Unravelling the complex magnetic structure of multiferroic pyroxene \( \text{NaFeGe}_2\text{O}_6 \): A combined experimental and theoretical study

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Magnetism of multiferroic pyroxene \( \text{NaFeGe}_2\text{O}_6 \) has been systematically investigated by neutron powder diffraction, magnetization measurements, density-functional theory (DFT) band-structure calculations, and Monte-Carlo simulations for the ensuing spin Hamiltonian. We found that \( \text{NaFeGe}_2\text{O}_6 \) first reveals one-dimensional spin-spin correlations in the paramagnetic state which is confirmed through magnetic diffuse scattering. Upon cooling, a sinusoidal spin-density wave sets in at 13 K and further transforms into a cycloidal configuration below 11.6 K. The cycloidal magnetic configuration with spins lying in the \((ac)\) plane, characterized by the \( \mathbf{k}\) vector \((\alpha, 0, \gamma)\), is responsible for multiferroicity in \( \text{NaFeGe}_2\text{O}_6 \) through the inverse Dzyaloshinsky-Moriya (DM) mechanism. On the microscopic level, a significant intrachain coupling \( J_1 \approx 12\) K, which is likely related to the one-dimensional spin-spin correlations, competes with two well-balanced interchain couplings of about 2 K, giving rise to magnetic frustration as well as incommensurability, while a moderate single-ion anisotropy triggers the intermediate spin-density-wave state between 11.6 and 13 K. We finally discuss the origin of multiferroicity in \( \text{NaFeGe}_2\text{O}_6 \) based on symmetry analysis.

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I. INTRODUCTION

Spin-driven multiferroics, where significant coupling between magnetic order and electric polarization emerges due to simultaneous symmetry breaking induced mainly by the incommensurate magnetic structure [1], have drawn a great deal of attention in recent years. Several theoretical models, such as inverse Dzyaloshinsky-Moriya (DM) (or spin-current model) [2, 3] and spin-dependent \( p-d\) orbitals hybridization [4], have been put forward to explain this fascinating phenomenon. Although the inverse DM model essentially has captured the behavior of many multiferroic materials, such as \( \text{TbMnO}_3 \) [5] and \( \text{AgFeO}_2 \) [6], in which the spin configuration is cycloidal with the propagation vector lying in the spin plane, it failed to account for multiferroicity in systems with proper screw magnetic symmetry. More recently, the mechanism of ferroaxiality of crystal structure has been proposed to explain the experimentally observed multiferroic properties in \( \text{Cu}_3\text{Nb}_2\text{O}_8 \) [7], \( \text{CaMn}_2\text{O}_{12} \) [8], and \( \text{RbFe(MoO}_4)_2 \) [9], where a proper screw magnetic structure with spin plane perpendicular to the propagation vector has been found. In addition, Kaplan and Mahanti [10] have shown that the extended inverse DM effect in some specific systems contributes to microscopic electric polarization in both cycloidal and proper-screw helical systems, and this observation has been used to account for the multiferroicity in some delafossites [11].

As one of the main minerals of the Earth’s crust and upper mantle, pyroxenes with the chemical formula \( \text{AM}_2\text{O}_6 \) (\( A = \) mono- or divalent metal, \( M = \) transition metal, \( T = \) Ge or Si) have gained revitalized attention of condensed-matter physicists, since recently a number of magnetic pyroxenes have been found to show multiferroicity or magnetoelastic effect due to geometric magnetic frustration arising from the competition between intra- and inter-chain exchange interactions [12–17]. Later on, subsequent investigations on pyroxenes indicated that only \( \text{NaFeGe}_2\text{O}_6 \) [14], \( \text{SrMnGe}_2\text{O}_6 \) [16], and the mineral aegirine [12] are truly multiferroic.

\( \text{NaFeGe}_2\text{O}_6 \) crystallizes in the space group \( \text{C}2/\text{c}1' \) and can be regarded as a system showing both frustration and magnetic low dimensionality due to its special crystal structure, in which zig-zag chains of edge-sharing \( \text{FeO}_6 \) octahedra are bridged by corner-linked \( \text{GeO}_4 \) tetrahedral chains (Fig. 1). Previous investigations, based on magnetic-susceptibility measurements, have shown that \( \text{NaFeGe}_2\text{O}_6 \) first demonstrates a low-dimensional feature with a broad susceptibility maximum around 35 K, followed by the long-range antiferromagnetic (AFM) ordering at 13 K [18]. More recently, a successive long-range AFM magnetic transition at 11.6 K was identified through a specific-heat measurement [19], revealing the rich and complex magnetic properties of \( \text{NaFeGe}_2\text{O}_6 \). The AFM transition at 11.6 K is accompanied by a spontaneous electric polarization, as evidenced through electric polarization measurement on both powder and single-crystal samples [14, 15]. Neutron diffraction has previously been employed to investigate the magnetic structure of \( \text{NaFeGe}_2\text{O}_6 \) powders and single crystals below 11.6 K. Although reports from two distinct research groups concurred on the incommensurate cycloidal spin configuration, they proposed different propagation vectors, \( \mathbf{k}_1 \approx (0.3357, 0, 0.0814) \) versus \( \mathbf{k}_2 \approx (0.323, 1.0, 0.08) \) [18, 19]. The intermediate-temperature magnetic structure between 11.6 K and 13 K remains unknown. To understand the complex magnetic properties of \( \text{NaFeGe}_2\text{O}_6 \), it is vital to figure out the correct magnetic structures of both ordered states, what exchange interactions are involved and how strong they are.

Here, we present unambiguous determination of the hitherto debated magnetic structure below 11.6 K, and uncover the magnetic configuration between 11.6 K and 13 K using...
resolution pulsed neutron diffraction. We further identify the presence of one-dimensional spin-spin correlations via magnetic diffuse scattering in the paramagnetic state well above 13 K. A combination of density-functional calculations and Monte-Carlo simulations enables us to quantify the microscopic spin Hamiltonian and obtain relevant magnetic interactions in NaFeGe$_2$O$_6$. Finally, we discuss possible mechanisms for multiferroicity in terms of the magnetic symmetry.

II. METHODS

Polycrystalline NaFeGe$_2$O$_6$ was synthesized by a solid-state reaction. The stoichiometric mixture of reagent-grade Na$_2$CO$_3$, Fe$_2$O$_3$, and GeO$_2$ was ground in an agate mortar and pelletized. The pellets were placed into alumina crucibles and heated in air at 1273 K for 100 hours and cooled down to room temperature. Intermediate regrinding and reheating were performed in order to improve the purity of the sample.

The temperature-dependent magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design, MPMS-7T). The dc magnetic susceptibility was recorded from 2 to 350 K in zero-field-cooled (ZFC) and field-cooled (FC) procedures in a magnetic field of 1 T. The specific-heat measurement was carried out using a relaxation technique with a Quantum Design Physical Property Measurement System (PPMS) in the temperature range of 2-300 K on cooling. The pelletized sample was mounted on a sample platform with Apiezon N-grease for better thermal contact.

Temperature-dependent powder x-ray diffraction (XRD) data were collected with a RIGAKU Smartlab diffractometer in the high-resolution parallel beam mode using a Ge (220)\texttimes 2 monochromator for CuK$_\alpha$ radiation and Oxford Phenix cold stage giving access to sample temperatures as low as 12 K. The neutron powder diffraction (NPD) data were collected at the ISIS pulsed neutron and muon facility of the Rutherford Appleton Laboratory (UK), on the WISH diffractometer located at the second target station [20]. A powder sample (~ 4.1 g) was loaded into a 6 mm diameter cylindrical vanadium can and measured in the temperature range of 1.5 - 150 K using an Oxford Instrument Cryostat. The data at 1.5, 20, 50, 100 and 150 K were collected for 1 hour, and typical scans between these temperatures were carried out with an exposition time of 30 minutes with steps of 1 K in the temperature range of 2-10 K and 0.2 K for measurements between 10 and 15 K.

Rietveld refinements of the crystal and magnetic structures were performed using the Fullprof program [21] against the data measured in the detector banks at the average 2$\theta$ values of 58°, 90°, 122°, and 154°, each covering 32° of the scattering plane. Group-theoretical calculations were done using ISODISTORT [22] and Bilbao Crystallographic Server (Magnetic Symmetry and Applications [23]) software.

Magnetic exchange couplings were analyzed using density-functional (DFT) band-structure calculations performed in the FPLO [24] and VASP [25, 26] codes. Perdew-Burke-Ernzerhof flavor of the exchange-correlation potential was chosen [27]. The $k$ mesh with up to 64 points in the symmetry-irreducible part of the first Brillouin zone was used providing full convergence with respect to the number of $k$-points. Correla-
tion effects in the Fe 3d shell were taken into account on the mean-field level via the DFT+U procedure with the on-site Coulomb repulsion \( U_d = 6 - 8 \text{ eV} \) and Hund’s exchange \( J_d = 1 \text{ eV} \) [28, 29].

Exchange couplings \( J_{ij} \) enter the spin Hamiltonian

\[
H = \sum_{\langle ij \rangle} J_{ij} S_i S_j + \sum_i A_i (S_i^z)^2
\]

where \( S = \frac{5}{2} \) and the summation is over bonds \( \langle ij \rangle \). The values of \( J_{ij} \) were obtained by a mapping procedure using energies of collinear spin configurations [30]. A similar mapping procedure for orthogonal spin configurations yields magnetic anisotropy parameters \( A_i \) when spin-orbit (SO) coupling is included within the DFT+U+SO approach.

Thermodynamic properties of the resulting spin model were analyzed by classical Monte-Carlo simulations using the spinmc algorithm of the ALPS package [31]. Finite \( L \times L \times L \) lattices with \( L \leq 8 \) and periodic boundary conditions were used.

III. RESULTS

A. Magnetic properties

The temperature dependence of the magnetic susceptibility of NaFeGe\(_2\)O\(_6\) measured in a magnetic field of 1 T is shown in Fig. 2 (a). An obvious broad maximum at \( \sim 38 \) K resembles the behavior of a linear-chain Heisenberg antiferromagnet, in agreement with the chain-like structural features [32]. In fact, similar low-dimensional features have also been observed in other pyroxenes, such as NaCrGe\(_2\)O\(_6\) [33]. With further decreasing temperature, a drop around 11.6 K occurs. As marked by the dashed and dashed-dotted lines in the inset, two distinct magnetic transitions at \( T_{N1} = 11.6 \text{ K} \) and \( T_{N2} = 13 \text{ K} \) can be clearly seen in the Fisher’s heat capacity \( d(\chi T)/dT \), suggesting two magnetically ordered states. This result is consistent with the previous studies [14, 19].

Experimental magnetic susceptibility was fitted with the Curie-Weiss law between 200 and 350 K. This yields an effective moment \( \mu_{eff} = 6.16(8) \text{ \mu_B} \), consistent with the calculated spin-only value of 5.92 \( \text{ \mu_B} \) for Fe\(^{3+}\) cations in the high-spin state, in agreement with the previous report [14]. The negative Weiss temperature of \( \Theta = -117(1) \text{ K} \) indicates predominant antiferromagnetic interactions and reveals a considerable reduction in the Néel temperature, \( \Theta/T_N \gtrsim 10 \), which may be due to the low-dimensionality and/or frustration.

In order to further characterize these magnetic phase transitions, we performed heat capacity measurement. Figure 2 (b) shows the temperature dependence of the specific heat \( (C_p) \) of NaFeGe\(_2\)O\(_6\). The two successive cusps at 11.6 and 13 K are indicative of two magnetic phase transitions, in good agreement with our magnetic susceptibility result. No apparent anomaly can be observed around 38 K, implying that the broad maximum at 38 K should be attributed to short-range magnetic correlations.

![Figure 2](image)

B. Neutron diffraction

According to our temperature-dependent x-ray diffraction and the WISH backscattering data collected in the temperature range of 1.5-150 K, NaFeGe\(_2\)O\(_6\) crystallizes with \( C2/c1' \) symmetry and has no symmetry change down to 1.5 K. At 150 K, the lattice parameters are: \( a = 10.0092(1) \text{ \AA}, b = 8.9124(1) \text{ \AA}, c = 5.50895(5) \text{ \AA}, \beta = 107.5189(9)^\circ \). Magnetic Bragg reflections appear below \( T_{N2} = 13 \text{ K} \) (ICM2 phase) in the NPD data, as shown in Fig. 3, and they can be indexed by an incommensurate propagation vector \( \mathbf{k} \sim (\alpha, 0, \gamma) \) with \( \alpha = -0.6999(8) \) and \( \gamma = 0.0649(2) \) at 12.2 K. The value of \( \mathbf{k} \) shows a slightly temperature-dependent behavior, as indicated in Fig. 4. On further cooling, additional magnetic reflections appear below \( T_{N1} = 11.6 \text{ K} \) (ICM1 phase), and the magnetic reflections exhibit an obvious temperature-dependent behavior. These reflections can also be indexed by the same incommensurate vector \( \mathbf{k} \) albeit with a slightly different \( \alpha \) and \( \gamma \) values (Fig. 4 (a) and (b)). At 1.5 K, the refined \( \mathbf{k} \) is \( (-0.6702(1), 0, 0.08028(5)) \). It is clear that the ICM2 phase only appears within the very narrow temperature range 11.6 - 13 K.

Previous neutron diffraction experiments on both powder and single crystals failed to resolve this phase [18] The presence of magnetic Bragg reflections in our neutron diffraction
data is consistent with the magnetic susceptibility and heat capacity measurements, showing the existence of two ordered magnetic states. The propagation vector of the ICM1 phase we obtained is, in fact, equivalent to the vector $k'=(0.323, 1.0, 0.08)$ reported in Ref. 18. By applying a reciprocal translation $(-1, -1, 0)$, one can transform $k'$ into $k = (-0.67, 0.0, 0.8)$.

We have performed symmetry analysis in order to determine the magnetic structures of NaFeGe$_2$O$_6$. Starting with the parent space-group $C2/c1'$ and propagation vector $k = (a, 0, \gamma)$ in the B plane of the Brillouin zone, through ISODISTORT, two active magnetic irreducible representations, mB1 and mB2, as well as their corresponding subgroups were obtained. For ICM1 phase, we found that magnetic superspace group $Cc1'(a, 0, \gamma)0s$ (basis=$(-1,0,0,0),(0,-1,0,0),(0,0,-1,0),(0,0,0,1)$, origin=$(0,0,0,0)$), generated from single active mB1 irreducible representation, can be adopted to describe the magnetic structure. Such symmetry fixes the phase difference between atom Fe1 (0,y,0.25) and Fe2 (0,−y,0.75) to be $(1+\gamma)*\pi$. The refinement of magnetic structure at 1.5 K was carried out by taking into account this symmetry constraint. The final refinement of neutron diffraction data is shown in Fig. 5. It turns out that cycloidal magnetic symmetry with moment confined into the (ac) plane was obtained. The refined total magnetic moment at 1.5 K is 3.857(8) $\mu_B$, considerably smaller than the theoretical value expected for $S = 5/2$ of Fe$^{3+}$. In fact, this value is very close to the total magnetic moment with 4.09(4) $\mu_B$ refined from a single crystal NaFeGe$_2$O$_6$ reported in Ref.[18]. Such a reduction, observed very often in cycloidal spin systems, is likely a consequence of spin fluctuations and covalency. The magnetic symmetry, as represented in Fig. 1, breaks the inversion symmetry and preserves the mirror plane symmetry perpendicular to the unique b axis, leading to the magnetic point group $m1'$ which allows the existence of a ferroelectric polarization. Indeed this magnetic symmetry corroborates with the observation of multiferroicity in a previous report[14, 15].

The magnetic symmetry for ICM2 phase belongs to the same irreducible representation as ICM1 (mB1), but with a distinct magnetic order parameter direction $(a,0)$. This corresponds to magnetic superspace group $C2/c1'(a,0,\gamma)0s$ (basis=$(-1,0,0,0),(0,0,0),(0,0,1),(0,0,0)$, origin=$(0,0,0,0)$) which conserves the inversion symmetry and twofold screw axis. We therefore found that a sinusoidally modulated magnetic structure is suitable to refine our neutron magnetic scattering data at 12.2 K. The refinement leads to a spin moment of 1.55(2) $\mu_B$ along the a axis. The final refined neutron diffraction pattern is shown in Fig. 4 and the corresponding magnetic configuration is illustrated in Fig. 1. One can immediately see that it does not break the space inversion and gives rise to a centrosymmetric magnetic point group $2/m1'$. Such magnetic structure cannot lead to any long range electric polarization, in accordance with the previous polarization measurement. The temperature-dependent magnetic moment of NaFeGe$_2$O$_6$ over the temperature 1.5 to 14 K is shown in Fig. 4 (c) where the magnetic moment for the ICM2 phase (SDW) is taken by a quadratic mean of the refined moment.

Having demonstrated the low dimensional character of the magnetism in NaFeGe$_2$O$_6$, we now look into some micro-
scopically for short-range magnetic correlations from neutron diffraction. As shown in Fig. 6, the magnetic diffuse scattering in NaFeGe$_2$O$_6$ extracted from the difference of neutron diffraction data collected at 20 K and 100 K shows a maximum around $d = 5.1$ Å ($1.4$ Å$^{-1}$), signaling the presence of short-range magnetic correlations. The feature with sharp rise at low Q and gradual decrease toward high Q is characteristic of one-dimensional correlations. The nearest Fe$^{3+}$ intrachain distance is about 3.257 Å, suggesting that this 1D magnetic correlation originates from the intrachain magnetic ordering of Fe cations along the $c$ axis. In the family of magnetic pyroxenes, the presence of one-dimensional magnetic correlations in CaMnGe$_2$O$_6$ has been evidenced through the analysis of magnetic neutron diffuse scattering data based on an analytical one-dimensional AFM model [17]. The model is represented by

$$S(Q) = f(Q)^2 \sum_i \langle S_0 S_i \rangle \frac{\sin(QR_i)}{QR_i}$$

(2)

where $f(Q)$ is the magnetic form factor of Fe$^{3+}$ in the dipole approximation, $R_i$ represents the distance between the sites along the 1D chain. The exponential decrease and the AFM spin pair correlations $\langle S_0 S_i \rangle$ with the spin distance $d_i$ and correlation length $\xi$ is expressed as

$$\langle S_0 S_i \rangle = (-1)^{S_0 S_i} \exp\left(-\frac{d_i}{\xi}\right)$$

(3)

We fitted such a model against the experimental data and the best fit is given in Fig 6. The correlation length of 8.0 ±0.4 Å can account for the short-range magnetic correlations along the $c$ axis. In fact, the onset temperature of 1D magnetic correlation is likely much higher than 38 K (observed in magnetic susceptibility curve) as weak neutron magnetic diffuse scattering at 50 K is still present. Another evidence of 1D spin correlations could be gained from thermal expansion. As shown in Fig. 7, the temperature-dependent lattice volume of NaFeGe$_2$O$_6$ refined from XRD data exhibits apparent negative thermal expansion below 57 K. This anomaly can be attributed to magnetostriction effect related to 1D magnetic ordering [17].
has been proved to be effective in several systems for change paths between the atom sites Fe1 (0, 0.9036(2), 0.25) and Fe2 (0, −0.0964(2), 0.75) in a primitive setting.

| S_i | S_j | d(Fe-Fe) | R   | Contribution to $\xi_{ij}$ |
|-----|-----|----------|-----|-----------------------------|
| Fe1 | Fe1 | 6.69 Å   | (1,0,0) | $J_3 e^{-i k_x}$ |
|     |     |          | (-1,0,0) | $J_5 e^{i k_x}$ |
|     |     |          | (0,1,0)  | $J_3 e^{-i k_x}$ |
|     |     |          | (0,-1,0) | $J_5 e^{i k_x}$ |
| Fe1 | Fe2 | 3.257 Å  | (0,0,0)(0,0,1) | $J_1 (1 + e^{-i k_z})$ |
|     |     |          | (-1,0,0)(0,-1,1) | $J_2 (e^{i k_y} + e^{i(2 k_y - k_z)})$ |
| Fe2 | Fe1 | 3.257 Å  | (0,0,0)(0,-1) | $J_1 (1 + e^{i k_z})$ |
|     |     |          | (1,0,0)(1,-1) | $J_2 (e^{-i k_y} + e^{i(2 k_y + k_z)})$ |
| Fe2 | Fe2 | 6.69 Å   | (1,0,0)  | $J_3 e^{-i k_x}$ |
|     |     |          | (-1,0,0) | $J_5 e^{i k_x}$ |
|     |     |          | (0,1,0)  | $J_3 e^{-i k_x}$ |
|     |     |          | (0,-1,0) | $J_5 e^{i k_x}$ |

C. Mean-field approach

The crystal structure of NaFeGe$_2$O$_6$ is made up of FeO$_6$ octahedra, which share their edges to form zig-zag chains parallel to the c axis. As shown in Fig. 1, these chains are stacked along both the a and b axes with the adjacent chains linked via GeO$_4$ tetrahedra. Therefore, within each chain, the nearest Fe$^{3+}$ ions make Fe-O-Fe superexchange (SE) interaction $J_1$ while between chains only $Fe - O - O - Fe$ superexchange (SSE) occurs. Such special atomic arrangement leads to two kinds of SSE paths: double path for $J_2$ with the shortest interchain Fe-Fe distance 5.64 Å and single path for $J_3$ with the Fe-Fe distance about 6.69 Å.

Using mean-field and classical spin approximation, which has been proved to be effective in several systems [34–36], we now investigate the ordered spin configurations to look for the magnetic ground state. Consider a primitive cell, the spin Hamiltonian of exchange interaction between ion i in the cell at $R$ and ion j in the cell at $R'$ is given by

$$H = \sum_{i,j} \sum_{R,R'} J_{ij}^{RR'} S_i^R S_j^{R'}$$

(4)

where $J_{ij}^{RR'}$ is the exchange integral between spin $S_i$ and $S_j$. We employ the method of Freiser [34] to figure out the ground state of a system. Due to the translational symmetry of the matrix of $J_{ij}^{RR'}$, suppose $\sigma^R$ represents the mean spins at site i in a cell with lattice vector $R$, the ordered spin configuration can be expressed in terms of the Bloch spin functions

$$\sigma^R_i = \sum_k \sigma_k^i e^{-i k R}$$

(5)

Then, the spin-spin interaction energy $\xi_{ij}$ between two spin functions $\sigma_i^R$ and $\sigma_j^R$ can be expressed as

$$\xi_{ij} = \sum_R J_{ij}^{RR} e^{-i k R}$$

(6)

The diagonalization of quadratic part of the mean-field free energy retains an eigenvalue problem

$$\sum_j \{ \sum_{R,R'} J_{ij}^{RR'} e^{-i k R'} \} \sigma_j = \lambda(k) \sigma_i$$

(7)

The eigenvalues are inversely proportional to the possible transition temperatures while the corresponding eigenvectors yield the spin configuration. Therefore for a given set of spin exchange parameters, one can evaluate the value of vector $k$ which minimizes the lowest eigenvalue of the interaction matrix. The determined eigenvector is usually regarded as the first ordered state [36, 37].

In NaFeGe$_2$O$_6$, the spin-spin exchange energies associated with the matrix $\xi_{ij}$ from various spin exchange paths $J_1$, $J_2$ and $J_3$ between the two spin sites are summarized in Table I. We employed the program ENERMAG [38] to perform the diagonalization of the exchange matrix. In NaFeGe$_2$O$_6$, the dominant interaction $J_1$ is AFM. It is reasonable to only consider negative $J$s as the interactions between chains are AFM super-superexchange [39]. Some previous works on magnetic pyroxenes [40, 41] indicate a $J_1 > J_2 > J_3$ hierarchy of the magnetic exchange couplings via DFT calculations. By setting $J_1$=1 K, we have done the diagonalization of the matrix via considering various of exchange integrals and varying $k$ vector within the first Brillouin zone. We found that the incommensurate phase with vector (u,0,w) in centering setting has always the lowest eigenvalue when $J_2$ is two times larger than $J_3$ in magnitude, i.e. they produce the same bond energies as there are twice more $J_3$ couplings in the spin lattice. Because $J_2$ and $J_3$ compete to each other, the $J_2/ J_3 = 2:1$ regime implies strong frustration. As shown in Fig. 8, when the constraint $J_1:J_2:J_3=1:0.6:0.3$ is fulfilled, a $k$ vector with (−0.6, 0, 0.19) in centering setting, minimizing the lowest eigenvalue, is obtained. It is very similar to the $k$ vector indexed from NPD. By altering $J_2$ and $J_3$ relative to $J_1$ in the interval of [1,0], a magnetic phase diagram for NaFeGe$_2$O$_6$ was derived. The red region in the phase diagram (Fig. 8) stands for the $k=0$ phase which captures several magnetic pyroxenes such as NaCrGe$_2$O$_6$, NaCrSi$_2$O$_6$ [33, 42] and CaMnGe$_2$O$_6$ [17], in which AFM chains are ferromagnetically ordered. Magnetic phase colored with yellow addresses magnetic structure, often
found in many pyroxenes such as CaM(Si,Ge)$_2$O$_6$ (M=Fe, Co, Ni). In these compounds, spins within chains are ferromagnetically coupled while between chains they are antiferromagnetically aligned. Between these two regions, an ICM phase occurs as a consequence of strong magnetic frustration in the triangular configuration formed by $J_1$, $J_2$ and $J_3$ paths. The quantitative description of the exchange interactions based on DFT calculations is given in the following section.

D. Microscopic magnetic exchange

Previous studies reported several sets of crystallographic data for NaFeGe$_2$O$_6$ [18]. We performed DFT calculations for all of them and found only minor differences in the exchange couplings. The effect of Hubbard $U_d$ is more pronounced, but it pertains to absolute values of $J$’s and does not change their hierarchy.

By evaluating the exchange couplings in the crystallographic unit cell of NaFeGe$_2$O$_6$ (4 magnetic atoms) and in the doubled cell (8 magnetic atoms), we established that three exchanges, $J_1 - J_3$, are sufficient for the minimum microscopic descriptions as further long distance interactions are well below 0.1 K. The resulting couplings are summarized in Table II. As for the three main couplings, their sizes can be juxtaposed with the experiment by calculating the Curie-Weiss temperature,

$$\Theta = \frac{S(S+1)}{3} \sum_i z_i J_i = \frac{35}{6} (J_1 + J_2 + 2J_3),$$

where $z_i$ stands for the number of couplings per Fe site. The $\Theta$ values in Table II show the best agreement with the experiment for $U_d = 7$ eV that yields $J_2/J_1 = 0.31$ and $J_1/J_3 = 0.17$. On the structural level, this hierarchy conforms to the increase in the Fe–Fe distances and to the fact that $J_2$ involves the double GeO$_4$ bridge (two tetrahedra linking the FeO$_6$ octahedra), whereas in the case of $J_3$ only a single bridge is involved. For comparison, in Cr-based pyroxenes interactions via the double tetrahedral bridges are predominant as well [40].

Given two couplings $J_1$, two couplings $J_2$, and four couplings $J_3$ per Fe site, NaFeGe$_2$O$_6$ should be far from magnetic one-dimensionality, because $J_{\text{inter}}/J_{\text{intra}} = (J_2 + 2J_3)/J_1 = 0.66$. On the other hand, $J_2$ and $J_3$ form triangular loops and compete. The fact that $2J_3 = 4.2$ K is similar to $J_2 = 3.8$ K renders NaFeGe$_2$O$_6$ strongly frustrated. This frustration not only triggers incommensurate long-range ordering, but also introduces short-range order in the paramagnetic state, as we present below.

Regarding the long-range ordered state, simple classical minimization leads to an incommensurate state with the propagation vector $\mathbf{k} = (-0.675, 0, 0.09)$ in good agreement with the experimental $\mathbf{k} = (-0.67, 0, 0.08)$ at 1.5 K. Monte-Carlo simulations produce magnetic susceptibility with a broad maximum and the magnetic transition taking place well below this maximum. By keeping the $J_2/J_1$ and $J_3/J_1$ ratios from DFT and adjusting $J_1$ as well as other parameters, we arrive at the best fit with $g = 1.99$ and $J_1 = 9.6$ K that corresponds to the susceptibility maximum at 38 K and $T_N \simeq 12$ K. Note that this model features only one magnetic transition, because no anisotropy terms have been involved.

We also calculated magnetic susceptibility for a single spin chain with the same value of $J_1 = 9.6$ K and $g = 2.0$. As shown in Fig. 9, it reproduces the overall shape of the experimental susceptibility data but does not fit the absolute values. This confirms that the susceptibility maximum in NaFeGe$_2$O$_6$ is related to the magnetic one-dimensionality, yet the interchain couplings are clearly non-negligible. This is also obvious by the fact that the system eventually orders 3D.

Finally, we estimate single-ion magnetic anisotropy. To this end, we fix spins along a given direction and rotate the reference spin in the plane perpendicular to this direction [30]. This yields $a$ direction as the magnetic easy axis. For $b$ and $c$ directions, the energy increases by 0.50 K and 0.62 K, respectively. This is a relatively small value given the fact that, in contrast to $J$’s, it is not normalized by $S^2$. However, it is of the same scale as in other Fe$^{3+}$ oxide compounds [29]. The easy-axis anisotropy naturally explains the formation of the SDW state with spins along $a$ in the ICM2 phase, because in the presence of anisotropy a collinear structure is preferred at elevated temperatures over a non-collinear one. The cycloid in the ICM1 phase features a component along the $a$ direction, which is also consistent with the calculated single-ion anisotropy.

IV. DISCUSSION

Magnetic behavior of NaFeGe$_2$O$_6$ is well captured by a model of coupled spin chains with a weak single-ion

| $d_{Fe-Fe}$ | $U_d = 6$ eV | $U_d = 7$ eV | $U_d = 8$ eV |
|:-----------:|:------------:|:------------:|:------------:|
| $J_1$      | 3.25        | 15.0        | 12.3        | 10.2        |
| $J_2$      | 5.64        | 4.5         | 3.8         | 3.1         |
| $J_3$      | 6.70        | 2.5         | 2.1         | 1.9         |
| $\Theta$   | 144         | 119         | 100         |

FIG. 9. Fit of the magnetic susceptibility with the 3D spin model including $J_1$, $J_2$, and $J_3$, as explained in the text. The susceptibility of a spin chain with $g = 2.0$ and the same $J_1$ as in the 3D fit is shown with the dashed line for reference.
We have examined other recently discovered pyroxenes, where structural chains of transition-metal octahedra are present. On the other hand, the interchain interactions are highly variable leading, e.g., to a quasi-1D regime in LiFeSi2O6 and an essentially 3D regime in LiFeGe2O6. In both cases, only one type of the interchain interactions is present, and no frustration occurs. Therefore, different types of commensurate and collinear magnetic structures have been observed. NaFeGe2O6 stands apart from other transition-metal pyroxenes investigated hitherto, because it features two well-balanced interchain interactions. This gives rise to magnetic frustration triggering the incommensurate magnetic states. Similar microscopic scenario may be relevant to SrMnGe2O6 as an incommensurate magnetic structure has been revealed there through neutron diffraction.

The presence of single-ion anisotropy seems to be crucial for the occurrence of two magnetic transitions and the formation of the collinear SDW state that precedes the constant-moment cycloidal state at low temperatures. Similar phases have been observed in systems like Ca3Co2O6 [43, 44] and Li2NiW2O8 [45], where magnetic ions bear a strong single-ion anisotropy. Although Fe3+ with its half-filled d-shell is by far less anisotropic than Ni2+ or Co3+, the anisotropy energy of less than 1 K (and less than 1% of the leading exchange coupling J1) is already sufficient for driving similar physics. The main difference is the incommensurate and non-collinear ground-state magnetic configuration driven by the isotropic exchange couplings Ji in NaFeGe2O6, whereas in systems with stronger anisotropy, a commensurate and collinear state favored by the anisotropy occurs.

Let us now discuss the electric polarization in NaFeGe2O6 from symmetry viewpoint based on the determined magnetic superspace group. Both magnetic susceptibility and neutron diffraction reveal that NaFeGe2O6 undergoes an AFM transition at 11.6 K, and its magnetic superspace group Cc1′(α, 0, γ)0s breaks both spatial inversion and time reversal. Such a cycloidal magnetic symmetry allows electric polarization within the (ac) plane (Fig. 10(b)), in good agreement with the experimental observation, and can be explained by the theory of inverse DM effect or spin-current model. However, this mechanism does not account for the observation of a small polarization (less than 2 µC/m2) along the b-axis in a synthetic single crystal [15]. In principle, the symmetry analysis of NaFeGe2O6 allows the presence of a magnetic moment along the b-axis and indicates that both cycloidal and proper screw components are presumably present, as illustrated in Fig. 10(a). We have examined other recently developed mechanisms for explaining multiferroicity in materials showing proper screw magnetic symmetry. A cycloidal spin arrangement (Fig. 10(b)) based on $P \propto (A \cdot r_{ij})(S_i \times S_j)$ gives no electric polarization along the b-axis, because the mirror plane contains $r_{ij}$ [6, 10, 46, 47]. In light of the ferroaxial mechanism, the proper screw component can lead to $P_z \propto A \cdot (r_{ij} \cdot (S_i \times S_j))$ along the b-axis. However, because of the existence of the mirror plane perpendicular to the b-axis, as explained schematically in Fig. 10(c), the opposite spin chirality renders this electric polarization zero. As a result, the magnetic superspace group demonstrates that electric polarization can only be present in the (ac) plane. A signal in a pyrocurrent measurement can be due to an impurity phase or a misalignment of the crystal. It is likely that the observed b-component of the polarization has such extrinsic origin due to an impurity phase, like hematite ($α$-Fe2O3) and maghemite ($γ$-Fe2O3) that have been identified in the crystal on which the pyrocurrent measurement of Ref. [15] was performed.

V. CONCLUSION

In conclusion, we have investigated the magnetic structures of NaFeGe2O6 experimentally and theoretically. A microscopic magnetic model of coupled spin chains with weak but relevant single-ion anisotropy is established to understand the origin of successive incommensurate spin structures below 11.6 and 13 K, unravelled by high-resolution neutron diffraction, and to explain the presence of one-dimensional spin correlations in the paramagnetic state, evidenced through magnetic neutron diffuse scattering. Two well-balanced interchain couplings are responsible for the magnetic frustration and incommensurate spin configuration while weak single-ion anisotropy determines spin orientations and stabilizes the intermediate-temperature SDW state. A magnetic phase diagram in terms of different exchange couplings in and between chains, capturing the documented magnetic structures reported in pyroxenes so far, are presented. We also identified that the polarization can only be present in the (ac) plane in NaFeGe2O6 by examining different models with respect to our determined magnetic symmetry.

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[1] D. Khomskii, “Trend: Classifying multiferroics: Mechanisms and effects,” Physics 2, 20 (2009).
[2] M. Mostovoy, “Ferroelectricity in spiral magnets,” Phys. Rev. Lett. 96, 067601 (2006).
[3] H. Katsura, N. Nagaosa, and A. V. Balatsky, “Spin current and magnetoelectric effect in noncollinear magnets,” Phys. Rev. Lett. 95, 057205 (2005).
[4] T. H. Ariwa, “Ferroelectricity induced by proper-screw type magnetic order,” J. Phys. Soc. Jap. 76, 073702 (2007).
[5] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Ariwa, and Y. Tokura, “Magnetic control of ferroelectric polarization,” Nature 426, 55–58 (2003).
[6] N. Terada, D. D. Khalyavin, P. Manuel, Y. Tsujimoto, K. Knight, P. G. Radaelli, H. S. Suzuki, and H. Kitazawa, “Spiral-spin-driven ferroelectricity in a multiferroic delafossite AgFeO2,” Phys. Rev. Lett. 109, 077203 (2012).
[7] R. D. Johnson, Sunil Nair, L. C. Chapon, a. Bombardi, C. Vecchini, D. Prabhakaran, a. Thoothroody, and P. G. Radaelli, “Cu4Nb2O8: A multiferroic with chiral coupling to the crystal structure,” Phys. Rev. Lett. 107, 137205 (2011).
[8] R. D. Johnson, L. C. Chapon, D. D. Khalyavin, P. Manuel, P. G. Radaelli, and C. Martin, “Giant improper ferroelectricity in the ferroaxial magnet CaMn7O12,” Phys. Rev. Lett. 108, 067201 (2012).
[9] A. J. Hearmon, F. Fabrizi, L. C. Chapon, R. D. Johnson, D. Prabhakaran, S. V. Streltsov, P. J. Brown, and P. G. Radaelli, “Electric field control of the magnetic chiralities in ferroaxial multiferroic RbFe(MoO4)2,” Phys. Rev. Lett. 108, 237201 (2012).
[10] T. A. Kaplan and S. D. Mahanti, “Canted-spin-coupled electric dipole: A local symmetry theory,” Phys. Rev. B 83, 1–10 (2011).
[11] N. Terada, “Magnetic and ferroelectric orderings in multiferroic α-NaFe2O5,” J. Phys.: Condens. Matter 26, 453202 (2014).
[12] S. Jodlauk, P. Becker, J. A. Mydosh, D. I. Khomskii, T. Lorenz, S. V. Streltsov, D. C. Hezel, and L. Bohatý, “Pyroxenes: a new class of multiferroics,” J. Phys.: Condens. Matter 19, 432201 (2007).
[13] S. V. Streltsov and D. I. Khomskii, “Electronic structure and magnetic properties of pyroxenes (Li,Na)TM(Si,Ge)2O6: Low-dimensional magnets with 90 bonds,” Phys. Rev. B 77, 064405 (2008).
[14] I. Kim, B. G. Jeon, D. Patil, S. Patil, G. Néert, and K. H. Kim, “Observation of multiferroic properties in pyroxene NaFe2Ge2O6,” J. Phys.: Condens. Matter 24, 306001 (2012).
[15] M. Ackermann, L. Andersen, T. Lorenz, L. Bohatý, and P. Becker, “Anisotropy study of multiferroicity in the pyroxene NaFe2Ge2O6,” New J. Phys. 17, 13045 (2015).
[16] L. Ding, C. V. Colin, C. Darie, and P. Bordet, “SrMGe2O6 (M = Mn, Co): a family of pyroxene compounds displaying multiferroicity,” J. Mater. Chem. C 4, 4236 (2016).
[17] L. Ding, C. V. Colin, C. Darie, J. Robert, F. Gay, and P. Bordet, “One-dimensional short-range magnetic correlation in the magnetoelectric pyroxene CaMnGe2O6,” Phys. Rev. B 93, 064423 (2016).
[18] G. J. Redhammer, A. Senyshyn, M. Meven, G. Roth, S. Prinz, A. Pachler, G. Tippelt, C. Pietzonka, W. Treutmann, M. Hoelzel, B. Pedersen, and G. Ahntauer, “Nuclear and incommensurate magnetic structure of NaFeGe2O6 between 5 k and 298 k and new data on multiferroic NaFeSi2O6,” Phys. Chem. Miner. 38, 139 (2011).
[19] T. V. Drokin, G. a. Petrakovskii, L. Keller, J. Schifer, a. D. Balaev, a. V. Kartashev, and D. a. Ivanov, “Modulated magnetic structure in quasi-one-dimensional chiralpyroxene NaFe2Ge2O6,” J. Exp. Theor. Phys. 112, 121 (2011).
[20] L. C. Chapon et al., “Wish: The new powder and single crystal magnetic diffractometer on the second target station,” Neutron News 22, 22–25 (2011).
[21] J. Rodrigez-Carvajal, “Recent advances in magnetic structure determination by neutron powder diffraction,” Phys. B Condens. Matter 192, 55 (1993).
[22] B. J. Campbell, H. T. Stokes, Tanner D. E., and D. M. Hatch, “Isodisplice: a web-based tool for exploring structural distortions,” J. Appl. Crystallogr. 39, 607 (2006).
[23] J. M. Perez-Mato, S. V. Gallego, E. S. Tasci, L. Elcoro, G. de la Flor, and M. I. Aroyo, “Symmetry-based computational tools for magnetic crystallography,” Annu. Rev. Mater. Res. 45, 217 (2015).
[24] K. Koepenrik and H. Eschrig, “Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme,” Phys. Rev. B 59, 1743–1757 (1999).
[25] G. Kresse and J. Furthmüller, “Efficiency of ab initio total energy calculations for metals and semiconductors using a plane-wave basis set,” Computational Materials Science 6, 15 – 50 (1996).
[26] G. Kresse and J. Furthmüller, “Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set,” Phys. Rev. B 54, 11169–11186 (1996).
[27] J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” Phys. Rev. Lett. 77, 3865–3868 (1996).
[28] A. N. Vasilev et al., “1/3 magnetization plateau and frustrated ferrimagnetism in a sodium iron phosphite,” Phys. Rev. B 93, 134401 (2016).
[29] A. A. Tsirlin, I. Rousochatzakis, D. Filimonov, D. Batuk, M. Frontzek, and A. M. Abakumov, “Spin-reorientation transitions in the Cairo pentagonal magnet Bi4Fe5O13F3,” Phys. Rev. B 96, 094420 (2017).
[30] H. Xiang, C. Lee, H.-J. Koo, X. Gong, and M.-H. Whangbo, “Magnetic properties and energy-mapping analysis,” Dalton Trans. 42, 823–853 (2013).
[31] A.F. Albuquerque et al., “The ALPS project release 1.3: Open-source software for strongly correlated systems,” J. Magn. Magn. Mater. 310, 1187–1193 (2007).
[32] G. Néert, O. Fabelo, K. Forsberg, C. V. Colin, and J. Rodriguez-Carvajal, “Structural and magnetic proper-
ties of the low-dimensional fluoride $\beta$-FeF$_3$(H$_2$O)$_2$H$_2$O," Dalton Trans. 44, 14130–14138 (2015).

[33] G. Néert, C. Ritter, M. Isobe, O. Isnard, a. Vasiliev, and Y. Ueda, “Magnetic and crystal structures of the one-dimensional ferromagnetic chain pyroxene NaCrGe$_2$O$_6$,” Phys. Rev. B 80, 024402 (2009).

[34] M. J. Freiser, “Thermal variation of the pitch of helical spin configurations,” Phys. Rev. 123, 2003 (1961).

[35] D. Dai, M. Whangbo, N. Carolina, S. Uni, and H. Koo, “Analysis of the spin exchange interactions and the ordered magnetic structures of lithium transition metal phosphates LiMPO$_4$ (M = Mn, Fe, Co, Ni) with the olivine structure,” Inorg. Chem. 44, 2407 (2005).

[36] D. D. Khalyavin, P. Manuel, J. F. Mitchell, and L. C. Chapon, “Spin correlations in the geometrically frustrated RBaCo$_4$O$_7$ antiferromagnets: Mean-field approach and monte carlo simulations,” Phys. Rev. B 82, 094401 (2010).

[37] J. M. Luttinger and L. Tisza, “Theory of dipole interaction in crystals,” Phys. Rev. 70, 954 (1946).

[38] N. El Khayati, R. C. El Moursli, J. Rodriguez-Carvajal, G. Andre, N. Blanchard, F. Bourée, G. Collin, and T. Roisnel, “Crystal and magnetic structures of the oxyphosphates MFePO$_3$ (M = Fe, Co, Ni, Cu): analysis of the magnetic ground state in terms of superexchange interactions,” Eur. Phys. J. B 22, 429 (2001).

[39] J.B. Goodenough, Magnetism and the chemical bond (Interscience, New York, 1963).

[40] O. Janson, G. Néert, M. Isobe, Y. Skourski, Y. Ueda, H. Rosner, and A. A. Tsirlin, “Magnetic pyroxenes LiCrGe$_2$O$_6$ and LiCrSi$_2$O$_6$: Dimensionality crossover in a nonfrustrated S=3/2 heisenberg model,” Phys. Rev. B 90, 214424 (2014).

[41] C. Lee, J. Kang, J. Hong, J. H. Shim, and M. H. Whangbo, “Analysis of the difference between the pyroxenes LiFeSi$_2$O$_6$ and LiFeGe$_2$O$_6$ in their spin order, spin orientation, and ferrotoroidal order,” Chem. Mater. 26, 1745 (2014).

[42] G. Néert, I. Kim, M. Isobe, C. Ritter, A. N. Vasiliev, K. H. Kim, and Y. Ueda, “Magnetic and magnetoelectric study of the pyroxene NaCrSi$_2$O$_6$,” Phys. Rev. B 81, 184408 (2010).

[43] S. Agrestini, L. C. Chapon, A. Daoud-Aladine, J. Schefer, A. Gukasov, C. Mazzoli, M. R. Lees, and O. A. Petrenko, “Nature of the magnetic order in Ca$_3$Co$_2$O$_6$,” Phys. Rev. Lett. 101, 097207 (2008).

[44] S. Agrestini, C. L. Fleck, L. C. Chapon, C. Mazzoli, A. Bombardi, M. R. Lees, and O. A. Petrenko, “Slow magnetic order-order transition in the spin chain antiferromagnet Ca$_3$Co$_2$O$_6$,” Phys. Rev. Lett. 106, 197204 (2011).

[45] K. M. Ranjith, R. Nath, M. Majumder, D. Kasinathan, M. Skoulatos, L. Keller, Y. Skourski, M. Baenitz, and A. A. Tsirlin, “Commensurate and incommensurate magnetic order in spin-1 chains stacked on the triangular lattice in Li$_2$NiW$_2$O$_8$,” Phys. Rev. B 94, 014415 (2016).

[46] N. Terada, D. D. Khalyavin, J. M. Perez-Mato, P. Manuel, D. Prabhakaran, A. Daoud-Aladine, P. G. Radaelli, H. S. Suzuki, and H. Kitazawa, “Spin and orbital orderings behind multiferroicity in delafossite and related compounds,” Phys. Rev. B 89, 184421 (2014).

[47] N. Terada, D. D. Khalyavin, P. Manuel, Y. Tsujimoto, and A. A. Belik, “Magnetic ordering and ferroelectricity in multiferroic 2HAgFeO$_2$: Comparison between hexagonal and rhombohedral polytypes,” Phys. Rev. B 91, 094434 (2015).