0 diffractometer with CuK _{α} radiation (graphite monochromator) at a temperature $T = 300 \text{ K}$. The Mössbauer studies were carried out at room temperature on powder samples 5–10 mg/cm² in thickness in the natural iron content using a ⁵⁷Co(Cr) source. Magnetic measurements were performed using a SQUID magnetometer on a sample with a weight of 195 mg in the temperature range 4.2–300 K. The electrical resistivity was measured at 300 K.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The x-ray diffraction analysis shows that the composition of the synthesized material is NaFeGe₂O₆. The

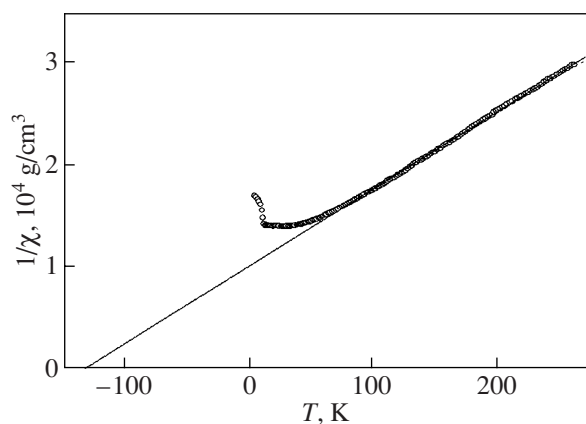


Fig. 1. Temperature dependence of the inverse magnetic susceptibility of NaFeGe₂O₆ polycrystals.

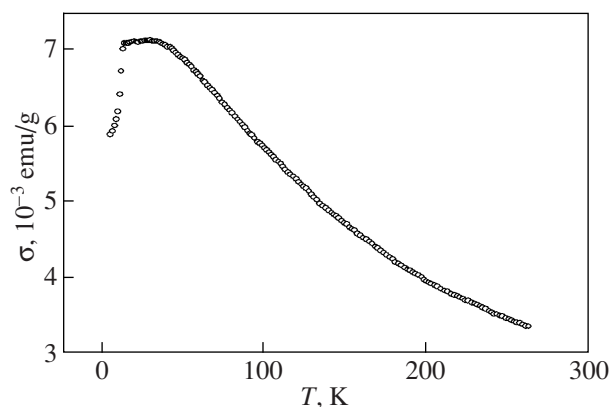


Fig. 2. Temperature dependence of the magnetization of a NaFeGe₂O₆ polycrystal.

lattice parameters of the NaFe metagermanate are as follows: $a = 10.008 \text{ \AA}$, $b = 8.948 \text{ \AA}$, $c = 5.523 \text{ \AA}$, and $\beta = 107.59^\circ$, which agree with the data from [1]. There are impurity-phase traces in the x-ray diffraction pattern.

The resistivity of the compound was measured at $T = 300 \text{ K}$ to be $\rho \approx 10^{11} \Omega \text{ cm}$. As the sample temperature decreases, the resistivity increases.

The results of magnetic measurements of NaFeGe₂O₆ ceramic samples are presented in Figs. 1 and 2 and in the table. Figure 1 shows the temperature dependence of the inverse magnetic susceptibility $\chi^{-1}(T)$. The measurement was carried out using a SQUID magnetometer in a magnetic field of 100 Oe on a sample cooled to 4.2 K in a zero magnetic field. In a high-temperature region, the inverse susceptibility $\chi^{-1}(T)$ can be described by the Curie–Weiss law. The asymptotic Néel temperature, determined by extrapolating the $\chi^{-1}(T)$ straight line in the high-temperature region to the intercept with the T axis, is $\Theta = -135 \text{ K}$, the Curie–Weiss constant $C = 0.0135 \text{ K}$, which corresponds to an effective magnetic moment (molar value) $\mu_{\text{eff}} = 5.89\mu_{\text{B}}$ (μ_{B} is the Bohr magneton). Using available values of the orbital angular momentum and spin for the magnetic Fe³⁺ ion ($L = 0$ and $S = J = 5/2$, respectively), one can calculate the effective magnetic

moment. Assuming that the spectroscopic splitting factor $g = 2$, we have $\mu_{\text{eff}} = 5.91\mu_{\text{B}}$. The satisfactory agreement between the calculated and experimental values of the effective magnetic moment indicates that the trivalent iron ions determine the paramagnetic properties and that other impurity magnetic ions are small in amount. The observed anomalies of the magnetic susceptibility χ and the magnetization σ of polycrystalline NaFeGe₂O₆ at $\sim 15 \text{ K}$ (Figs. 1, 2) indicate a magnetic phase transition to the antiferromagnetic state.

The Mössbauer spectrum of the NaFeGe₂O₆ compound shown in Fig. 3 is a quadrupole doublet with a splitting of $0.34 \pm 0.03 \text{ mm/s}$, an isomer chemical shift of $0.40 \pm 0.02 \text{ mm/s}$ with respect to the metallic iron $\alpha\text{-Fe}$, and an absorption line half-maximum width of $0.30 \pm 0.03 \text{ mm/s}$. This value of the isomer shift is characteristic of a high-spin Fe³⁺ ion in the octahedral coordination. The quadrupole splitting indicates that the oxygen octahedron around the iron cation is distorted.

The Mössbauer spectrum exhibits additional absorption lines indicated in Fig. 3 by arrows. These lines indicate the presence of a magnetically ordered impurity phase, which agrees with the x-ray diffraction data. The hyperfine structure parameters of the spectrum of this phase correspond to hematite $\alpha\text{-Fe}_2\text{O}_3$. From the area of the spectrum of the “impurity” sextet, it follows that the hematite phase accounts for less than 5%.

In the crystalline structure of diopside, the oxygen octahedra containing iron cations form zigzag chains extended along the c axis [1]. The octahedra are bound by shared edges, thus forming 90° indirect exchange coupling between the nearest neighboring iron cations (Fig. 4). In a plane perpendicular to the c axis, the iron cations can interact through extended indirect bonds Fe–O–Ge–O–Fe (Fig. 5). Thus, one can expect that the intrachain interaction through Fe–O–Fe short bonds will be much stronger than the interchain interaction. In

Data obtained from measurements of the magnetic susceptibility of a NaFeGe₂O₆ powder

Θ , K	C , K	μ_{calc} , μ_{B}	μ_{exper} , μ_{B}	T_{max} , K	T_{N} , K
-135	0.0135	5.91	5.89	25	15

Note: Θ is the asymptotic Néel temperature, C is the Curie–Weiss constant, μ_{calc} is the calculated effective magnetic moment, μ_{exper} is the experimental effective magnetic moment, T_{max} is the temperature corresponding to the maximum magnetization, and T_{N} is the Néel temperature.

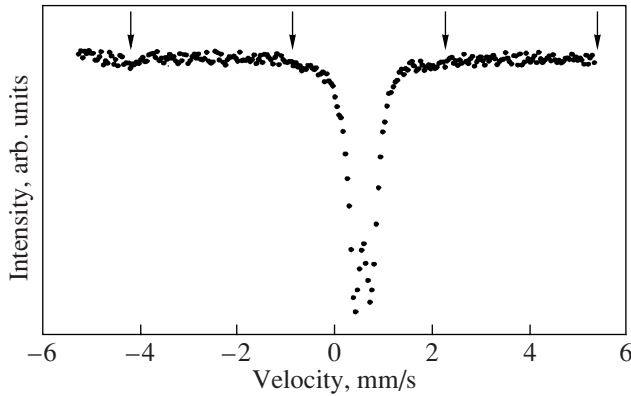


Fig. 3. Mössbauer spectrum of $\text{NaFeGe}_2\text{O}_6$. The arrows indicate the positions of the sextet lines of the impurity hematite phase $\alpha\text{-Fe}_2\text{O}_3$.

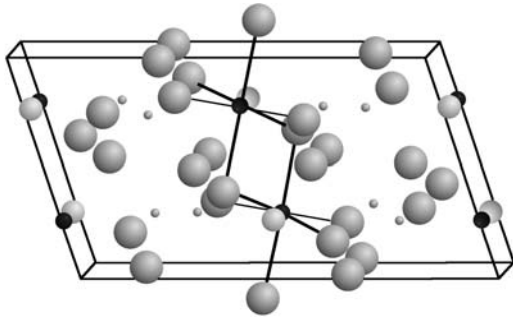


Fig. 4. Intrachain bonds Fe-O-Fe in the $\text{NaFeGe}_2\text{O}_6$ structure (bold lines). All lines show the octahedral surroundings of a central Fe cation consisting of oxygen anions. The ion size increases along the series of Ge, Fe, Na, and O.

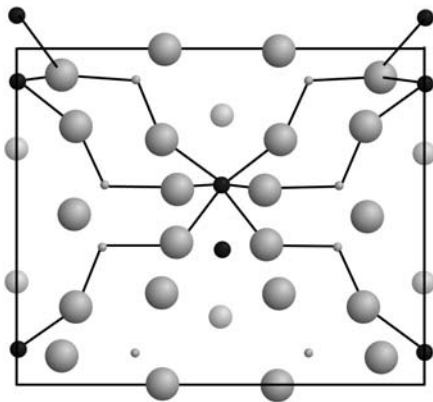


Fig. 5. Interchain bonds Fe-O-Ge-O-Fe of a central Fe cation with Fe cations belonging to the four neighboring chains in $\text{NaFeGe}_2\text{O}_6$. The ion size increases along the series of Ge, Fe, Na, and O.

this case, we can estimate the strength of the intrachain interaction using the known relation between the asymptotic Néel temperature and the maximum exchange integral in the system [2]

$$k\Theta = \frac{2}{3}S(S+1)zJ_1, \quad (1)$$

where the number of nearest neighbors in the chain $z = 2$. This estimate gives $J_1 = -11.5$ K for the experimental value $\Theta = -135$ K.

The magnetic ordering temperature T_N depends on the interchain interaction [3]

$$kT_N = \frac{4}{3}S(S+1)J_1 \frac{1}{I}, \quad (2)$$

where $I = 0.64(J_1/J_{2a})^{1/2}[1 + 0.253 \ln(J_{2a}/J_{2b})]$. Here, $J_{2a, 2b}$ are the exchange integrals in the a and b directions (perpendicular to the chain) determining the interchain interaction. For the diopside structure, we have $J_{2a} = J_{2b}$; so, the above formula is simplified to $I = 0.64(J_1/J_{2a})^{1/2}$. Using these formulas, we find that the interchain interaction $J_2 = -0.072$ K at the experimental value $T_N = 15$ K.

Thus, the interchain interaction in the $\text{NaFeGe}_2\text{O}_6$ compound is two orders of magnitude less than the intrachain interaction.

In the diopside structure, each iron cation has eight extended bonds Fe-O-Ge-O-Fe with six iron cations belonging to the four neighboring chains. Thus, each iron cation has four intralayer bonds J_2^{intra} belonging to one ab layer and four interlayer bonds J_2^{inter} . Since all the interactions are antiferromagnetic, the intralayer interactions are in competition with the interlayer interactions; i.e., the Néel temperature is determined by the difference between the exchange integrals $J_2^{\text{intra}} - J_2^{\text{inter}} = J_2 = -0.072$ K. The diopside magnetic structure is dependent on the relation between the exchange integrals, if $J_2^{\text{intra}} > J_2^{\text{inter}}$, then the ordering in the ab layer is antiferromagnetic. If $J_2^{\text{inter}} > J_2^{\text{intra}}$, the ordering is ferromagnetic.

4. CONCLUSIONS

Polycrystalline $\text{NaFeGe}_2\text{O}_6$ has been synthesized by the solid-phase reaction method. The x-ray diffraction, magnetic, electrical, and Mössbauer measurements have shown that this compound is a dielectric with an antiferromagnetic ordering temperature $T_N = 15$ K. It exhibits a diopside monoclinic structure containing trivalent iron cations in a high-spin state with octahedral coordination to oxygen. From analyzing the exchange interactions in the nearest neighbor approxi-

mation, it follows that the crystal magnetic structure is an ensemble of iron cation chains with an intrachain cation–cation exchange integral $J_1 \approx -11.5$ K and an interchain interaction $J_2 \approx -0.07$ K. Due to the competition between the intra- and interlayer exchange interactions of chains, the antiferromagnetic ordering temperature is low.

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