

# Quasi-one-dimensional pyroxene $\text{NaFeGe}_2\text{O}_6$ : the magnetic structure and magnetic phase diagram

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We present the additional results of neutron diffraction measurements on  $\text{NaFe}^{3+}\text{Ge}_2\text{O}_6$ . The temperature dependence of the  $\text{NaFeGe}_2\text{O}_6$  specific heat in the absence of the external magnetic field ( $H = 0$ ) exhibits a sharp maxima at the temperatures  $T_1 = 11.6$  K and  $T_2 = 13$  K. The results of neutron diffraction are confirmed the existing two magnetic phases in zero magnetic field. In this compound there is antiferromagnetic long-range order, Neel temperature  $T_N = 13$  K. The iron-containing pyroxene neutron diffraction data indicate the incommensurate magnetic structure at the temperatures 1.6 – 11.5 K. It consists of antiferromagnetically coupled a pairs of the  $\text{Fe}^{3+}$  spins with helical modulation within the  $a$ - $c$  plane of the crystal lattice. The magnetic structure is unclear at the temperature range  $11.5 \text{ K} > T > 13 \text{ K}$ .

**Keywords:** pyroxene  $\text{NaFeGe}_2\text{O}_6$ , incommensurate magnetic structure, magnetic phase diagram, neutron scattering.

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Представлены результаты дополнительного исследования соединения  $\text{NaFe}^{3+}\text{Ge}_2\text{O}_6$  методом упругого рассеяния нейтронов. Исследование температурной зависимости теплоемкости в отсутствие внешнего магнитного поля показало наличие двух фазовых переходов при температурах  $T_1 = 11,5$  К и  $T_2 = 13$  К. Изучение упругого рассеяния нейтронов подтвердило существование двух магнитных фазовых переходов в нулевом магнитном поле. В соединении  $\text{NaFeGe}_2\text{O}_6$  имеет место переход из парамагнитного состояния в упорядоченное при  $T_N = 13$  К. При температуре  $T_c = 11,5$  К образец подвергается дополнительному фазовому переходу в состояние с несоизмеримой магнитной структурой, представляющей собой антиферромагнитную спираль, сформированную из пар спинов ионов  $\text{Fe}^{3+}$  с геликоидальной модуляцией в плоскости  $a$ - $c$  кристаллической решетки. Магнитная структура соединения не известна в температурном диапазоне  $11,5 \text{ К} > T > 13 \text{ К}$ .

**Ключевые слова:** пироксен  $\text{NaFeGe}_2\text{O}_6$ , несоизмеримая магнитная структура, магнитная фазовая диаграмма, нейтронное рассеяние

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## Introduction

Pyroxenes are formed a broad class of materials for physical investigations. The pyroxenes compounds have a chemical formula  $\text{ABX}_2\text{O}_6$  ( $A = \text{Na, Li and Ca}$ ;  $B = \text{Mg, Cr, Cu, Ni, Fe, etc.}$ ;  $X = \text{Ge, Si}$ ). If the A position is occupied by the monovalent cations ( $\text{Na, Li}$ ), B adopts attitude of the trivalent metals ( $\text{Fe, Cr, etc.}$ ). If the A position is occupied by the divalent cation ( $\text{Ca}$ ), in this case B adopts attitude of the divalent cation ( $\text{Ni, Fe, Co, etc.}$ ). Some pyroxenes are a rock forming minerals and they have been studied in geosciences. The most of the germanates and silicates (for ex.,  $\text{NaFe}^{3+}\text{Ge}_2\text{O}_6$ ,  $\text{LiFe}^{3+}\text{Ge}_2\text{O}_6$ ) are attracted significant interest in solid state physics due to their low dimensional magnetic systems [1, 2].

The new interest to these physical systems is appeared in spintronics — new direction in the modern electronics — due to the discovery of the strong interaction between the magnetic and electric subsystems in the compounds  $\text{NaFeSi}_2\text{O}_6$ ,  $\text{LiFeSi}_2\text{O}_6$  and  $\text{LiCrSi}_2\text{O}_6$  which are formed a new class of multiferroics [3].

The pyroxene-type compounds exhibit a variety of different magnetically ordered states (table 1). The most of them are antiferromagnetic [4 – 16]. There is ferromagnetic (for ex.,  $\text{NaCr}^{3+}\text{Ge}_2\text{O}_6$ ) [17 – 19]. Some pyroxene compounds show the orbital driven spin gap state (for ex.,  $\text{NaTiSi}_2\text{O}_6$ ) [21]. The variety of pyroxene magnetic properties are connected with the features of the crystal structure witch is allowed the existing of a magnetic frustration.

Table 1

The magnetic states in pyroxenes compounds		
Compounds	Magnetically ordered state	References
NaV <sup>3+</sup> Ge <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 22$ K)	[4, 5]
LiV <sup>3+</sup> Ge <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 24$ K)	[4 – 7]
NaV <sup>3+</sup> Si <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 17$ K)	[4]
LiV <sup>3+</sup> Si <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 22$ K)	[4]
LiFe <sup>3+</sup> Ge <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 20$ K)	[8 – 10]
NaFe <sup>3+</sup> Ge <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 13$ K), incommensurate magnetic structure at 1.6 – 11.5 K	[11 – 14]
NaFe <sup>3+</sup> Si <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 5$ K)	[14 – 16]
LiFe <sup>3+</sup> Si <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 18$ K)	[8, 15, 16]
NaCr <sup>3+</sup> Ge <sub>2</sub> O <sub>6</sub>	ferromagnetic long-range order ( $T_c = 6$ K)	[17 – 19]
LiCr <sup>3+</sup> Ge <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 4$ K)	[17]
LiCr <sup>3+</sup> Si <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 11$ K)	[17]
NaCr <sup>3+</sup> Si <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 3$ K)	[17, 19, 20]
NaTi <sup>3+</sup> Si <sub>2</sub> O <sub>6</sub>	spin-singlet ground state ( $T_c = 210$ K)	[21, 22]
LiTi <sup>3+</sup> Si <sub>2</sub> O <sub>6</sub>	spin-singlet ground state ( $T_c = 230$ K)	[21]
CaCu <sup>2+</sup> Ge <sub>2</sub> O <sub>6</sub>	spin-singlet ground state ( $T_c = 40$ K)	[23]
CaFe <sup>2+</sup> Si <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 38$ K)	[24, 25]
CaCo <sup>2+</sup> Si <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 10$ K)	[26]
CaNi <sup>2+</sup> Si <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 20$ K)	[26]
CaCo <sup>2+</sup> Ge <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 18$ K)	[25]
CaMn <sup>2+</sup> Ge <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 12$ K)	[25]
CaNi <sup>2+</sup> Ge <sub>2</sub> O <sub>6</sub>	antiferromagnetic long-range order ( $T_N = 18$ K)	[25]

We investigated the iron containing metagermanate NaFeGe<sub>2</sub>O<sub>6</sub> with clinopyroxene crystal structure (a monoclinic space group C2/c,  $Z = 4$ ), which was first described at room temperature in [27]. The nuclear structure is remained the same down to 2,5 K [14]. The lattice parameters at room temperature are  $a = 10,01$  Å;  $b = 8,94$  Å;  $c = 5,52$  Å;  $\beta = 108$  e [27].

The crystal structure consists of one-dimensional zigzag chains of edge-sharing FeO<sub>6</sub> octahedra which running parallel the crystallographic  $c$  axis. The GeO<sub>4</sub> tetrahedra are connected into infinite chains extended along the crystallographic  $c$  axis. The two types of chains alternate along the crystallographic  $b$  axis.

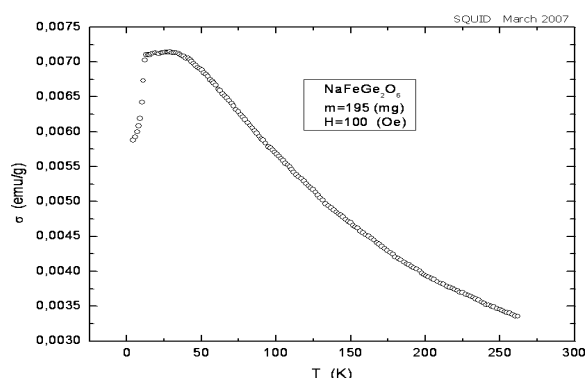


Fig. 1. Temperature dependence of the magnetization in NaFeGe<sub>2</sub>O<sub>6</sub>.

The magnetism of the pyroxene NaFeGe<sub>2</sub>O<sub>6</sub> is determined by spins on Fe<sup>3+</sup> ions ( $S = 5/2$ ).

We measured the temperature dependence of the magnetization  $\sigma(T)$  in magnetic field 0,01 T by a superconducting quantum interference device (SQUID) magnetometer between 4.2 and 300 K [11]. Bulk magnetic measurements of the temperature dependence of the magnetization show a broad maximum near 25 K (fig. 1), which is the characteristic property of low dimensional magnetic spin systems.

In previous papers we found the incommensurate magnetic structure due to the magnetic exchange interactions competitions in the polycrystalline NaFeGe<sub>2</sub>O<sub>6</sub> [12, 13]. This result was confirmed on a NaFeGe<sub>2</sub>O<sub>6</sub> single crystal [14].

To subsequent study the magnetic phase transitions and the magnetic structure in this compound it has been used the neutron scattering measurements.

### Sample preparation and experimental procedure

Polycrystalline NaFeGe<sub>2</sub>O<sub>6</sub> was obtained by a solid-state reaction method from the stoichiometric mixture of Na<sub>2</sub>CO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, GeO<sub>2</sub> at the temperatures of 800 – 900 °C in air at four stages each with a duration of 24 h. The sample was free from magnetic impurities, which were not detected in the x-ray diffraction patterns.

The neutron scattering experiments in the temperature range of 1.6 – 100 K were performed on the cold neutron powder diffractometer DMC [28] at Swiss spallation neutron source SINQ [29]. 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 [30]. 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.

Experimental results and their discusson

Table 2

We measured the temperature dependence of the specific heat  $C_p(T)$  between 2 and 300 K and the magnetic field 0 and 9 T [13]. The calorimetric investigations in the temperature range of 2 – 300 K in magnetic fields up to 9 T were performed using a Quantum Design PPMS 6000 instrument at Krasnoyarsk Shared Usage Scientific Center.

The temperature dependence of the NaFeGe<sub>2</sub>O<sub>6</sub> specific heat in the absence of the external magnetic field ( $H=0$ ) exhibits a sharp maxima at the temperatures  $T_1 = 11.6$  K and  $T_2=13$  K (fig. 2). There are two phase transitions in this clinopyroxene-type NaFeGe<sub>2</sub>O<sub>6</sub> compound at  $H = 0$ . The position of the first maximum ( $T_1 = 11.6$  K) in the  $C_p(T)$  curve depends on magnetic field. The position of the second maximum ( $T_2 = 13$  K) is not depend on magnetic field range of 0 – 9 T.

Also the magnetic susceptibility measurements had showed that the magnetic structure modification takes place near temperature  $T_1 = 11.6$  K [13].

Using neutron powder diffraction the magnetic order below  $T_N \approx 13$  K was confirmed again in the NaFeGe<sub>2</sub>O<sub>6</sub> [31, 32]. The fig. 3 shows the temperature dependence of the integrated intensity of the strongest magnetic peak  $(0, 0, 0) \pm k$  in the diffraction pattern of the neutron magnetic scattering in the NaFeGe<sub>2</sub>O<sub>6</sub>. This magnetic peak does not overlap with any other peaks and the fit program can easily determine the intensity. The phase transition which take a place in the NaFeGe<sub>2</sub>O<sub>6</sub> and is shown on the temperature dependence of the specific heat at  $T_2 = 13$  K (fig. 2) corresponds to the transition from paramagnetic to antiferromagnetic state, so  $T_2 = T_N = 13$  K. The temperature of the magnetic ordering  $T_N$  is low due to the competition between the intra- and interlayer exchange interactions of chains which were analyzed in [11].

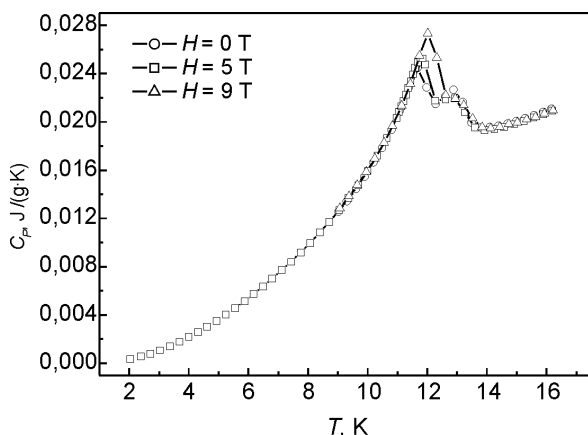


Fig. 2. Temperature dependence of the specific heat of NaFeGe<sub>2</sub>O<sub>6</sub> in magnetic field  $H = 0, 5, 9$  T.

The neutron scattering results for NaFeGe<sub>2</sub>O<sub>6</sub> spin arrangement at 1.6 K

Propagation vector	$\mathbf{k} = (0.3357(4), 0, 0.0814(3))$
Moment arrangement:	helical modulation of antiferromagnetically coupled pairs
The ordered moment per Fe <sup>3+</sup> ion	$M = 2.55(1) \mu_B$
Plane of moments	close to a-c plane (small component along b)
Reliability factors of refinement	$R_p = 4.5, \chi^2 = 4.43$

Neutron powder diffraction experiments ( $\lambda = 2.4576$  Å) results in NaFeGe<sub>2</sub>O<sub>6</sub> magnetic structure study are listed in table 2. The magnetic structure wave vector  $\mathbf{k} = (0.3357(4), 0, 0.0814(3))$  at 1.6 K.

On the basis of neutron diffraction measurements we concluded that the NaFeGe<sub>2</sub>O<sub>6</sub> magnetic structure is incommensurate and consists of antiferromagnetically coupled Fe<sup>3+</sup> pairs with helical modulation within the a-c plane of the crystal lattice (fig. 3). The NaFeGe<sub>2</sub>O<sub>6</sub>

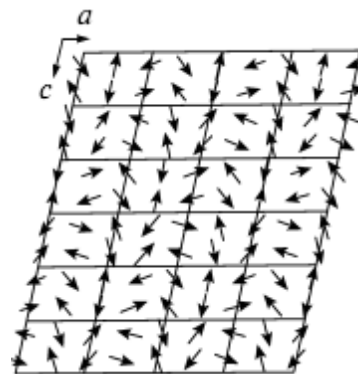


Fig. 3. Magnetic structure below  $T_1 = 11.6$  K in NaFeGe<sub>2</sub>O<sub>6</sub>.

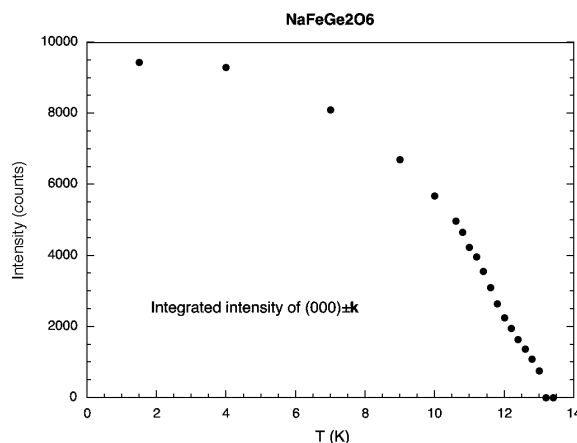


Fig. 4. Temperature dependence of the integrated intensity of the Bragg magnetic peak  $(0, 0, 0) \pm \mathbf{k}$  on the NaFeGe<sub>2</sub>O<sub>6</sub> neutron diffraction pattern. The Neel temperature is  $T_N = 13$  K.

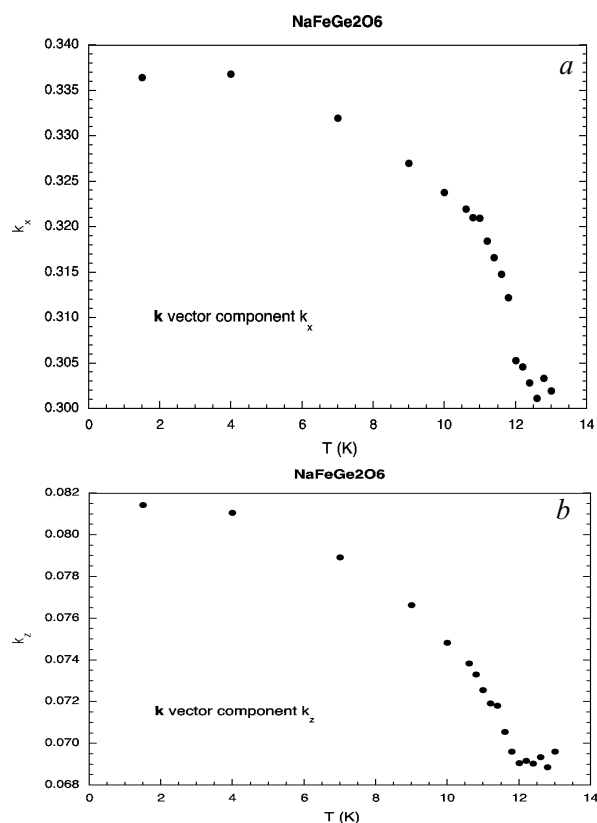


Fig. 5. Temperature dependence of the wave vectors  $k_x$  (a) and  $k_z$  (b) of the magnetic structure for  $\text{NaFeGe}_2\text{O}_6$ .

helical magnetic structure is apparently due to the “competition” of exchange interactions of different atomic neighbors of  $\text{Fe}^{3+}$  ions [33].

This magnetic structure is the same up to 11.6 K. In the integrated intensity curve there is a change of slope at 12 K, indicating the second phase transition (fig. 4).

The fig. 5 shows components of the  $\mathbf{k}$  vector: the component  $k_x$  (fig. 5a) and the component  $k_z$  (fig. 5b). The temperature dependence of  $k_x$  and  $k_z$  also show two phase transitions. Between 13 and 12 K the components of  $k$  are slowly changing. At 12 K both components start to increase quite steeply and then settle at the low temperature values at 1.6 K. The evolution of the  $\mathbf{k}$  vector was determined only by use of the magnetic peak positions and no magnetic model was involved.

It is not possible to refine a full magnetic model at magnetic field  $H = 0$  because the magnetic intensities are too small in the reason of the experimental data close to the ordering temperature  $T_N$ . There are no dramatic changes of relative intensities of different magnetic peaks above and below 12 K. So we may conclude that the two magnetic phases must be closely related.

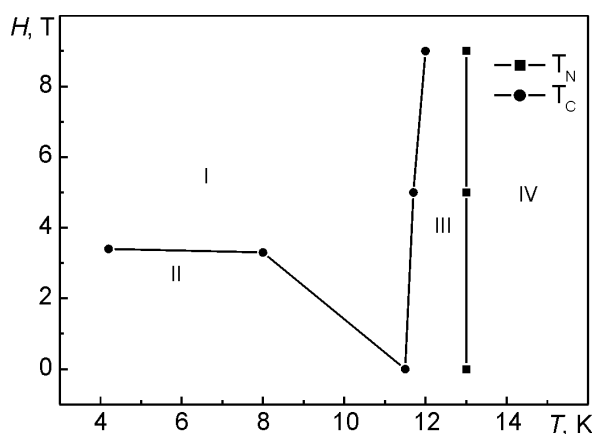


Fig. 6. Phase diagram of the magnetic state in  $\text{NaFeGe}_2\text{O}_6$ . Magnetic structure is incommensurate in region II and paramagnetic in region IV. It is unknown in regions I and III.

On the basis of the experimental data of the compound  $\text{NaFeGe}_2\text{O}_6$  we plot the phase diagram of the magnetic state (fig. 6). Magnetic structure is incommensurate in region II and paramagnetic in region IV. It is unknown in regions I and III.

### Conclusion

The magnetic structure and phase transitions of the sodium iron germanate  $\text{NaFeGe}_2\text{O}_6$  was studied by neutron diffraction.

In summary we conclude that the neutron diffraction results are in a good agreement with the data of the specific heat measurements. There are clear changes in the temperature dependence of the integrated intensity curve at 12 K indicating two ordered magnetic phases in zero magnetic field.

Below  $T_N \approx 13$  K the compound  $\text{NaFeGe}_2\text{O}_6$  undergoes a phase transition disorder — order (from the paramagnetic state to antiferromagnetic state).

The magnetic structure of  $\text{NaFeGe}_2\text{O}_6$  is not determined in the temperature range  $11.6 \text{ K} > T > 13 \text{ K}$  and the magnetic field  $H = 0$ . It is not possible to refine by the neutron diffraction experiment because the magnetic intensities are too small.

Below  $T_1 = 11.6$  K the magnetic structure undergoes to an incommensurate structure. Antiferromagnetically coupled pairs of  $\text{Fe}^{3+}$  moments show an helical modulation according to the magnetic propagation vector  $\mathbf{k}$  within the  $ac$  plane and no modulation along  $b$ .

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**Literature**

1. Streltsov S.V., Khomskii D.I. Electronic structure and magnetic properties of pyroxenes (La, Na)TM(Si,Ge)<sub>2</sub>O<sub>6</sub>: Low-dimensional magnets with 90° bonds. *Phys. Rev.*, 2008, B 77, p. 064405-1 – 064405-11.
2. Katanin A.A., Irhin V.Yu. Magnetic order and spin fluctuation in low-dimensional system. *Uspekhi Fiz. Nauk* 2007, v. 177, p. 639 – 662.
3. Jodlauk S., Becker P., Mydosh J.A., Khomskii D.I., Lorenz T., Streltsov S.V., Hezel D.C., Bohaty L. Pyroxenes: a new class of multiferroics. *J. Phys. Cond. Matter* 2007, v. 19, p. 432201 – 432210.
4. Vasiliev A.N., Ignatchik O.L., Isobe M., Ueda Y. Long range Neel order in quasi-one-dimensional vanadium-based (s=1) pyroxenes (Li,Na)V(Si,Ge)<sub>2</sub>O<sub>6</sub>. *Phys. Rev.* 2004, B 70, p. 132415-1 – 132415-4.
5. Emirdag-Eanes Mehtap, Kolis Joseph W. Hydrothermal synthesis, characterization and magnetic properties of NaVGe<sub>2</sub>O<sub>6</sub> and LiVGe<sub>2</sub>O<sub>6</sub>. *Mater. Research Bull.* 2004, v. 39, p. 1557 – 1567.
6. Mila F., Zhang F.C. On the origin of biquadratic exchange in spin 1 chain. *Eur. Phys. J.* 2000, B16, p. 7 – 10.
7. Millet P., Mila F., Zhang F.C., Mambrini M., Van Oosten A.B., Pashchenko V.A., Sulpice A., Stepanov A. Biquadratic interactions and spin-Peierls transition in spin-1 chain LiVGe<sub>2</sub>O<sub>6</sub>. *Phys. Rev. Lett.* 1999, v. 83, p. 4176 – 4179.
8. Redhammer G.J., Roth G., Treutmann W., Hoelzel M., Paulus W., Andre G., Pietzonka C., G. Amthauer. The magnetic structure of clinopyroxenes-type LiFeGe<sub>2</sub>O<sub>6</sub> and revised data on multiferroic LiFeSi<sub>2</sub>O<sub>6</sub>. *J. Solid State Chem.* 2009, v. 182, p. 2374 – 2384.
9. Redhammer G.J., Roth G., Paulus W., Andre G., Lottermoser W., Amthauer G., Treutmann W. The crystal and magnetic structure of Li-aegirine LiFe<sub>3</sub>+Si<sub>2</sub>O<sub>6</sub>: temperature-dependent study. *Phys. Chem. Minerals*, 2001, v. 28, p. 337 – 346.
10. Drokina T.V., Petrakovskii G.A., Bayukov O.A., Bovina A.F., Shimchak R., Velikanov D.A., Kartashev A.V., Volkova A.L., Ivanov D.A., Stepanov G.N. Properties of clinopyroxene LiFeGe<sub>2</sub>O<sub>6</sub>. *Phys. Solid State*, 2010, v. 52, p. 2250 – 2253.
11. Drokina T.V., Bayukov O.A., Petrakovskii G.A., Velikanov D.A., Bovina A.F., Stepanov G.N., Ivanov D.A. Synthesis and properties of NaFeGe<sub>2</sub>O<sub>6</sub>. *Phys. Solid State*, 2008, v. 50, p. 2141 – 2144.
12. Drokina T., Petrakovskii G., Keller L., Schefer J., Ivanov D. Magnetic structure and properties of pyroxene NaFeGe<sub>2</sub>O<sub>6</sub>. *China. Rare Metals*, 2009, v. 28, p. 398 – 400.
13. Drokina T.V., Petrakovskii G.A., Keller L., Schefer J., Balaev A.D., Kartashev A.V., Ivanov D.A. Modulated magnetic structure in quasi-one-dimensional clinopyroxene NaFeGe<sub>2</sub>O<sub>6</sub>. *JETP* 2011, v. 112, p. 121 – 126.
14. Redhammer G.J., Senyshyn A., Meven M., Roth G., Prinz S., Pachler A., Tippelt G., Pietzonka C., Treutmann W., Hoelzel M., Pedersen B., Amthauer G. Nuclear and incommensurate magnetic structure of NaFeGe<sub>2</sub>O<sub>6</sub> between 5 K and 298 K and new date on multiferroic NaFeSi<sub>2</sub>O<sub>6</sub>. *Phys. Chem. Minerals* 2010, DOI 10.1007/s00269-010-0390-3 (Springer).
15. Baum E., Treutmann W., Behruzi M., Lottermoser W., Amthauer G. Structural and magnetic properties of the clinopyroxenes NaFeSi<sub>2</sub>O<sub>6</sub> and LiFeSi<sub>2</sub>O<sub>6</sub>. *Zeitsch. Fur Kristal.* 1988, v. 183, p. 273 – 284.
16. Baker P.J., Lewtas H.J., Blundell S.J., Lancaster T., Franke I., Hayes W. Pratt F.L., Bohary L., Becker P. Muon-spin relaxation and heat capacity measurements on the magneto-electric and multiferroic pyroxenes LiFeSi<sub>2</sub>O<sub>6</sub> and NaFeSi<sub>2</sub>O<sub>6</sub>. *Phys. Rev.* 2005, B 81, p. 214403-1 – 214403-5.
17. Vasiliev A.N., Ignatchik O.L., Sokolov A.N., Hiroi Z., Isobe M., Ueda Y. Long-range magnetic order in quasi-one-dimensional chromium-based (s=3/2) pyroxenes (Li,Na)Cr(Si,Ge)<sub>2</sub>O<sub>6</sub>. *Phys. Rev.*, 2005, B 72, p. 012412-1 – 012412-4.
18. Vasiliev A.N., Ignatchik O.L., Sokolov A.N., Hiroi Z., Isobe M., Ueda Y. Long-range magnetic order in quasi-one-dimensional oxides NaCrSi<sub>2</sub>O<sub>6</sub> and NaCrGe<sub>2</sub>O<sub>6</sub>. *JETP Letters*, 2003, v. 78, p. 1039 – 1042.
19. Nenert G., Ritter C., Isobe M., Isnard O., Vasiliev A.N., Ueda Y. Magnetic and crystal structures of the one-dimensional ferromagnetic chain pyroxene NaCrGe<sub>2</sub>O<sub>6</sub>. *Phys. Rev.* 2009, B 80, p. 024402-1 – 024402-7.
20. Nenert G., Kim I., Isobe M., Ritter C., Vasiliev A.N., Kim K.H., Ueda Y. Magnetic and magnetoelectric study of the pyroxene NaCrSi<sub>2</sub>O<sub>6</sub>. *Phys. Rev.* 2010, B 81, p. 184408-1 – 184408-4.
21. Isobe M., Ninomiya E., Vasiliev A.N., Ueda Y. Novel Phase Transition in Spin-1/2 Linear Chain Systems: NaTiSi<sub>2</sub>O<sub>6</sub> and LiTiSi<sub>2</sub>O<sub>6</sub>. *J. Phys. Soc. Jpn.* 2002, v. 71, p. 1848 – 1851.
22. Popoviã Z.S., Đljivanëanin P.V., Vukajloviã Filip R. Sodium pyroxene NaTiSi<sub>2</sub>O<sub>6</sub>: possible haldane spin-1 chain system. *Phys. Rev. Lett.* 2004, v. 93, p. 036401-1 – 036401-4.
26. Sasago Y., Hase M., Ushinokya K., Tokunaga M., Miura N. Discovery of spin-singlet ground state with an energy gap in CaCuGe<sub>2</sub>O<sub>6</sub>. *Phys. Rev.* 1995, B 52, p. 3533 – 3539.
27. Coey J.M.D., Ghose S. Magnetic order in hedenbergite: CaFe<sup>2+</sup>Si<sub>2</sub>O<sub>6</sub>. *Solid State Commun.* 1985, v. 53, p. 143 – 145.
28. Redhammer G.J., Roth G., Treutman W., Paulus W., Andre G., Pietzonka C., Amthauer G. Magnetic ordering and spin structure in Ca-bearing clinopyroxenes CaM<sup>2+</sup>(Si, Ge)<sub>2</sub>O<sub>6</sub>, M=Fe, Ni, Co, Mn. *J. Solid State Chem.*, 2008, v. 18, p. 13163 – 3176.
29. Durand G., Vilminot S., Rabu A., Derory A., Lamboour J.P., Ressouche E. Synthesis, structure, and magnetic properties of CaMSi<sub>2</sub>O<sub>6</sub> (M = Co, Ni) compounds and their solid solutions. *J. Solid State Chem.*, 1996, v. 124, p. 374 – 378.
30. Solovyova L.P. and Bakakin V.V. X-ray investigation of Na, Fe-metagermanate NaFeGe<sub>2</sub>O<sub>6</sub>. *Krystallographiya*, 1967, v. 12, p. 591 – 594.
31. Fischer P., Keller L., Scheffer J., Kohlbrecher J. Neutron diffraction at SINQ. *Neutron News* 2000, v. 11, p. 19 – 21.
32. Fischer W.E. SINQ - The spallation neutron source, a new research facility at PSI. *Physica*, 1997, B 234 – 236, p. 1202 – 1208.

33. Rodriguez-Cravalaj Recent Advances in Magnetic Structure Determination by Neutron Powder Diffraction. J Physica B: Condens. Matter. 1993, v. 192, p. 55 – 69.
31. Drokina T., Petrakovskii G., Keller L., Schefer J. Investigation of the magnetic structure in NaFeGe<sub>2</sub>O<sub>6</sub> using neutron powder diffraction. Journal of Physics: Conference Series. 2010, v. 251, p. 012016 – 012020.
32. Schefer J., Keller L., Drokina T., Petrakovskii G. Incommensurate magnetic structure of NaFeGe<sub>2</sub>O<sub>6</sub> pyroxene investigated by neutron powder diffraction. Thesis. International conference on Neutron Scattering (ICNS 2009). 3 – 7 May, 2009. Knoxville, Tennessee, USA.
33. Izumov Yu.A. Diffraction of Neutrons on Long-Period structures 1987, (Energoatomizdat, Moscow), 200 p.

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