MAGNETISM AND FERROELECTRICITY

Properties of Clinopyroxene LiFeGe$_2$O$_6$

T. V. Drokina[a,b,*], **G. A. Petrakovskiĭ**[a,b], **O. A. Bayukov**[a,b], **A. F. Bovina**[a], **R. Shimchak**[c],
D. A. Velikanov[a,b], **A. V. Kartashev**[a], **A. L. Volkova**[a], **D. A. Ivanov**[a], **and G. N. Stepanov**[a]

[a] *Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok 50,*
Krasnoyarsk, 660036 Russia
* e-mail: tvd@iph.krasn.ru
[b] *Siberian Federal University, pr. Svobodny 79, Krasnoyarsk, 660041 Russia*
[c] *Institute of Physics, Polish Academy of Sciences, al. Lotnikow 32/46, Warsaw, 02-668 Poland*
Received February 26, 2010; in final form, April 8, 2010

Abstract—The polycrystalline compound LiFeGe$_2$O$_6$ has been synthesized by the solid-phase reaction. The X-ray diffraction, Mössbauer, calorimetric, and magnetic investigations have been carried out. The Mössbauer spectrum at 300 K represents a single quadrupole doublet. The isomer shift with respect to the metal iron α-Fe is 0.40 mm/s, which is characteristic of the Fe^{3+} high-spin ion in the octahedral coordination. The quadrupole splitting of 0.42 mm/s indicates a distortion of the oxygen octahedron around the iron cation. The results of the measurement of the temperature dependence of the heat capacity in the range 2–300 K have shown the presence of the only anomaly with a maximum at $T_m \sim 20.5$ K, which indicates the occurrence of a magnetic phase transition in this point. The data of the measurement of the temperature dependence of the magnetization have confirmed that the magnetic order with the dominant antiferromagnetic interaction of magnetically active ions exists in LiFeGe$_2$O$_6$ at a temperature below 20.5 K. The investigation of the temperature dependence of the heat capacity in the magnetic field H up to 9 T has demonstrated that the external factor insignificantly changes the order–disorder transition point (at $H = 9$ T, there occurs a shift of ~0.5 K toward the low-temperature range).

1. INTRODUCTION

The properties of the synthesized LiFeGe$_2$O$_6$ compound belonging to the family of rock-forming minerals and relating to pyroxenes are investigated. Interest to materials with pyroxene structures is firstly associated with quasi-one-dimensionality of their magnetic subsystems [1, 2]. It is known that the pyroxene lattice is formed by the chains of magnetically active cations with different degrees of the interchain exchange coupling realized through the GeO$_4$ tetrahedra [1, 3]. In this case, the exchange interaction inside the chain of magnetically active cations, as a rule, is stronger than the resulting interchain interaction. The striking representative of such systems is, for example, diopside NaFeGe$_2$O$_6$ [4].

Another feature of the magnetic properties of pyroxenes is the presence of a complex interrelated totality of intrachain J and interchain J_1 exchange interactions with frustrations.

Interest in the pyroxene structures also has increased since the report about the dependence of the electric properties on the magnetic field in materials NaFeSi$_2$O$_6$, LiFeSi$_2$O$_6$, and LiCrSi$_2$O$_6$ [3].

In connection with the aforementioned, the further investigation of the properties of pyroxenes is of interest.

The crystal structure of the LiFeGe$_2$O$_6$ compound at room temperature belongs to the monoclinic crystal system and has the space group $P2_1/c$ with unit cell parameters $a = 9.873$ Å, $b = 8.795$ Å, $c = 5.372$ Å, and $\beta = 106.92°$ [5].

LiFeGe$_2$O$_6$ is clinopyroxene, in the crystal structure of which the GeO$_4$ tetrahedra are connected with one another by the vertexes into the chains elongated along axis c. The polyhedra around the Fe atoms are the octahedra. By means of common edges, they form continuous zigzag ribbons also along axis c. In the direction of axis b, the ribbons of two kinds are alternated.

The first data on the magnetic properties of the LiFeGe$_2$O$_6$ compound are reported in [6, 7], where, based on the SQUID-measurements, the temperature of the antiferromagnetic ordering is determined ($T_N \approx 20$ K). The authors point to the presence of the magnetic impurity in the studied sample uncontrollable by the X-ray structural analysis and optical microscopy [6]. From the data of the neutron diffraction investigations of LiFeGe$_2$O$_6$, the magnetic structure with translation vector $\mathbf{k} = (1/2, 0, 0)$ and the magnetic moment $4.48(5)\mu_B$ (at $T = 5$ K) arranged in a–c plane at an angle of 91.0° to axis c is suggested [6]. It is shown that the intrachain Fe–O–Fe exchange interaction is anti-

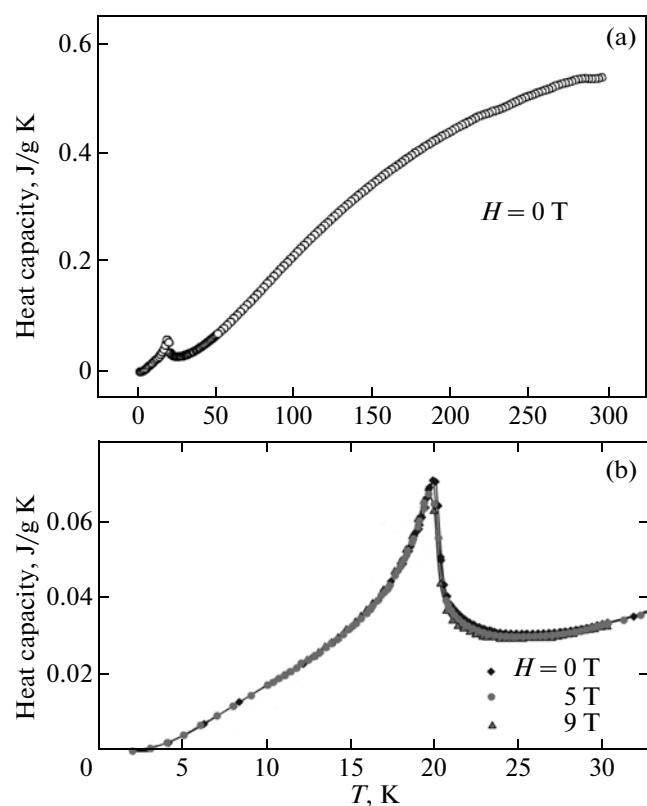**Fig. 1.** Temperature dependences of the heat capacity of the $LiFeGe_2O_6$ compound.

ferromagnetic, while the interchain exchange interaction between the magnetically active ions performed through the $(GeO_4)_A$ and $(GeO_4)_B$ tetrahedra, differing by the bending angles of the tetrahedral chains, has different signs.

In this work, we present the results of the Mössbauer, calorimetric, and magnetic measurements of the $LiFeGe_2O_6$ compound.

2. SYNTHESIS OF THE SAMPLES AND EXPERIMENTAL TECHNIQUE

Polycrystalline LiFe germanate was synthesized by the solid-phase reaction under the standard pressure. The samples were prepared from the charge via mixing and milling the powder-like oxides: 11.3 wt % Li_2CO_3, 24.5 wt % Fe_2O_3, and 64.2 wt % GeO_2. The pellets with diameter $d = 12$ mm and thickness $h = 3–4$ mm were fabricated from the oxide mixture under the pressure. The pellets were subjected to the high-temperature treatment in the following mode: 24 h, 600°C; 24 h, 650°C; 24 h, 700°C; 24 h, 750°C; 24 h, 800°C, 24 h, 850°C; and 24 h, 900°C. In order to increase the uniformity of the samples, the pellets after each annealing were milled, thoroughly ground, and pressed again.

The X-ray structural analysis of the powders was performed at 300 K on a DRON-2.0 diffractometer (CuK_α radiation, graphite monochromator) at the Kirensky Institute of Physics of the Siberian Branch of the Russian Academy of Sciences (Krasnoyarsk, Russia).

The Mössbauer investigations were performed on an MS-1104Em spectrometer at the Kirensky Institute of Physics of the Siberian Branch of the Russian Academy of Sciences (Krasnoyarsk, Russia) at room temperature with the $Co^{57}(Cr)$ source for the powders $5–10$ mg/cm^2 thick according to the natural iron content.

The magnetic measurements were performed on the SQUID magnetometers at the Kirensky Institute of Physics of the Siberian Branch of the Russian Academy of Sciences (Krasnoyarsk, Russia) and the Institute of Physics of the Polish Academy of Sciences (Warsaw, Poland) in the temperature range 4.2–300 K in the fields up to 6 T.

The calorimetric investigations were performed on a Quantum Design PPMS 6000 installation at the Center of the Collective Use, Krasnoyarsk Scientific Center, in the temperature range 2–300 K in the magnetic fields up to 9 T.

3. RESULTS AND DISCUSSION

The X-ray diffraction data at $T = 300$ K confirmed that the synthesized material has the composition $LiFeGe_2O_6$, belongs to the monoclinic crystal system, and has the space group $P2_1/c$ with the unit cell parameters $a = 9.882$ Å, $b = 8.793$ Å, $c = 5.380$ Å, and $\beta = 108.88°$, which agrees with the data [5]. The quality of the samples was verified by the X-ray structural analysis and nuclear γ-resonance using an optical microscope. The necessity of this verification is caused by the overlap of the intensity peaks of the reflected X-rays of the $LiFeGe_2O_6$ and α-Fe_2O_3 compounds (α-Fe_2O_3 is the most probable additional magnetic phase). Our samples under study contain no magnetic impurities revealed by the X-ray structural analysis and γ-resonance as well as with the help of the optical microscope.

The Mössbauer spectrum of the $LiFeGe_2O_6$ compound is a single quadrupole doublet. The splitting is 0.42 mm/s, the isomer shift is 0.40 mm/s with respect to metal iron α-Fe, and the full width of the absorption line at the half-maximum is 0.34 mm/s. The chemical shift is characteristic of the Fe^{3+} high-spin ion located in the octahedral coordination. The magnitude of the quadrupole splitting indicates the distortion of the oxygen octahedron around the iron cation.

We measured the specific heat of $LiFeGe_2O_6$ and followed its variation with temperature. At $T = 300$ K, specific heat C_p is 0.53 J/g K. The temperature dependence of $C_p(T)$ is presented in Fig. 1a. The only anom-
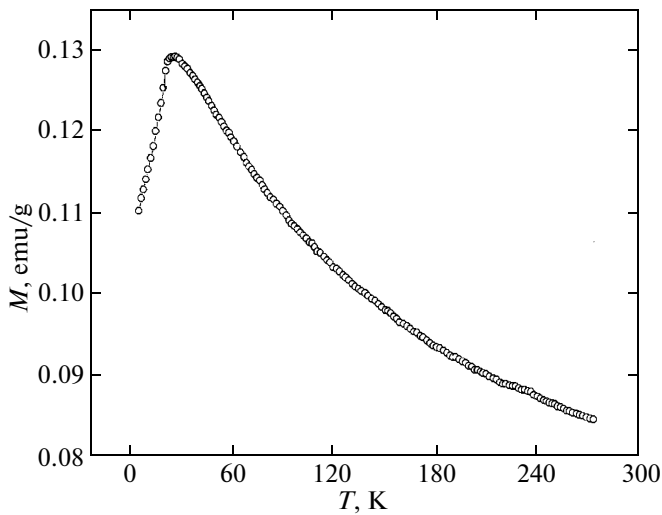
Fig. 2. Temperature dependence of the magnetization of LiFeGe$_2$O$_6$ at $H = 500$ Oe.
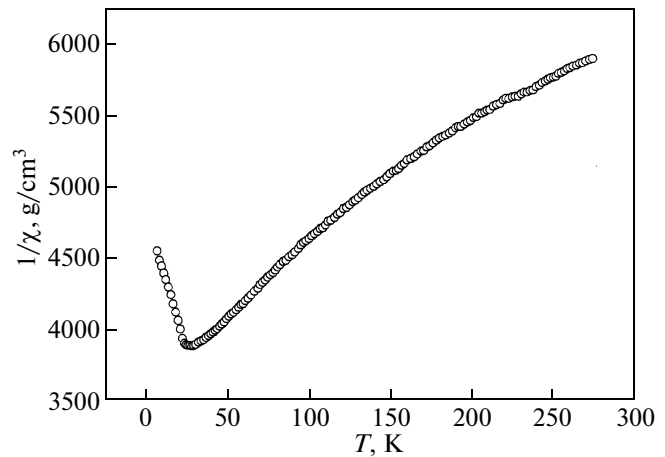
Fig. 3. Temperature dependence of the inverse susceptibility of LiFeGe$_2$O$_6$.

aly is found in the region $T_m \sim 20.5$ K, which indicates the existence of the second-order phase transition. A more detail investigation of this portion in the magnetic fields (Fig. 1b) showed that constant magnetic field $H = 9$ T leads to a decrease in the phase transition temperature by 0.5 K.

The results of the magnetic measurements for the LiFeGe$_2$O$_6$ ceramic samples are presented in Figs. 2 and 3. The curves that characterize the magnetic properties of LiFeGe$_2$O$_6$ have the shape typical of the antiferromagnets. The temperature dependence of magnetization (Fig. 2) is peaked at $T_{\max} \approx 24$ K. At low temperatures, the anomaly is observed for the temperature dependence of inverse magnetic susceptibility $1/\chi$, which is associated with the antiferromagnetic ordering of LiFeGe$_2$O$_6$. The temperature dependence of $1/\chi$ (Fig. 3) of the LiFeGe$_2$O$_6$ compound at high temperatures (above ~100 K) cannot be described by the linear function, which does not allow us to determine the asymptotic Néel temperature Θ_N with a sufficient accuracy. We can notice that it is negative and rather high (probably, $\Theta_n < -100$ K). For the exact determination of the asymptotic Néel temperature, the measurements of the susceptibility at higher temperatures are necessary ($T > 300$ K).

The investigations of the influence of the magnetic field on the temperature dependence of magnetization in the range up to 6 T do not allow us to conclude that the magnetic field affects the temperature of the paramagnetic–antiferromagnetic phase transition.

We carried out the measurements of the field dependence of magnetization of LiFeGe$_2$O$_6$ at 10 and 17 K. The results of measurements coincide with the data [6]. The field dependence deviates from the linear

law in the range 2.5–4.0 T, which can be associated with the spin-flip effect.

Thus, the investigation of the magnetic properties showed that the energy of dominating exchange interaction has a negative sign, and the Néel temperature is $T_N \approx 20.5$ K. The phase transition temperature of the magnetically ordered state coincides with the data obtained from the measurement of heat capacity (Fig. 1) as well as with the data of magnetic measurements [6]. The peak of heat capacity at $T = 20.5$ K (Fig. 1) corresponds to the order–disorder phase transition.

4. CONCLUSIONS

The LiFeGe$_2$O$_6$ compound was synthesized by the solid-phase reaction. The X-ray structural, Mössbauer, calorimetric, and magnetic investigations of the LiFeGe$_2$O$_6$ polycrystal were carried out.

According to the data of the Mössbauer measurements, the cations of the magnetically active trivalent iron ions at $T = 300$ K are in the high-spin state and octahedral coordination by oxygen. The quadrupole splitting of 0.42 mm/s indicates a distortion of the oxygen octahedron around the iron cation.

The heat capacity was measured, and its temperature dependence was investigated. It was shown that, in the temperature range from 4.2 to 300 K, there is the only magnetic phase transition to the antiferromagnetic state at $T \approx 20.5$ K. The magnetic field in the range from 0 to 9 T shifts the point of the order–disorder transition by 0.5 K into the low-temperature region.

REFERENCES

1. S. V. Streltsov and D. I. Khomskii, Phys. Rev. B: Condens. Matter **77**, 064405 (2008).

2. A. A. Katanin and V. Yu. Irkhin, Usp. Fiz. Nauk **177** (6), 639 (2007) [Phys.—Usp. **50** (6), 613 (2007)].

3. S. Jodlauk, P. Becker, J. A. Mydosh, D. I. Khomskii, T. Lorenz, S. V. Streltsov, D. C. Hezel, and L. Bohaty, J. Phys.: Condens. Matter **19**, 432201 (2007).

4. T. V. Drokina, O. A. Bayukov, G. A. Petrakovskiĭ, D. A. Velikanov, A. F. Bovina, G. N. Stepanov, and D. A. Ivanov, Fiz. Tverd. Tela (St. Petersburg) **50** (11), 2050 (2008) [Phys. Solid State **50** (11), 2141 (2008)].

5. M. Behruzi and T. Hahn, in *Information Centre for Diffraction Data 26-1440* (Technishe Hochschule, Aachen, Germany, 1974).

6. G. J. Redhammer, G. Roth, W. Treutmann, M. Hoelzel, W. Paulus, G. Andre, C. Pietzonka, and G. Amthauer, J. Solid State Chem. **182**, 2374 (2009).

7. A. L. Volkova and T. V. Drokina, in *Abstracts of Papers of the Conference of Students, PhD Students, and Young Scientists of Physics (NKSF-XXXVIII), Krasnoyarsk, 2009*, p. 28.

Translated by N. Korovin