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Pyroxenes: a new class of multiferroics**S Jodlauk¹, P Becker¹, J A Mydosh², D I Khomskii², T Lorenz²,
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Online at stacks.iop.org/JPhysCM/19/432201**Abstract**

Pyroxenes with the general formula $AMSi_2O_6$ ($A =$ mono- or divalent metal, $M =$ di- or trivalent metal) are shown to be a new class of multiferroic materials. In particular, we have found so far that $NaFeSi_2O_6$ becomes ferroelectric in a magnetically ordered state below ~ 6 K. Similarly, magnetically driven ferroelectricity is also detected in the Li homologues, $LiFeSi_2O_6$ ($T_C \sim 18$ K) and $LiCrSi_2O_6$ ($T_C \sim 11$ K). In all these monoclinic systems the electric polarization can be strongly modified by magnetic fields. Measurements of magnetic susceptibility, pyroelectric current and dielectric constants (and their dependence on magnetic field) are performed using a natural crystal of aegirine ($NaFeSi_2O_6$) and synthetic crystals of $LiFeSi_2O_6$ and $LiCrSi_2O_6$ grown from melt solution. For $NaFeSi_2O_6$ a temperature versus magnetic field phase diagram is proposed. Exchange constants are computed on the basis of *ab initio* band structure calculations. The possibility of a spiral magnetic structure caused by frustration to be the reason for the origin of the multiferroic behaviour is discussed. We propose that other pyroxenes may also be multiferroic, and that the versatility of this family offers an exceptional opportunity to study general conditions for and mechanisms of magnetically driven ferroelectricity.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Multiferroic materials, which are simultaneously (ferro)magnetic, ferroelectric and ferroelastic, have very interesting physical properties and promise important applications. They are

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presently attracting considerable attention [1–6]. There exist several different classes of multiferroics [5], a very interesting type being the recently discovered [7, 8] systems in which ferroelectricity appears only in certain magnetically ordered states, typically, although not necessarily, spiral ones [6]. Even though their electric polarization P is usually not large, one can easily influence it by comparatively weak magnetic fields. It is this magnetic ‘switching’ of P which makes multiferroics potentially very useful in device applications. At present relatively few such materials are known: some of them [7–11] are multiferroic in zero magnetic field, while others develop an electric polarization only if a magnetic field is applied [12–14]. These compounds belong to different crystallographic classes, and although some general rules governing their behaviour are already established [6], there is as yet no complete or general understanding of the origin of multiferroic behaviour.

Here we report the discovery and study of a new class of multiferroics, which opens a fresh possibility to investigate the systematics of this phenomenon. Interestingly, this class—pyroxenes—form a very important group of minerals: they provide more than 20 vol% of the Earth’s crust and upper mantle to a depth of 400 km [15, 16]. In addition, with certain combinations of cations they create such well-known semiprecious stones as the famous Chinese jade and they even are found as constituents of extraterrestrial materials such as lunar and Martian rocks and meteorites [17, 18]. Pyroxenes belong to the silicates of the general composition $AMSi_2O_6$ where A stands for mono- or divalent metals while M represents di- or trivalent metals. Their crystal structures possess orthorhombic or monoclinic symmetries which can accept a wide variety of M and A elements, especially the 3d-transition metals. In most cases Si may be also substituted by Ge. Thus, pyroxenes offer a quite broad and flexible class of materials for physical investigations. Until now detailed investigations of these systems have been mainly focused on mineralogical and crystallographic aspects. Only recently did their magnetic properties attract some attention, in particular due to the observation of the orbitally driven spin gap state in $NaTiSi_2O_6$ [19, 20]. Most pyroxenes seem to be antiferromagnetic [21], yet complete magnetic structures are only known for few members of this class.

The specific features and the variety of magnetic properties of pyroxenes are determined by their crystal structure, shown in figure 1. The main building blocks are one-dimensional zig-zag chains of edge-sharing $[MO_6]$ octahedra running along the crystallographic c -axis. Within the (110) and $(\bar{1}10)$ planes these chains are connected by chains of $[SiO_4]$ (or $[GeO_4]$) tetrahedra. Important here is that, besides the quasi-one-dimensionality of the $[MO_6]$ chains, the relative packing of the magnetic chains forms a triangular-type magnetic lattice in each (110) plane, see figure 1(c), giving rise to a magnetic frustration. A similar frustration is present in the $(\bar{1}10)$ plane. Such geometric frustration can in principle lead to complex magnetic structures, in particular, commensurate or incommensurate spiral ordering, which, according to our present understanding, may be favourable for magnetically induced ferroelectricity [6]. So based upon their crystal structure pyroxenes are excellent candidates for multiferroic behaviour. Another beneficial feature of these materials is that they are usually good insulators (transparent crystals of green, yellow or brown colour), which is important for ferroelectric materials.

We find that indeed at least three members of this family, $NaFeSi_2O_6$, $LiFeSi_2O_6$ and $LiCrSi_2O_6$ become ferroelectric in a magnetically ordered state. In all of them the ferroelectricity can be strongly modified by the application of magnetic fields along different crystallographic directions.

2. Experimental details and methods

$NaFeSi_2O_6$ has been studied on different samples cut from a high-quality natural single crystal from Mount Malosa, Malawi, of size $10 \times 10 \times 80$ mm³, while for $LiFeSi_2O_6$ and $LiCrSi_2O_6$

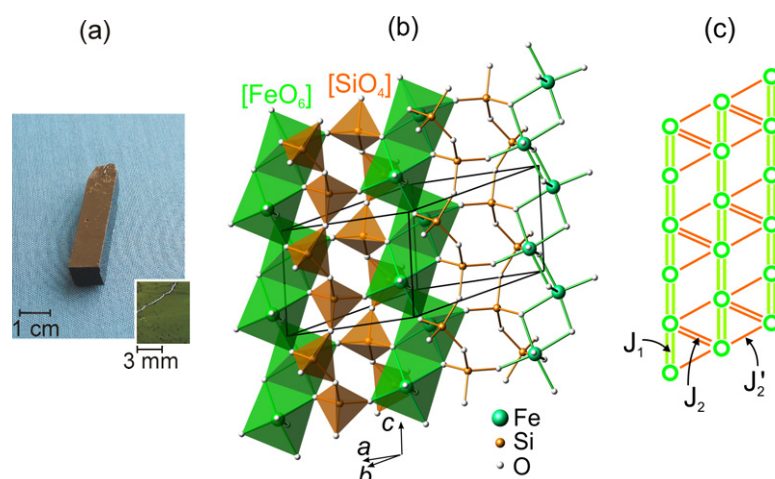


Figure 1. (a) Natural aegirine ($\text{NaFeSi}_2\text{O}_6$) crystal from a pegmatite of alkaline rocks of Mount Malosa, Malawi. In thin sections (see inset) the aegirine crystal is green and transparent. (b) The main features of the crystal structure are chains of edge-sharing $[\text{FeO}_6]$ octahedra (green) and chains of corner-sharing $[\text{SiO}_4]$ tetrahedra (orange) running along the c -direction (structure data from [22]). The linkage between iron atoms of neighbouring chains is visualized in the right part using the stick-and-ball representation. Sodium atoms are left out for clarity. Black lines denote the unit cell. The crystal structures of $\text{LiFeSi}_2\text{O}_6$ and $\text{LiCrSi}_2\text{O}_6$ are similar, but with space group symmetry $P2_1/c$ [23], while it is $C2/c$ for $\text{NaFeSi}_2\text{O}_6$. (c) Schematic elements of the magnetic subsystem. The double green lines represent the intrachain exchange interaction J_1 arising from two equivalent Fe–O–Fe paths. Despite the geometric zig-zag arrangement of the $[\text{FeO}_6]$ octahedra, one may expect for Fe^{3+} a uniform J_1 , since both the bond distances and the bond angles do not alternate along the chain direction and all 3d-orbitals of Fe^{3+} are half-filled. The interchain exchange J_2 (double yellow lines) and J'_2 (single yellow lines) arise from the Fe–Fe coupling via two and one $[\text{SiO}_4]$ tetrahedra, respectively.

we used synthetic single crystals. The chemical composition and homogeneity of our natural crystal of aegirine were analyzed by electron microprobe (JEOL 8900RL) on a (001) plate yielding the compositional formula $\text{Na}_{1.04}\text{Fe}_{0.83}\text{Ca}_{0.04}\text{Mn}_{0.02}\text{Al}_{0.01}\text{Ti}_{0.08}\text{Si}_2\text{O}_6$. Transparent single crystals of $\text{LiFeSi}_2\text{O}_6$ (light green) and $\text{LiCrSi}_2\text{O}_6$ (emerald green) were grown from melt solution with dimensions reaching $4 \times 2 \times 0.5 \text{ mm}^3$.

The magnetic susceptibility, pyroelectric current (typical peak heights: 50 fA–5 pA, typical baselines: 20–400 fA with noise of order 10 fA) and capacitance were measured by a vibrating sample magnetometer (Quantum Design PPMS), an electrometer (Keithley 6517 A) and a capacitance bridge (Andeen-Hagerling 2500 A), respectively. For the dielectric investigations plate-like samples coated with gold or silver electrodes were used. The dielectric constant ϵ' was calculated from the measured capacitance. The pyroelectric current was recorded without an applied electric field at a heating rate of $+1 \text{ K min}^{-1}$ for $\text{NaFeSi}_2\text{O}_6$ and $+4 \text{ K min}^{-1}$ for $\text{LiFeSi}_2\text{O}_6$ and $\text{LiCrSi}_2\text{O}_6$ after having cooled the sample in a static electric poling field of at least 200 V mm^{-1} . Typical leakage currents caused by the poling field amount to about 50 fA, meaning that the resistivities of our crystals are larger than $10^{14} \Omega \text{ m}$. By reversing the poling field the pyroelectric origin of the measured current and the ferroelectric switching of polarization was established. The polarization was completely reversible in $\text{NaFeSi}_2\text{O}_6$ and in $\text{LiFeSi}_2\text{O}_6$. In our small single crystals of $\text{LiCrSi}_2\text{O}_6$ the full reversal of pyrocurrent was not reached but only a reduction of $\sim 50\%$, most probably due to the domain wall pinning. This feature has to be checked for larger crystals. For calculating the polarization P by integration

of the pyroelectric current, a non-polarization-caused baseline (dependent on sample and measurement geometry) was eliminated.

For the band structure calculations we used the tight-binding linearized muffin-tin (MT) orbitals method and the LSDA + U approximation, which takes into account the on-site Coulomb correlations (U) in a mean-field way. We utilized the values of the Hubbard $U = 4.5$ eV and Hund's rule $J_H = 1$ eV obtained by the same calculation scheme described in [24]. The exchange interaction parameters were computed as a second derivative of the energy variation at small spin rotations [25].

3. Results

3.1. $\text{NaFeSi}_2\text{O}_6$

On $\text{NaFeSi}_2\text{O}_6$ (that is monoclinic with space group symmetry $C2/c$ in the paramagnetic state [22]) we measured the magnetic susceptibility in magnetic fields applied along all three crystallographic axes. The results for χ_a and χ_b are shown in figure 2(a). The measurements of χ_c resemble those for χ_a and are not shown. The inverse susceptibility $1/\chi_a$ taken in a field of 1 T is presented in figure 2(b). The susceptibility data show nearly paramagnetic (Curie–Weiss) behaviour down to a temperature of about 50 K and the clear onset of antiferromagnetic ordering at 8 K. A negative Weiss temperature $\Theta \approx -29$ K signals a net antiferromagnetic exchange interaction. The value of the effective magnetic moment μ_{eff} amounts to $5.69\mu_B$ close to the theoretically expected value of $g\sqrt{S(S+1)}\mu_B = 5.92\mu_B$ for the spin-only value of the Fe^{3+} ($S = 5/2$) magnetic moments. While χ_a (and χ_c) for low magnetic fields exhibit a maximum indicating the antiferromagnetic order, only a kink is observed for χ_b . This is a strong indication, that (at least for low magnetic fields) the spins of the Fe^{3+} -ions lie within the ac -plane. By applying higher magnetic fields the transition temperature (T_N) is reduced and the anomaly strongly broadens until it is not resolvable anymore in a field of 8 T. Another intriguing feature of the susceptibility data is an additional anomaly at around 6 K. Its position slightly decreases towards lower temperatures with increasing field and it vanishes for fields of more than about 4 T. As will be illustrated below, this behaviour is related to the onset of a spontaneous electrical polarization in $\text{NaFeSi}_2\text{O}_6$.

Measurements of the pyroelectric current and of the dielectric constants were performed on three mutually perpendicular plate-like samples (sample surfaces range from 40–80 mm², typical thickness is about 1 mm) with face normals along b , c , and $(b \times c)$, which does not coincide with a in a monoclinic unit cell. For each sample the magnetic field was applied along b , c , and $(b \times c)$. In figures 2(c) and (d) we present the electric polarization P_b along b and P_c along c measured in different magnetic fields H applied either along the $(b \times c)$ or the b direction (P_b for $H \parallel c$ is similar to P_b for $H \parallel (b \times c)$ and not shown). From these data we recognize that $\text{NaFeSi}_2\text{O}_6$ becomes ferroelectric below $T_{\text{FE}} = 6$ K, with the polarization $P \parallel b$. The onset temperature T_{FE} and the magnitude of P_b are suppressed by the field $H \parallel (b \times c)$, but hardly change for $H \parallel b$. This is confirmed by a well-defined peak of the longitudinal component ϵ'_b of the relative dielectric tensor along b (figure 2(e)), which is strongly suppressed by a magnetic field applied within the ac -plane, but only weakly shifts to lower temperature for $H \parallel b$. This anisotropic magnetic field dependence of the ferroelectric ordering fully corresponds to that of the magnetic ordering observed in the susceptibility measurements. When the polarization P_b is suppressed by $H \parallel (b \times c)$, a (smaller) spontaneous polarization P_c appears instead. A similar polarization P_c is also generated by $H \parallel c$. Thus, a field H applied within the ac -plane leads to a gradual rotation of the polarization from b to c -direction, see figure 2(f), while a magnetic field applied along the b -direction does not

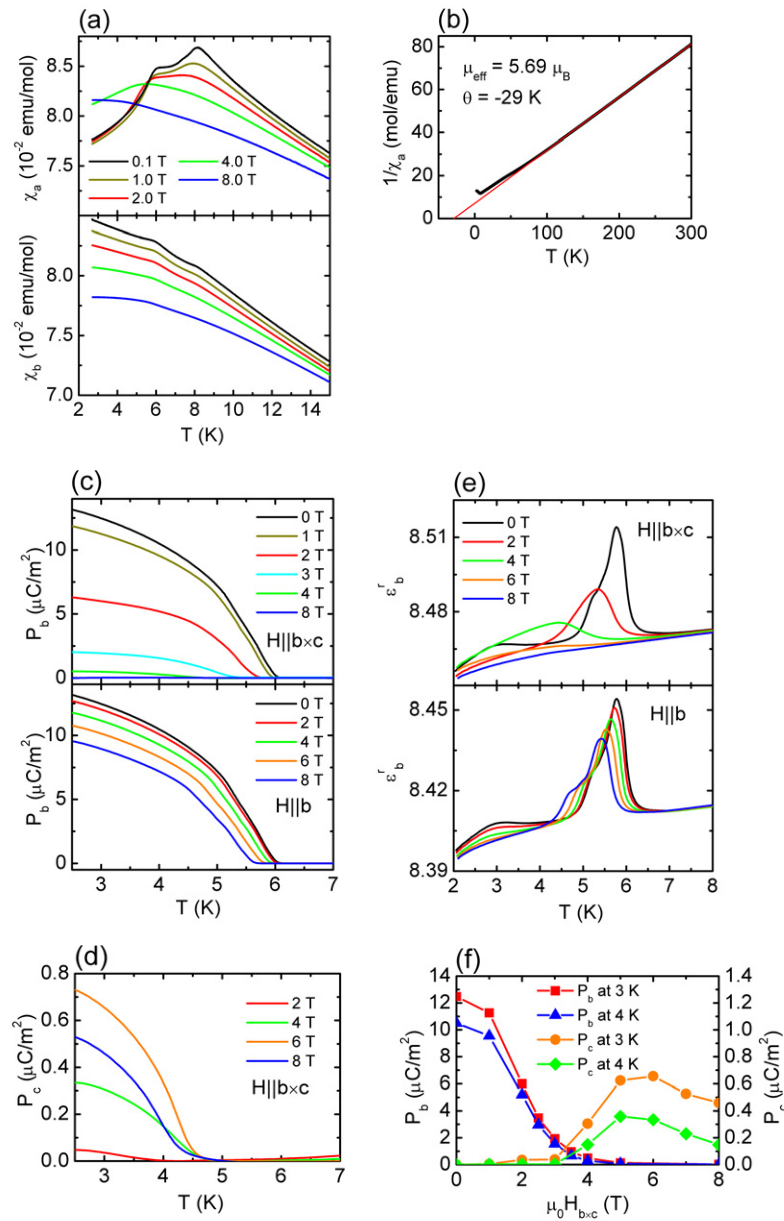


Figure 2. Magnetic and ferroelectric properties of NaFeSi₂O₆: representative temperature dependences of the magnetic susceptibility ((a) and (b)), spontaneous electric polarization ((c) and (d)) and the longitudinal component of the dielectric tensor ϵ_b^r (e) measured for different magnetic field strengths and orientations as indicated in the figure. Panel (f) displays the polarizations P_b and P_c as a function of a magnetic field $H \parallel (b \times c)$ at selected temperatures.

create any measurable P_c . An electric polarization $P_{b \times c}$ along $(b \times c)$ could not be detected, independent of the direction and strength of the applied magnetic field. The proposed phase diagram of the magnetoelectric behaviour of NaFeSi₂O₆ is given in figure 3.

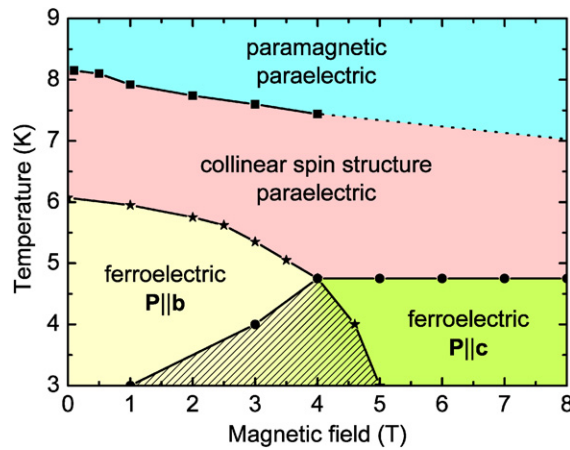


Figure 3. Temperature versus magnetic field (applied in the ac -plane) phase diagram for $\text{NaFeSi}_2\text{O}_6$ illustrating the multiferroic behaviour.

3.2. $\text{LiFeSi}_2\text{O}_6$ and $\text{LiCrSi}_2\text{O}_6$

For the Li-pyroxenes $\text{LiFeSi}_2\text{O}_6$ and $\text{LiCrSi}_2\text{O}_6$ (with space group symmetry $P2_1/c$ below 228 K and 335 K, respectively, and $C2/c$ above these temperatures [26]) we measured χ_c as well as the pyroelectric current and dielectric constants on thin (~ 0.5 mm) plate-like samples with $\{010\}$ surfaces of about 10 mm^2 and 4 mm^2 , respectively, in magnetic fields applied along c . As presented in figure 4(a), $\text{LiFeSi}_2\text{O}_6$ shows paramagnetic behaviour down to a temperature of 18 K, where at low applied magnetic field the clear onset of antiferromagnetic ordering is observed. The onset temperature gradually decreases to 14 K when increasing the magnetic field to 14 T. The strong low-temperature increase of χ_c around 6 T indicates a spin-flop transition, where the orientation of the spins changes from parallel c to perpendicular c . Figure 4(b) presents the measured pyroelectric current and the corresponding electric polarization along the b -direction of the crystal. While there is essentially no pyroelectric current in zero magnetic field, we find pronounced peaks in the pyroelectric current for finite fields. For $H > 0$, we also observe small precursors of negative sign in the pyroelectric current. Their origin is not yet clear, but they cannot be attributed to ferroelectric behaviour, since—in contrast to the large peaks—they neither change sign nor shape or size when the electric poling field is reversed. With increasing magnetic field these peaks shift to lower temperatures similar to the shift of the antiferromagnetic ordering temperatures observed in χ_c . Integrating the difference of the pyroelectric current in finite and zero magnetic field reveals a clear development of a spontaneous electric polarization P_b below the magnetic ordering temperature in finite magnetic fields. However, due to small negative pyroelectric currents in finite fields for temperatures below the peak, the calculated polarization decreases again and even changes sign with further decreasing temperature. Whether or not this unexpected behaviour is intrinsic requires further studies on larger crystals.

The magnetic susceptibility χ_c of $\text{LiCrSi}_2\text{O}_6$ (figure 4(c)) shows a different behaviour. Around 20 K we observe a broad maximum of χ_c , as is typical for low-dimensional spin systems. Below 11 K, a sharp increase of χ_c sets in indicating a long-range magnetic order with a small ferromagnetic component. This indicates a slightly canted antiferromagnetic spin structure. The maximum spontaneous magnetic moment of about $0.005\mu_B$ suggests a canting angle of about 0.1° of the total spin moment of $3\mu_B$ per Cr^{3+} . Similar to $\text{LiFeSi}_2\text{O}_6$, we find

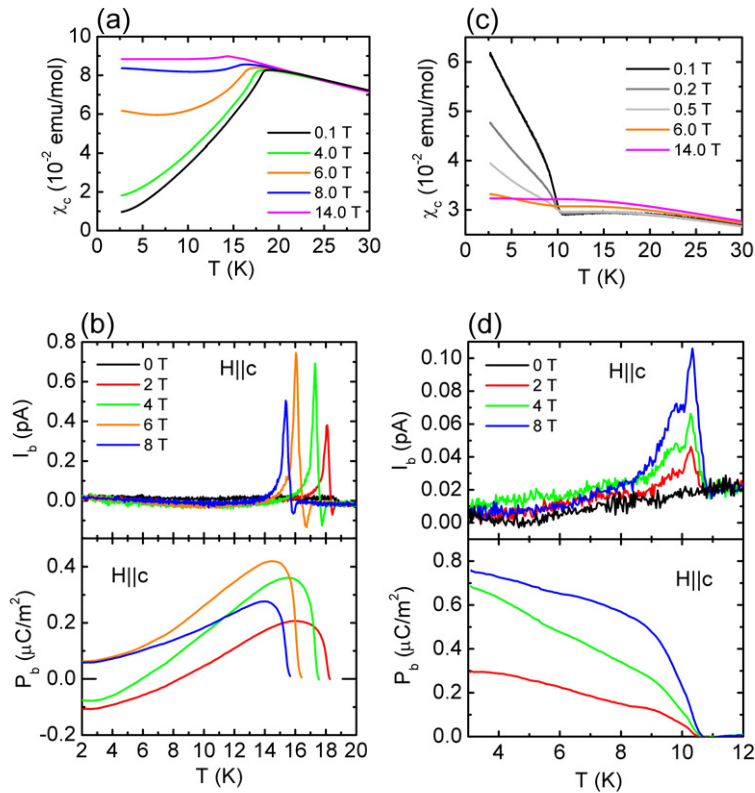


Figure 4. Selected temperature dependences of the magnetic susceptibility χ_c , pyroelectric current I_b and electric polarization P_b of LiFeSi₂O₆ ((a) and (b)) and LiCrSi₂O₆ ((c) and (d)) for different magnetic fields applied along the c -direction. The small current peaks of negative sign in panel (b) are not of pyroelectric origin (see section 2).

an electric polarization P_b along b in an applied magnetic field along c while P_b remains zero without a magnetic field. The pyroelectric current and the resulting electric polarization of LiCrSi₂O₆ (figure 4(d)) show a sharp phase transition slightly below 11 K that coincides with the temperature of magnetic ordering. In contrast to LiFeSi₂O₆ we observe neither a shift of the onset temperatures of magnetic ordering nor of the electric polarization with increasing magnetic field. The magnitude of the electric polarization monotonically grows with increasing magnetic field up to the highest applied field of 8 T.

4. Discussion

According to the data presented above we identify at least three members of the large pyroxene family that develop magnetically driven ferroelectricity, which strongly depends on the applied magnetic field. The ferroelectric behaviour was established by reversing the static electric poling field (see section 2). The explanation of the appearance of ferroelectricity in magnetic states requires the specific knowledge of the corresponding magnetic structure. The early data on the magnetic structure of NaFeSi₂O₆ are presented in [22, 27], and those for LiFeSi₂O₆ in [27, 28] (for LiCrSi₂O₆ no information on the magnetic structure is available in literature). The proposed structures, all being antiferromagnetic, are nevertheless different, even for the

same material. In [22] it was suggested that in aegirine the spins of the one-dimensional zig-zag chains in the c -direction are ferromagnetic, with the neighbouring chains being antiparallel. In [27] the same magnetic coupling scheme, but also a model of purely antiferromagnetic coupling within and between the chains, was considered for both, $\text{NaFeSi}_2\text{O}_6$ and $\text{LiFeSi}_2\text{O}_6$, based upon magnetization and Mössbauer investigations. And in [28] the authors conclude that the spins are antiferromagnetically ordered both intrachain and interchain for $\text{LiFeSi}_2\text{O}_6$, but the detailed magnetic structure was not revealed. At the same time several peaks in the neutron scattering spectra of $\text{NaFeSi}_2\text{O}_6$ observed in [22] remain unexplained, and the authors themselves speculate that they may be connected with a possible incommensurate superstructure caused by frustration. In the absence of unambiguous data on the magnetic structure we can only assume that there may indeed exist a spiral structure in these materials, possibly in addition to the main features found in [22, 27, 28]. Actually, a spiral structure should be expected from the ‘triangular’ topology seen in figure 1(c) and also from the values of the exchange constants. The latter were determined from *ab initio* band structure calculations which we carried out using the LSDA + U method (see section 2). For $\text{NaFeSi}_2\text{O}_6$ we obtained the intrachain exchange integral $J_1 = 8.5$ K and the interchain coupling $J_2 = 1.6$ K; $J'_2 = 0.8$ K, and for $\text{LiFeSi}_2\text{O}_6$ $J_1 = 7.0$ K, $J_2 = 3.4$ K; $J'_2 = 1.9$ K—all antiferromagnetic, in full agreement with the Goodenough–Kanamori rules. For such values of exchange one expects a spiral magnetic structure for the triangular lattice [29].

Based upon our exchange scheme we can propose a scenario which would explain the appearance of ferroelectricity by the existence of spiral magnetic structures in $\text{NaFeSi}_2\text{O}_6$ (and probably in $\text{LiFeSi}_2\text{O}_6$ and $\text{LiCrSi}_2\text{O}_6$ as well), consistent with the general considerations of [6]. However, we cannot exclude other possible mechanisms, e.g. magnetostriction [5, 6]. The features of the observed polarization in all three materials, $\text{NaFeSi}_2\text{O}_6$, $\text{LiFeSi}_2\text{O}_6$ and $\text{LiCrSi}_2\text{O}_6$, indicate that the crystals remain monoclinic in their magnetically and electrically ordered phase, and therefore the phase transition follows a simple group–subgroup path. In $\text{NaFeSi}_2\text{O}_6$ the loss of inversion symmetry of the paraelectric phase (point group $2/m$) at T_{FE} results in the polar point groups 2 ($\mathbf{P} \parallel \mathbf{b}$) or m (\mathbf{P} perpendicular \mathbf{b}), depending upon the applied magnetic field. So far in the Li-compounds spontaneous polarization was observed parallel \mathbf{b} in finite field, but it is not clear whether for $H = 0$ the polarization is simply absent (or very small), or along another direction. At present our available single crystals do not allow a definite conclusion. Another open question is whether the presence of non-centrosymmetric $[\text{SiO}_4]$ tetrahedra plays some role in providing the mechanism of ferroelectricity in pyroxenes.

5. Conclusions

We have found a new class of multiferroic materials among the geologically important pyroxenes with the general formula AMSi_2O_6 . So far, three members of this large family of compounds— $\text{NaFeSi}_2\text{O}_6$, $\text{LiFeSi}_2\text{O}_6$ and $\text{LiCrSi}_2\text{O}_6$ —show magnetically induced ferroelectricity. Both the magnitude and direction of the polarization can be strongly modified by a magnetic field. In the absence of reliable data on magnetic structure we cannot exactly identify the source of multiferroic behaviour in the pyroxenes, but we suggest that its origin may be connected with a spiral magnetic structure caused by their magnetic frustration. The existence of many compounds with the pyroxene structure advances the hope that other materials of this large family would also display multiferroic behaviour at yet higher temperatures. The fact that this phenomenon is observed in materials that are very important in geology adds a new ingredient to our findings. One can only speculate whether the physics disclosed here may have important outgrowths for geophysics, e.g. concerning cold extraterrestrial objects. However, even irrespective of this potentially important interplay, the

very fact of the observation of a whole new class of (nearly) isostructural multiferroic materials has a substantial interest and should lead to a new and better understanding of this fascinating phenomenon.

Acknowledgments

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