Crystal and magnetic structures, phase transitions in quasi-one-dimensional pyroxenes $Na_{0.5}Li_{0.5}FeGe_2O_6$

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A B S T R A C T

The possibility of cation substitution in pyroxenes allows the investigation the gradual change of structural and magnetic properties under doping in these compounds. Here, $Na_{0.5}Li_{0.5}FeGe_2O_6$ was prepared by the standard solid-phase reaction method and has been investigated using X-ray and neutron powder diffraction, and further characterized by magnetic and calorimetric measurements. The crystal structure of $Na_{0.5}Li_{0.5}FeGe_2O_6$ at 300 K is monoclinic $C2/c$ ($a = 10.0333(1)$, $b = 8.8136(1)$, $c = 5.5295(9)$ Å, $\beta = 108.921(1)°$). Calorimetric investigations indicate a displacive first order phase transition at $T = 271 \pm 1$ K which is accompanied by the appearance of superstructure reflections in the X-ray patterns. At this transition $Na_{0.5}Li_{0.5}FeGe_2O_6$ undergoes a space group change from $C2/c$ to $P2_1/c$ ($a = 9.9692(3)$, $b = 8.8545(3)$, $c = 5.4752(2)$ Å, $\beta = 108.494(1)°$). Magnetic order has been found below the Néel temperature $T_N \approx 18$ K and has been refined from neutron diffraction. The quasi-low-dimensional magnetic spin system $Na_{0.5}Li_{0.5}FeGe_2O_6$ exhibits a collinear antiferromagnetic structure with the space group P_a2_1/c and the doubling of the unit cell along the crystallographic a-axis of the pyroxene crystal (propagation vector $\boldsymbol{k} = (1/2, 0, 0)$). The critical modes which are responsible for the phase transition from $C2/c$ to $P2_1/c$ symmetry and for the magnetic transition from paramagnetic to antiferromagnetic state have been determined and their role in the transition is described. They are also the relevant mechanism driving the magnetic order in $LiFeGe_2O_6$.

1. Introduction

The pyroxenes compounds have the general chemical formula ABX_2O_6 (A = Na, Li and Ca; B = Mg, Cr, Cu, Ni, Fe, etc.; X = Ge, Si). They cover a broad class of a materials and have shown a variety of different magnetically ordered states (antiferromagnetic [1–4], ferromagnetic [3,5], modulated magnetic structure [6,7], spin gap state [8]). The variety of magnetic properties is connected to the features of the crystal structure which allows the existence of competing magnetic exchange interactions. Some pyroxene compounds have attracted significant theoretical interest due to their one-dimensional magnetism [9] and the structural phase transitions as a function of temperature and pressure [10–13]. Further,

special interest to these systems comes from the properties of some pyroxene compounds ($NaFeGe_2O_6$, $NaFeSi_2O_6$, $LiFeSi_2O_6$ and $LiCrSi_2O_6$) which exhibit a strong interaction between the magnetic and electric order [14,15].

The crystal structure and magnetic properties of the compounds $NaFeGe_2O_6$, $LiFeGe_2O_6$ have been studied in the past years [2,6,7,10,16,17]. The general crystal structures of pyroxenes consist of the isolated chains of FeO_6 edge-sharing octahedra which lie parallel to the crystallographic $\boldsymbol{c}$ axis. The corner-sharing GeO_4 tetrahedra form infinite chains extended along the crystallographic $\boldsymbol{c}$ axis. These two types of chains alternate along the crystallographic $\boldsymbol{b}$ axis.

The room temperature crystal of $NaFeGe_2O_6$ is monoclinic with the space group $C2/c$ [17]. The crystal structure of the clinopyroxenes $LiFeGe_2O_6$ is monoclinic with the space group $P2_1/c$ at 300 K. $LiFeGe_2O_6$ undergoes a phase transition from $C2/c$ to $P2_1/c$ symmetry at $T = 789$ K [10]. Noteworthy, the $C2/c$ and $P2_1/c$ structures differ in the configuration of the tetrahedral chains: in

$P2_1/c$ pyroxenes there are different, in $C2/c$ pyroxenes structure they are symmetric equivalent.

The magnetism of these chain pyroxenes is determined by the magnetic moment of the Fe^{3+} ions ($S=5/2$). $NaFeGe_2O_6$ clinopyroxenes orders below $T_N \approx 13$ K and the magnetic structure has been determined using neutron powder diffraction [6,16,7]. It is incommensurateand consists of antiferromagnetically coupled Fe^{3+} pairs with helical modulation within the [0,1] plane of the crystal lattice at 1.6 K $> T >$ 11.5 K [16]. $LiFeGe_2O_6$ orders below $T_N \approx 20$ K [2]. The magnetic structure of $LiFeGe_2O_6$ is different to that observed for $NaFeGe_2O_6$. It does not exhibit an incommensurate modulation, but is a collinear antiferromagnetic structure with magnetic unit cell doubled along the $\boldsymbol{a}$-direction in the crystal [2].

Cation substitution influences structural and electronic properties of the pyroxenes and the study of intermediate phases often allows to identify the fundamental interactions driving the phase transitions and the influence of chemical pressure on the electronic properties. $Na_{0.5}Li_{0.5}FeGe_2O_6$ solid solution was first prepared by Novikov et al. [18] However, the detailed crystallographic structure and the magnetic ground state have been unknown so far.

In this paper, in order to characterize the properties of the solid solution $Na_{0.5}Li_{0.5}FeGe_2O_6$, we report the results from X-ray and neutron powder diffraction, as well as magnetization and calorimetric measurements. The relevant structural phase transition from $C2/c$ to $P2_1/c$ symmetry, the low temperature $P2_1/c$ crystal structure (G_1 phase), the crystallographic details of the crystal structure $C2/c$ (G_0 phase), magnetic properties and magnetic structure with the space group P_a2_1/c (G_2 phase) of the $Na_{0.5}Li_{0.5}FeGe_2O_6$ are reported herein.

2. Experimental

2.1. Material synthesis

The samples of $Na_{0.5}Li_{0.5}FeGe_2O_6$ were prepared by the solid-phase reaction method from a stoichiometric mixture of oxides Fe_2O_3, Na_2CO_3, Li_2CO_3 and GeO_2. The powder was pressed into pellets which were subject to a high-temperature treatment at a maximum temperature of 1000 °C in air with several intermediate grindings. The chemical and phase composition of the pellet milled into the powder was examined by X-ray diffraction and shows a single phase.

2.2. X-ray diffraction

The X-ray powder diffraction data of $Na_{0.5}Li_{0.5}FeGe_2O_6$ for Rietveld analysis were collected between 133 K and 373 K with a Bruker D8 ADVANCE powder diffractometer (Cu-Kα radiation) and linear VANTEC detector. The step size of 2θ was 0.016°, and the total counting time of the scan was 3.6 h, with a 2θ range of $5° \leq 2\theta \leq 120°$. Additional 10 temperature steps for cell parameter evaluation were measured in the range from 133 K to 373 K with the total counting time 1.2 h. All refinements of the powder patterns were performed with TOPAS 4.2 (Bruker) [19].

2.3. Neutron diffraction

The neutron scattering experiments in the temperature range of 1.6–300 K, with a 2θ range of $5° \leq 2\theta \leq 92.7°$, and step width 0.1° were performed on the cold neutron powder diffractometer DMC [20] at the Swiss spallation neutron source SINQ [21]. The $Na_{0.5}Li_{0.5}FeGe_2O_6$ powder sample was enclosed in a cylindrical vanadium container under helium atmosphere and mounted in a helium cryostat. The neutron wavelength used was $\lambda=2.44955$ Å.

The data has been corrected for absorption and was refined using the FULLPROF program package with the main aim to determine the magnetic phase at low temperature [22].

2.4. Magnetic bulk measurements

The magnetic properties measurements were performed on an SQUID magnetometer in the temperature range 4.0–300 K in magnetic field of 500 Oe.

2.5. Calorimetric measurements

The temperature dependence of the heat capacity $\Delta C_p(T)$ of $Na_{0.5}Li_{0.5}FeGe_2O_6$ was measured using differential scanning microcalorimeter DSM-10 Ma (DSM) in the temperature range from 100 K to 400 K. The experiments were performed in a helium atmosphere on a powder sample with a weight of 47 mg in the dynamic mode with heating and cooling rates of 16 K/min. The sample was packed in an aluminum container without any heat conducting greases.

To obtain the integral thermodynamic characteristics associated with phase transition, initially, the heat flow through the sample and reference compound was recorded against temperature. Then, after elimination of background, the information on excess heat capacity ΔC_p was obtained by processing the calorimetric results. The average deviation of the experimental data from the smoothed curve $\Delta C_p(T)$ does not exceed 1%. The error in the determination of the integral characteristics (enthalpy and entropy) is around $\sim 10\%$.

3. Results and discussion

3.1. G_0 phase characterization

The X-ray powder pattern of $Na_{0.5}Li_{0.5}FeGe_2O_6$ at 300 K (G_0 phase) reveals that $Na_{0.5}Li_{0.5}FeGe_2O_6$ has the centrosymmetric $C2/c$ space group with 4 formula units per the cell and the lattice parameters are close to those of $NaFeGe_2O_6$ [7,17]. Therefore the crystal structure of $NaFeGe_2O_6$ was used as the starting model for the Rietveld refinement of the room temperature crystal structure of $Na_{0.5}Li_{0.5}FeGe_2O_6$. The site of Na-ion was occupied by Li- and Na-ions with fixed occupation $p_{Li}=0.5$ and $p_{Na}=0.5$, respectively. Anisotropic model of the preferred orientation effect with spherical harmonics 4 order was used [19]. The refinement was stable and gave low R-factors (Table 1, Fig. 1). Coordinates of atoms and main bond lengths are given in Tables 2 and 3 respectively. Additional Rietveld refinement of the G_0 phase using neutron data also showed good agreement between data and model (Fig. 2).

3.2. G_1 phase characterization

Analysis of X-ray patterns of $Na_{0.5}Li_{0.5}FeGe_2O_6$ measured from 133 K to 373 K showed the appearance of superstructure peaks at $T_1=271.5$ K which are forbidden in the G_0 phase with $C2/c$ space group (Fig. 3). This clearly indicates that the studied pyroxene undergoes a structural phase transition. The X-ray powder pattern at 133 K with increased statistics was used to obtain cell parameters and space group of the distorted phase G_1. In this phase $Na_{0.5}Li_{0.5}FeGe_2O_6$ has the centrosymmetric $P2_1/c$ space group with 4 formula units per cell and the cell parameters are close to those of $LiFeGe_2O_6$ [11] in G_1 phase, so this crystal structure was used as the starting model for Rietveld refinement. Anisotropic model of the preferred orientation effect with spherical harmonics 4 order was used. Small impurity of ice was detected on the pattern, and these peaks were accounted during refinement by using second