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Citation: TSIRLIN, A.A. ...et al., 2017. Spin-reorientation transitions in the Cairo pentagonal magnet Bi$_4$ Fe$_5$ O$_{13}$ F. Physical Review B, 96: 094420.

Additional Information:

- This paper was accepted for publication in the journal Physical Review B and the definitive published version is available at https://doi.org/10.1103/PhysRevB.96.094420

Metadata Record: https://dspace.lboro.ac.uk/2134/33695

Version: Accepted for publication

Publisher: © American Physical Society

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Spin-reorientation transitions in the Cairo pentagonal magnet Bi$_4$Fe$_2$O$_{13}$F

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Abstract

We show that interlayer spins play a dual role in the Cairo pentagonal magnet Bi$_4$Fe$_2$O$_{13}$F, on one hand mediating the three-dimensional (3D) magnetic order and on the other driving spin-reorientation transitions both within and between the planes. The corresponding sequence of magnetic orders unraveled by neutron diffraction and Mössbauer spectroscopy features two orthogonal magnetic structures described by opposite local vector chiralities, and an intermediate, partly disordered phase with nearly collinear spins. A similar collinear phase has been predicted theoretically to be stabilized by quantum fluctuations, but Bi$_4$Fe$_2$O$_{13}$F is very far from the relevant parameter regime. While the observed in-plane reorientation cannot be explained by any standard frustration mechanism, our ab initio band-structure calculations reveal strong single-ion anisotropy of the interlayer Fe$^{3+}$ spins that turns out to be instrumental in controlling the local vector chirality and the associated interlayer order.

I. INTRODUCTION

Frustrated magnets [1–3] host a plethora of remarkable collective phenomena, ranging from topological spin liquids, long-range entanglement and fractionalized excitations [4–10], to emergent electrodynamics and magnetic monopoles [11–13], and even to spin-induced ferroelectricity [14–16]. While the majority of geometrically frustrated magnets are based on spin triangles (or tetrahedra in 3D), pentagon-based magnets, which are far more difficult to implement in real materials [17], are now attracting increasing attention both in theory [18–27] and experiment [28–34].

The main interest so far has been on the Cairo pentagonal lattice, a periodic arrangement of irregular pentagons with two types of sites, one with three-fold and the other with four-fold connectivity (Fig. 1). Cairo-based models host various phases of classical and quantum nature [24], magnetization plateaux [22, 24, 26, 27], and Kosterlitz-Thouless transitions [22]. By now, there are two main realizations of this lattice, Bi$_2$Fe$_5$O$_9$ [28–31, 34] and Bi$_4$Fe$_5$O$_{13}$F [32]. A similar pentagonal topology can be also identified in the multiferroics RMn$_2$O$_5$ (R = Bi, Y, or rare-earth) [35–42] that are renown for their complex interplay of commensurate and incommensurate magnetic orders with ferroelectricity.

The symmetric version of the Cairo Heisenberg model has two exchange couplings, $J_{33}$ and $J_{13}$ (Fig. 1 a), and hosts three phases in the classical, large-$S$ limit [24]: a coplanar orthogonal phase (Fig. 1 b), a collinear ferrimagnet, and a mixed phase in between. Quantum fluctuations convert the latter to a non-magnetic and possibly spin-nematic phase for $S = 1/2$. Additionally, they introduce another collinear phase for small $J_{33}/J_{13}$ [24]. This phase features collinear antiferromagnetic order on all four-fold sites and on half of the three-fold sites, with the remaining half being disordered (Fig. 1 c).

Bi$_2$Fe$_5$O$_9$ and Bi$_4$Fe$_5$O$_{13}$F feature dumbbells of the 4-fold-sites. Two Fe1 atoms that comprise a dumbbell lie above and below the Fe2 plane, centered at a nodal point of the pentagonal lattice. Additionally, there are two inequivalent couplings between four-fold and three-fold sites, denoted by $J_{33}$ and $J_{13}$ (Fig. 1), but the classical phase diagram of this extended model is qualitatively the same (Fig. 7). Furthermore, the calculated interactions (reported here and in [25]) place the two compounds nearly on the same spot in the phase diagram, and deep inside the orthogonal phase. Despite this remarkable similarity, the two Cairo materials show qualitatively different behavior. Bi$_2$Fe$_5$O$_9$ orders in the anticipated orthogonal state below 238 K, but Bi$_4$Fe$_5$O$_{13}$F, where Cairo planes are interleaved by an additional layer of Fe3 sites, shows three successive transitions at $T_N \simeq 178$ K, $T_2 \simeq 71$ K, and $T_1 \simeq 62$ K [32], with three distinct magnetically ordered states that we refer to as phase I ($T < T_1$), phase II ($T_1 < T < T_2$), and phase III ($T_2 < T < T_N$). Phase I is orthogonal [32], whereas the nature of phases II and III is unknown to date.

In the following, we unravel the nature of these phases, and elucidate their origin. Our main findings are:

i) Phases I and III are both orthogonal and macroscopically non-chiral, but with opposite local vector chiralities, as defined in Fig. 1 b. Since the two states are degenerate at the level of the isotropic Heisenberg model,
FIG. 1. (a) The symmetric Cairo lattice with two exchange couplings, $J_{33}$ and $J_{43}$. (b–c) Orthogonal and collinear phases. Note the zero moment on half of the 3-fold sites in (c). The Fe1 sites 1–4 in (b) provide a measure of local vector chirality as $\chi = \langle \mathbf{T} \rangle / |\langle \mathbf{T} \rangle|$, where $\mathbf{T} = \mathbf{S}_1 \times \mathbf{S}_2 + \mathbf{S}_3 \times \mathbf{S}_4 + \mathbf{S}_4 \times \mathbf{S}_1$. Note that $\chi$ is defined on the plaquette centered by the 4 rotoinversion axis (and vertical Fe2$_1$ dimers). The adjacent plaquettes have opposite chirality, but they are centered by the 42 screw axis (and horizontal Fe2$_2$ dimers) and thus distinguished by symmetry. The overall magnetic structure is non-chiral. (d–f) Magnetic structures of Bi$_4$Fe$_5$O$_{13}$F in phases I, II, and III, respectively. The two types of the $J_{43}$ couplings are also indicated. The crystal and magnetic structures are visualized using VESTA [43].

anisotropy must play a role.

ii) The intermediate phase II features nearly collinear spins and drastically reduced moments on half of the Fe2 sites, reminiscent of the quantum collinear phase of [24]. This is unexpected given the large, ‘classical’ spin $S=5/2$ and the fact that we are far from the relevant corner of the phase diagram (Fig. 7).

iii) The onset of phase II upon cooling coincides with a significant growing of the magnetic moments on the interlayer Fe3 sites, which sit between the Cairo planes and normally act to mediate the 3D ordering between the planes, as e.g. in Ref. [44].

iv) Spin reorientation within the planes is accompanied by a change of the interlayer order from ferromagnetic (phase I) to antiferromagnetic (phase III).

While these features cannot be explained by any standard frustration mechanism involving purely isotropic (Heisenberg) interactions, our ab initio band-structure calculations reveal sizable single-ion anisotropy on the interlayer Fe$^{3+}$ spins. The Fe3 spins are absent in Bi$_3$Fe$_2$O$_9$ (where neighboring planes couple directly to each other), so the emerging physical picture is that the interlayer spins play a vital role for the order within the planes. Specifically, the III→II→I transitions can be understood as a reorientation of the nominally preferred orthogonal state, from one orientation (phase III) that satisfies the anisotropy on the in-plane spins to another orientation (phase I) that satisfies the anisotropy on the interlayer Fe3 spins, and in between the system must necessarily go through the quasi-collinear phase II. This in-plane spin re-orientation is accompanied by a change in the interlayer order that evolves from antiferromagnetic in phase III to ferromagnetic in phase I.

II. MAGNETIC ORDER

All measurements were performed on single-phase polycrystalline samples of Bi$_4$Fe$_5$O$_{13}$F prepared previously [32]. Neutron diffraction data were collected at the cold neutron powder diffractometer DMC (LNS PSI, Villigen, Switzerland) with the wavelength of 4.5082 Å in the $T$ range of 1.5 – 200 K in a He-cryostat. The magnetic structures were refined by the Rietveld method using the JANA2006 program [45]. The symmetry analysis of possible magnetic configurations was carried out in ISODISTORT [46].

Phases I–III share the same propagation vector $\mathbf{k} =$
TABLE I. Fractional coordinates of the Fe atoms in the magnetic supercell.

<table>
<thead>
<tr>
<th></th>
<th>(x/a)</th>
<th>(y/b)</th>
<th>(z/c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1</td>
<td>(\frac{1}{4})</td>
<td>(\frac{1}{4})</td>
<td>0.0783</td>
</tr>
<tr>
<td>Fe2</td>
<td>(\frac{1}{4})</td>
<td>(\frac{3}{4})</td>
<td>0.0783</td>
</tr>
<tr>
<td>Fe3</td>
<td>0.0057</td>
<td>0.8429</td>
<td>0</td>
</tr>
<tr>
<td>Fe4</td>
<td>0.3429</td>
<td>0.0057</td>
<td>0</td>
</tr>
</tbody>
</table>

TABLE II. Irreducible representations of \(P4_2/mbc\) for \(k = (\frac{1}{2}, \frac{1}{2}, 0)\), order parameter directions (OPD), magnetic space groups (mSG), and allowed magnetic moment components for the Fe positions (referred to the unit cell of the nuclear structure).

<table>
<thead>
<tr>
<th>Irrep</th>
<th>OPD</th>
<th>mSG</th>
<th>Fe1</th>
<th>Fe2</th>
<th>Fe3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mM_5) (\uparrow) (M_5) (\downarrow) (\uparrow)</td>
<td>((a, b)) (P_{Cccn})</td>
<td>((00z))</td>
<td>({xy0})</td>
<td>({00z})</td>
<td>none</td>
</tr>
<tr>
<td>(mM_3) (M_3) (\uparrow) (\downarrow) (\uparrow)</td>
<td>((a, b)) (P_{Cmmm})</td>
<td>((00z))</td>
<td>({xy0})</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>(mM_2) (\uparrow) (\downarrow) (\uparrow)</td>
<td>((a, a)) (P_{C2/m})</td>
<td>({xy0})</td>
<td>({00z})</td>
<td>({x0})</td>
<td></td>
</tr>
<tr>
<td>(mM_2) (\uparrow) (\downarrow) (\downarrow)</td>
<td>((a, b)) (P_{C2/m})</td>
<td>({xy0})</td>
<td>({00z})</td>
<td>({x0})</td>
<td></td>
</tr>
<tr>
<td>(mM_4) (\uparrow) (\downarrow) (\uparrow)</td>
<td>((a, b)) (P_{Cmm})</td>
<td>((00z))</td>
<td>({00z})</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>(mM_5) (\uparrow) (\downarrow) (\uparrow)</td>
<td>((a, a)) (P_{C2/n})</td>
<td>({xy0})</td>
<td>({xy0})</td>
<td>({x0})</td>
<td></td>
</tr>
<tr>
<td>(mM_3) (\uparrow) (\downarrow) (\downarrow)</td>
<td>((a, b)) (P_{C2/c})</td>
<td>({xy0})</td>
<td>({xy0})</td>
<td>({x0})</td>
<td></td>
</tr>
</tbody>
</table>

\((\frac{1}{2}, \frac{1}{2}, 0)\). The analysis of irreducible representations (irreps) for the \(P4_2/mbc\) nuclear structure with this propagation vector yields six irreps. Their corresponding magnetic space groups and allowed magnetic moment components for different positions of the Fe atoms are listed in Table II. All these symmetries were tested in the refinement of the \(T = 1.5\) K magnetic structure. The magnetic moments were found to be strictly confined to the \(ab\) plane.

The solution was only possible with the \(mM_5\) \(\uparrow\) \(\downarrow\) \(\uparrow\) irrep and tetragonal magnetic space group \(P_{C42/n}\). This magnetic structure can be described within the \(a_m = a - b\), \(b_m = a + b\), \(c_m = c\) magnetic supercell with five positions (Table I) for the magnetic Fe atoms shown in Fig. 1. We use polar angles \(\varphi\) to define orientations of magnetic moments within the plane, \(m_a = \mu \cos \varphi\) and \(m_b = \mu \sin \varphi\) along the \(a_m\) and \(b_m\) directions, respectively.

A. Phase I

At \(T = 1.5\) K, two magnetic structures, A and B, are possible, showing very similar arrangement of the magnetic moments in the pentagonal layers (Fig. 2). These structures can be transformed into each other by rotating all magnetic moments for about 90°. The main difference between these structures is the orientation of a given Fe1 moment approximately along \(a_m\) or \(b_m\) directions of the magnetic supercell. Although \(a\) and \(b\) (and, thus, \(a_m\) and \(b_m\)) are equivalent in the tetragonal structure, individual Cairo planes lack the tetragonal symmetry. Therefore, anisotropy renders \(a\) and \(b\) distinguishable locally.

With our earlier HRPT data [32], models A and B produced virtually the same refinement residuals. Model A was reported as the magnetic structure in phase I [32], whereas model B was regretfully overlooked in that study. With the DMC data at hand, we can take advantage of the better resolution and sensitivity, and select model B based on the lower refinement residuals, compare \(R_{\text{nucl}} = 0.023\), \(R_{\text{mag}} = 0.027\), and \(R_P = 0.055\) for the model A and \(R_{\text{nucl}} = 0.021\), \(R_{\text{mag}} = 0.020\), \(R_P = 0.050\) for the model B. The choice of model B is further corroborated by the analysis of magnetic anisotropy in Sec. III B.

Phase I (Fig. 1d) is an orthogonal state, with spins on the Fe1 and Fe12 sites as well as on the Fe21 and Fe22 sites being mutually orthogonal. The interlayer ordering is ferromagnetic, because Fe1 moments of the neighboring Cairo planes interact via Fe3. The antiferromagnetic alignment of Fe1 and Fe3 gives rise to the ferromagnetic arrangement of the Fe1 moments in the adjacent layers. At 1.5 K, the moments are about 4.0 \(\mu_B\) on the octahedrally coordinated Fe1 and Fe3 sites and 3.3 \(\mu_B\) on the tetrahedrally coordinated Fe2 sites. This difference is due to the stronger Fe–O hybridization for the tetrahedrally coordinated Fe atoms.

B. Phase II

The propagation vector \(k = (\frac{1}{2}, \frac{1}{2}, 0)\) is retained in the entire \(T = 1.5 – 180\) K temperature range. The refinements were performed assuming that the magnetic structures follow the same irrep and also maintain the order parameter direction and magnetic space group, which would be consistent with weak first-order nature of the transitions at \(T_1\) and \(T_2\) [32]. Satisfactory solutions were found at all temperatures indeed.
As $T$ increases toward $T_1$, the Fe1 and Fe2 moments remain roughly unchanged, whereas the moment on Fe3 decreases significantly and drops below $2\mu_B$ at 55 K (Fig. 3, left). Upon further heating, the magnetic structure changes abruptly entering phase II. All Fe1 sites preserve large moments of $3.2 - 3.8\mu_B$, whereas the Fe2 sites split into two groups. The Fe2 moments increase to $3.8\mu_B$, whereas the Fe2$_1$ moments decrease to about $1.2\mu_B$, only one third of their 1.5 K value.

Magnetic moments directions change as well. The in-plane magnetic structure of phase II resembles the quantum collinear phase described in Ref. 24. Deviations from collinearity are due to the fact that $J_{43} \neq J_{43}'$. In this case, local fields on the Fe2$_1$ site do not cancel, leading to the non-zero ordered moment on Fe2$_1$ and, consequently, to the slight departure of the Fe1$_1$ and Fe1$_2$ moments from the direction of the Fe2$_2$ moment. Therefore, our phase II can be regarded an instance of the collinear phase of the Cairo model for the imperfect realization of this model in Bi$_4$Fe$_5$O$_{13}$F [47]. The reasons behind the formation of this phase are rather unusual, though, and will be discussed in Sec. III B.

The second notable change upon the I→II transition is the evolution of the interlayer order from ferromagnetic to orthogonal, namely, the adjacent Fe1 moments of the two neighboring Cairo planes, which were parallel in phase I, become orthogonal in phase II. This is accompanied by the drastic reduction in the ordered moment on Fe3 (Fig. 3).

C. Phase III

The narrow region of phase II is followed by a broader region of phase III, where in-plane order again becomes orthogonal, whereas the interlayer order returns to collinear, but the overall magnetic structure is quite different from that in phase I. First, the interlayer order is now antiferromagnetic, i.e., adjacent Fe1 moments in the neighboring Cairo planes are antiparallel to each other. Concurrently, the Fe3 moment vanishes. At 100 K it refined to 0.29(25) $\mu_B$, which is insignificant given the experimental error bar. Therefore, we fixed the Fe3 moment to zero throughout the temperature range of phase III.

The differences between the in-plane order of phases I and III can be captured by introducing the local vector chirality $\chi$, which we define for the plaquette of four Fe1 spins as explained in the caption of Fig. 1. The magnetic unit cell contains four such plaquettes. Two of them are centered by the $\bar{4}$ rotoinversion axis, whereas the other two are centered by the $4_2$ screw axis. The overall $P_{C42}/n$ symmetry requires that adjacent plaquettes have opposite vector chiralities, thus rendering the overall magnetic structure non-chiral. However, each plaquette changes its local vector chirality upon going from phase I to phase III. We find $\chi = +c$ in phase I and $\chi = -c$ in phase III for the plaquettes centered by the $4_2$ rotoinversion axis (‘vertical Fe2$_2$ dimers’), and the other way around for the plaquettes centered by the $4_2$ axis (‘horizontal Fe2$_2$ dimers’).
D. Mössbauer spectroscopy

Magnetic structure analysis was supported by Mössbauer spectroscopy measurements. The $^{57}$Fe Mössbauer spectra (Fig. 4) were recorded in the temperature range $55 - 300$ K in a transmission mode with a $^{57}$Co/Rh $\gamma$-ray source using a constant acceleration spectrometer MS1104. At room temperature, the spectrum can be decomposed into 3 doublets with the nearly 40:40:20 ratio of the intensities corresponding to the Fe1, Fe2, and Fe3 positions, respectively (Table III).

Upon cooling below $T_N$, the spectra reveal an additional splitting indicative of the magnetic ordering. However, the spectrum at 100 K, in phase III, could not be accounted for by a combination of regular sextets. We find that about 20% of the spectral intensity corresponds to an unresolved sextet with a very weak hyperfine splitting. This signal arises from Fe3 sites that, according to the neutron data, feature negligible ordered moment above $T_2$. Below $T_2$, the Fe3 moments increase and a well-resolved sextet develops.

Below $T_2$, the spectrum is decomposed into 5 sextets (Table III). The reduced ordered moment on Fe21 manifests itself in the largely broadened signal. At 55 K, in phase I, the sextets of Fe21 and Fe3 become more narrow suggesting the formation of large magnetic moments on all Fe sites, which is again in agreement with the magnetic structures shown in Fig. 1.

### TABLE III. Parameters of the Mössbauer spectra for Bi$_4$Fe$_5$O$_{13}$F

<table>
<thead>
<tr>
<th>$I$ (%)</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta EQ$ (mm/s)</th>
<th>$\Gamma$ (mm/s)</th>
<th>$H$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T = 300$ K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe1 35</td>
<td>0.37</td>
<td>0.31</td>
<td>0.27</td>
<td>–</td>
</tr>
<tr>
<td>Fe2 38</td>
<td>0.23</td>
<td>0.78</td>
<td>0.26</td>
<td>–</td>
</tr>
<tr>
<td>Fe3 27</td>
<td>0.33</td>
<td>0.36</td>
<td>0.40</td>
<td>–</td>
</tr>
<tr>
<td>$T = 100$ K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe1$_1$ 23</td>
<td>0.45</td>
<td>0.06</td>
<td>0.32</td>
<td>42.4</td>
</tr>
<tr>
<td>Fe1$_2$ 17</td>
<td>0.46</td>
<td>0.21</td>
<td>0.52</td>
<td>40.2</td>
</tr>
<tr>
<td>Fe2 38</td>
<td>0.28</td>
<td>0.11</td>
<td>0.45</td>
<td>39.9</td>
</tr>
<tr>
<td>Fe3 22</td>
<td>0.41</td>
<td>0.18</td>
<td>0.60</td>
<td>22</td>
</tr>
<tr>
<td>$T = 63$ K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe1$_1$ 24</td>
<td>0.46</td>
<td>0.04</td>
<td>0.31</td>
<td>46.4</td>
</tr>
<tr>
<td>Fe1$_2$ 16</td>
<td>0.46</td>
<td>0.03</td>
<td>0.67</td>
<td>44.6</td>
</tr>
<tr>
<td>Fe2$_1$ 18</td>
<td>0.29</td>
<td>0.00</td>
<td>0.87</td>
<td>41.0</td>
</tr>
<tr>
<td>Fe2$_2$ 22</td>
<td>0.29</td>
<td>$\sim 0$</td>
<td>0.35</td>
<td>43.2</td>
</tr>
<tr>
<td>Fe3 21</td>
<td>0.47</td>
<td>$\sim 0.05$</td>
<td>0.93</td>
<td>24.1</td>
</tr>
<tr>
<td>$T = 55$ K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe1$_1$ 27</td>
<td>0.50</td>
<td>0.05</td>
<td>0.30</td>
<td>47.6</td>
</tr>
<tr>
<td>Fe1$_2$ 15</td>
<td>0.52</td>
<td>$\sim 0.03$</td>
<td>0.73</td>
<td>45.8</td>
</tr>
<tr>
<td>Fe2$_1$ 17</td>
<td>0.34</td>
<td>$\sim 0.23$</td>
<td>0.31</td>
<td>44.6</td>
</tr>
<tr>
<td>Fe2$_2$ 20</td>
<td>0.34</td>
<td>$\sim 0.26$</td>
<td>0.34</td>
<td>43.4</td>
</tr>
<tr>
<td>Fe3 21</td>
<td>0.48</td>
<td>0.13</td>
<td>0.58</td>
<td>28.3</td>
</tr>
</tbody>
</table>

III. MAGNETIC MODEL

A. Isotropic exchange couplings

The isotropic exchange couplings in Bi$_4$Fe$_5$O$_{13}$F were previously reported in Ref. [32]. However, using these values in numerical simulations of the magnetic susceptibility, we arrived at the too high $T_N = 250$ K compared to the experimental value of 178 K. Therefore, we revised the microscopic magnetic model using extensive density-functional (DFT) band-structure calculations [48] performed in the FPLO [49] and VASP [50, 51] codes. Total energies of collinear spin configurations were mapped onto the spin Hamiltonian, and exchange couplings were determined [52]. The accuracy of this approach was improved by choosing different values of the on-site Coulomb repulsion for the octahedrally coordinated Fe1 and Fe3 sites and for the tetrahedrally coordinated Fe2 sites, following different oxygen coordination and, therefore, different screening [53].

DFT-based exchange couplings were refined by Monte-Carlo simulation of the magnetic susceptibility. The optimized set of exchange parameters was obtained, with $J_{33} = 116$ K, $J_{43} = 38$ K, $J''_{43} = 57$ K, and the Fe1–Fe3...
inter-plane interaction $J_\perp = 8\,\text{K}$ (Fig. 1). Additionally, a weak second-neighbor interlayer Fe1–Fe1 interaction $J_{\perp,2} = 2\,\text{K}$ is present. This set of parameters reproduces the susceptibility down to 120 K (Fig. 5) and predicts $T_N \simeq 180\,\text{K}$ in perfect agreement with the experiment.

**B. Magnetic anisotropy**

Several anisotropic terms may occur in Bi$_4$Fe$_5$O$_{13}$F. Their calculation follows the same procedure [52] with the only exception that orthogonal spin configurations are used [53]. Symmetric exchange anisotropy corresponds to energies well below 0.1 K per Fe atom and is thus negligible. The antisymmetric exchange anisotropy, Dzyaloshinsky-Moriya (DM) interactions allowed on the $J_{43}$, $J'_{43}$, and $J_\perp$ bonds, are stronger, up to about 5 K per Fe atom, but their effect on the magnetic structure largely cancels out, because in the orthogonal structures of phases I and III the adjacent $J_{43}$ ($J'_{43}$) bonds feature same directions of the DM vectors, yet opposite spin rotations.

Single-ion anisotropy terms are believed to be small in Fe$^{3+}$ compounds due to the $d^5$ nature of the magnetic ion. Unexpectedly, we find that these terms are in fact non-negligible and central to the physics of Bi$_4$Fe$_5$O$_{13}$F. Single-ion anisotropy is obtained by fixing spins along a given direction and rotating the reference spin in the plane perpendicular to this direction [53]. Angular dependence of the energy, $E(\varphi)$, directly measures the single-ion anisotropy of the reference spin.

Fig. 6 shows single-ion anisotropies for different Fe sites. The single-ion anisotropy of Fe3 is much stronger than those of Fe1 and Fe2. This can be attributed to a large distortion of the Fe3O$_6$ octahedra [32]. The positions of the energy minima are compatible with the symmetry of the crystal structure, where mirror planes require that the $E(\varphi)$ curves are symmetric with respect to $\varphi = 45^\circ$ and $135^\circ$.

An immediate effect of the single-ion anisotropy terms is the selection between states A and B that can form in phase I. Here, the predominant single-ion anisotropy of Fe3 favors either $a_m$ or $b_m$ direction of a given Fe3 atom. The Fe1 spins choose same directions because of the isotropic coupling $J_\perp$. Therefore, the Fe1 spins should point along the $b_m$ axis, whereas the Fe2 spins should point along the $a_m$ axis, as seen in the state B that is pinpointed by our neutron data.

The single-ion anisotropy also plays central role for the selection of both in-plane and interlayer order in Bi$_4$Fe$_5$O$_{13}$F, as we explain below.

**C. In-plane order**

The classical phase diagram of the $J_{43} - J'_{43} - J_{33}$ model that describes the in-plane isotropic interactions is shown in Fig. 7. This model takes into account the two inequivalent Fe1–Fe2 couplings, $J_{43}$ and $J'_{43}$, and the fact that there are two Fe1 spins on each four-fold site of the lattice. The phase diagram has been obtained using Lyons and Kaplan’s [54] generalization of the Luttinger-Tisza method [55], see Ref. [53] for technical details. The phase diagram contains three main phases, the coplanar orthogonal phase, the collinear ferrimagnetic phase, and a mixed phase in between, which is non-coplanar. In the latter phase, the projections of the spins along an axis yields the ferrimagnetic configuration while the pro-
phase II requires the presence of anisotropy.

The anisotropy of Fe3 is more than 5 times stronger than that of Fe1 and Fe2. Therefore, at low temperatures, in phase I, Fe3 with its preferred directions at $\varphi = 0^\circ$ and $90^\circ$ puts the Fe1 moments along $a_m$ and $b_m$. It does not choose the flavor of vector chiral order per se, but the anisotropy of Fe2 selects $\chi = +c$ in phase I, as confirmed by a direct energy minimization.

Above $T_2$, in phase III, the preferred direction of Fe3 plays no role, and the Fe1 and Fe2 moments are left to form an orthogonal configuration, even though their preferred directions are not compatible with such a structure. For example, the preferred directions of Fe11 and Fe12 differ by $48.2^\circ$ only, whereas Fe21 and Fe22 moments prefer to be nearly collinear. However, deviations from the orthogonal structure cost a lot of exchange energy, because the exchange couplings are at least two orders of magnitude stronger than the anisotropy. A clear fingerprint of this competition between the orthogonal state and individual single-ion anisotropies is the large and unexpected difference in the magnetic moments of Fe11 and Fe12 in phase III. Indeed, the Fe11 moment is larger, because it is close to the preferred direction (the departure from the preferred direction is $\Delta \varphi = 5^\circ$ at 100 K). On the other hand, the moment on Fe12 is far away from its preferred direction ($\Delta \varphi = 47^\circ$) and thus 30% smaller.

A side effect of these energy considerations is that vector chiral order changes from $\chi = +c$ in phase I to $\chi = -c$ in phase III. The continuous transformation between these two phases necessitates the intermediate quasi-collinear phase II that exists in a narrow temperature range only.

### D. Interlayer order

Let us now turn to the interlayer order that can be described by an effective 1D model of the $\text{Fe}1_1$–$\text{Fe}3$–$\text{Fe}1_2$–$\text{Fe}2$–$\text{Fe}3$–$\text{Fe}1_1$– chain. It is essentially a ferrimagnetic structure, where $S'_1 = 5$ stands for the Fe1 dumbbell and $S'_2 = \frac{3}{2}$ stands for the Fe3 atom. The nearest-neighbor Fe1–Fe3 coupling $J_{12}$ is augmented by the next-nearest-neighbor Fe1–Fe1 coupling $J_{12}$ resulting in a sawtooth-chain geometry (Fig. 8).

Classical energy minimization for such a model gives rise to a non-collinear state with the angle $\psi$ between the neighboring spins given by

$$\cos \psi = \frac{J_{12} S_3}{2 J_{12} S'_1}.$$  (1)

Two $\psi$ rotations may be followed by another two $\psi$ rotations or by two $-\psi$ rotations. Therefore, there is infinite classical degeneracy in the $J_{12} - J_{12}$ sawtooth-chain model, because any sequence of pairwise $\psi$ and $-\psi$ rotations can occur. This situation is remarkably similar to kagome francisites [56], where same physics is observed on a 2D lattice, and the ground state is chosen (already on the classical level) by anisotropic terms in the spin Hamiltonian.

---

**FIG. 7.** Classical phase diagram of the isotropic $J_{43} = J'_{43} = J_{33}$ model, with two Fe1 spins on each four-fold site of the lattice, see text. The two available compounds are shown by the filled blue triangle (based on the parameters of [25]) and the filled red dot (based on the parameters given above).
In the case of Bi$_4$Fe$_5$O$_{13}$F, $J_{\perp}/J_{12} \approx 4$ and $S_3/S'_3 \approx \frac{1}{2}$ produce ferrimagnetic order along the $c$ direction at low temperatures (phase I, Fig. 8). At higher temperatures, $S_3$ decreases, and the $S_3/S'_3$ ratio decreases as well. Therefore, $2\psi$ departs from $360^\circ$ and eventually reaches $180^\circ$ in phase III, where $S_3 = 0$, and the interlayer order is antiferromagnetic (Fig. 8). Phase II is in the intermediate regime with $2\psi = 270^\circ$ (Fig. 8), i.e., the interlayer order is orthogonal with the $90^\circ$ configuration between the Fe1 moments in the adjacent planes.

Ground state selection requires anisotropic terms in the spin Hamiltonian. The $J_{\perp} - J_{12}$ sawtooth-chain model makes no difference between the commensurate (“canted”) state, where two $\psi$ rotations are followed by two $-\psi$ rotations, and the incommensurate (helical) state, where only $\psi$ rotations occur (Fig. 8, left). This degeneracy is lifted by anisotropy terms.

In Bi$_4$Fe$_5$O$_{13}$F, single-ion anisotropy of Fe1 and Fe3 is at play. This anisotropy favors same spin directions on all Fe3 atoms and, respectively, on all Fe1 atoms from every second Cairo plane. Therefore, the commensurate order along the $c$ direction is stabilized. It is worth noting that the DM coupling on the $J_{\perp}$ bonds would have an opposite effect and favor the incommensurate helical order, but such a coupling is smaller than the single-ion anisotropy terms providing the energy of $0.4$ K per Fe atom only [57]. Therefore, the single-ion anisotropy is crucial not only for the in-plane order, but also for the commensurate nature of the order between the Cairo planes.

**IV. DISCUSSION AND CONCLUSIONS**

The main picture emerging from the experimental data presented here is that the interlayer Fe3 spins in Bi$_4$Fe$_5$O$_{13}$F play a dual role, on one hand mediating the 3D ordering and on the other driving a reorienting of the order both within and between the planes. While details of this transition require further dedicated theoretical work, on the experimental side the effect of the Fe3 spins is crucial for the design of new Cairo-lattice magnets, because interlayer magnetic sites, which are often introduced for the sake of stabilizing the crystal structure [58], are not innocent and in fact play decisive role for the magnetic order.

The sequence of transitions in Bi$_4$Fe$_5$O$_{13}$F is reminiscent of the consecutive spin re-orientations in RMn$_2$O$_5$, where an intermediate collinear phase separates two non-collinear states. However, this collinear phase [37] is different from our phase II, because it does not show the characteristic reduction in the ordered moment on half of the Fe2 sites. Instead, it may be related to the collinear phases A and B of Fig. 7.

More generally, we show that magnetic order in the pentagonal geometry is largely influenced by even weak anisotropy terms. Despite structural similarities, different systems may eventually show very different types of magnetic order depending on the transition-metal ion. In the case of RMn$_2$O$_5$, the $d^5$ Mn$^{3+}$ ion is known to be more anisotropic than the $d^6$ Fe$^{3+}$ [59], and no direct analogies between Fe-based Cairo magnets and multiferric R'Mn$_2$O$_5$ manganites may occur.

Phase II of Bi$_4$Fe$_5$O$_{13}$F is quite unusual on its own. On one hand, it strongly resembles quantum collinear phase of the Cairo model [56]. As explained in Sec. II B, deviations from the collinearity in this phase are due to the imperfect nature of the Cairo lattice ($J_{43} \neq J'_{43}$). On the other hand, phase II in Bi$_4$Fe$_5$O$_{13}$F is not stabilized by quantum fluctuations and originates from competing single-ion anisotropies. Despite this different origin, phase II involves significant amount of fluctuations reflected in the low ordered moment on Fe21. It would be interesting to explore whether properties of phase II and especially its magnetic excitations are similar to those of the quantum collinear phase established in Ref. 56. Moreover, variable magnetic structures of Bi$_4$Fe$_5$O$_{13}$F may have effect on its hitherto unknown dielectric behavior.
ACKNOWLEDGMENTS

We are grateful to Prof. J.-M. Perez-Mato and Dr. Dmitry Khalyavin for valuable discussions on the magnetic structures and symmetries. DF and AA are grateful to the Russian Science Foundation (grant 14-13-00680) for support. AT was supported by the Federal Ministry for Education and Research through the Sofja Kovalevskaya Award of Alexander von Humboldt Foundation. This work is based on experiments performed at the Swiss spallation neutron source SINQ, Paul Scherrer Institut, Villigen, Switzerland.


[17] This is mostly because of the well-known incompatibility of the five-fold symmetry with lattice periodicity.


[34] S. R. Mohapatra, A. Swain, C. S. Yadav, S. D. Kaushik,


[47] We have also tested a different magnetic structure solution that would impose largely non-collinear spins in the spirit of phase I. To this end, the space group $P2_1/m$ was used (Pc-czn maintaining the crystal axes of Pc-A2/f). This solution, however, demonstrated an inferior fit of the magnetic reflections ($R_{\text{max}} = 0.030$ at $T = 65$ K) because spin directions for the Fe3 atoms were constrained by symmetry. A better fit might be achievable with the $P2_1/c$ magnetic space group, but it contains 10 independent crystallographic positions for the Fe atoms that renders the solution intractable.


[53] See Supplemental Material at [...] for: i) neutron diffraction patterns and their refinements; ii) details of electronic structure calculations; iii) details on the derivation of the phase diagram presented in Fig. 7; iv) theoretical evidence for the qualitatively different $T$-dependence of the Fe3 and Fe1/Fe2 moments. The Supplemental Material includes Refs. 60–65.


[57] For the sake of comparison with Fig. 6, we provide the overall coupling energy that is not normalized to $S = \pm \frac{1}{2}$.


[59] The typical single-ion anisotropy term for octahedrally coordinated Mn$^{3+}$ is $2 – 3K$ [66, 67] yielding the energy difference on the order of 10 K upon spin rotation, the energy scale similar to that of Fe3 in Fig. 6.


[64] R. J. McQueeney, J.-Q. Yan, S. Chang, and J. Ma, “Determination of the exchange anisotropy in perovskite antiferromagnets using powder inelastic neutron scatter-


Supplemental Material

FIG. S1. Refined neutron diffraction patterns at 1.5 K, 65 K, and 100 K.

FIG. S2. Temperature evolution of the magnetic order in the Cairo plane. The Cairo planes at $z = 0$ are shown.
TABLE S1. Refined magnetic moments at different temperatures. The vectors of magnetic moments are represented using spherical coordinates $(\mu, \theta, \phi)$, where $\mu$ is the magnetic moment value and $\theta$ and $\phi$ are the azimuthal and polar angles, respectively. The magnetic moment components are then expressed as follows: $m_a = \mu \sin \theta \cos \phi$, $m_b = \mu \sin \theta \sin \phi$, and $m_c = \mu \cos \theta$. The angle $\theta$ is fixed to 90° (all spins are in the ab plane), whereas $\phi$ is measured with respect to the $a_\text{m}$ direction.

<table>
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S1. ISOTROPIC EXCHANGE COUPLINGS

Isotropic exchange couplings were obtained from total energies of collinear and orthogonal spin configurations using the mapping procedure [52]. We chose the Perdew-Burke-Ernzerhof (PBE) flavor of the exchange-correlation potential [48], and included correlations on the mean-field DFT+U level. Different values of the on-site Coulomb repulsion parameter $U_d$ were applied for the octahedrally and tetrahedrally coordinated Fe sites. The choice of $U_d$ was justified by calculating magnetic exchange couplings in reference compounds LaFeO$_3$ (octahedrally coordinated Fe$^{3+}$ ions) and BaSrFe$_3$O$_8$ (tetrahedrally coordinated Fe$^{3+}$ ions). For both compounds, we obtained exchange couplings using different values of $U_d$, and estimated Néel temperatures by simulating magnetic susceptibility with theloop algorithm [60] of ALPS [61]. Note that the value of $U_d$ is also dependent on the band-structure code, given the different basis sets for 3d-orbitals. The results of FPLO calculations can be well reproduced in VASP by increasing $U_d$ for 1 eV, which is similar to our earlier experience [62].

In LaFeO$_3$, the FPLO calculations with $U_d = 6$ eV (or, respectively, the VASP calculations with $U_d = 7$ eV) yield $J_{ab} = 61$ K and $J_c = 54$ K for the couplings in the $ab$ plane and along the $c$ direction, respectively, resulting in the Néel temperature $T_N = 729$ K. This value is in perfect agreement with the experimental $T_N \approx 730$ K [63]. Our computed exchange couplings also reproduce the averaged exchange coupling $\bar{J} = 56.8$ K obtained from inelastic neutron scattering [64].

In BaSrFe$_3$O$_8$, honeycomb bilayers of the Fe$^{3+}$ ions are formed. Using $U_d = 8$ eV in FPLO or $U_d = 9$ eV in VASP, we obtained the in-plane coupling $J_{ab} = 103$ K, the coupling $J_c = 175$ K between the two layers of the bilayer, and the coupling $J_{\perp} = 0.7$ K between the bilayers. This set of exchange couplings yields $T_N = 700$ K in excellent agreement with the experimental value of 690 K [65]. If, on the other hand, $U_d = 6$ eV is used (FPLO), $T_N$ increases well above 800 K implying that higher values of $U_d$ are required for a proper description of the tetrahedrally coordinated Fe$^{3+}$ sites.

Using such optimized values of $U_d$, we calculated exchange couplings in Bi$_4$Fe$_5$O$_{13}$F. In Table S2, they are compared with the values obtained in Ref. [32], where same value of $U_d$ was applied to all Fe sites. While no qualitative changes are observed, the coupling $J_{33}$ between the two tetrahedrally coordinated Fe atoms is reduced substantially, because a higher value of $U_d$ is applied. This reduction has an immediate effect on the Néel temperature that equals to 250 K for the parameter set from Ref. [32] and 150 K for our new parameter set. An even better agreement with the experimental $T_N = 180$ K can be achieved by adjusting the weakest coupling $J_{\perp}$. We found that $J_{\perp} = 8$ K leads to the best agreement not only with the experimental $T_N$, but also with the magnetic susceptibility curve in general. We have also identified the second-neighbor coupling $J_{1,2}$ along the $c$ axis. It is responsible for the AFM interlayer order in phase III.

<table>
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<th>$J_i$</th>
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<td>3.06</td>
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<tr>
<td>6.11</td>
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TABLE S2. Exchange couplings in Bi$_4$Fe$_5$O$_{13}$F: the Fe–Fe distances $d_{Fe-Fe}$ (in Å), the Fe–O–Fe angles $\psi_{Fe-O-Fe}$ (in deg), and exchange couplings $J_i$ (in K) obtained from FPLO calculations. The values from Ref. [32] were obtained using $U_d = 7$ eV and $J_d = 1$ eV. The values in the current work are based on the optimized choice of $U_d$, 6 eV for the octahedrally coordinated Fe sites and 8 eV for the tetrahedrally coordinated Fe sites.

<table>
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<th>$\varphi_0$</th>
<th>$A$</th>
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<th>$A$</th>
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<tbody>
<tr>
<td>0.69</td>
<td>42.5</td>
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</table>

TABLE S3. Single-ion anisotropy of Fe$^{3+}$ ions parametrized using Eq. (2). The pre-factor $A$ is in K, and the phase shift $\varphi_0$ is in degrees, showing the position of the energy minimum (preferred spin direction) for a given atom.

S2. MAGNETIC ANISOTROPY

For calculating single-ion anisotropy, we used the same mapping approach [52] but exploited orthogonal spin configurations, where the spin of interest probes different directions in the $ab$ plane, whereas all other spins are along the $c$ direction, so that all interactions with other spins are canceled, and the effect of single-ion anisotropy is probed exclusively. While spin configurations of our choice eliminate all intersite interactions for Fe1 and Fe3, the calculations for Fe2 required two antiparallel spins on one $J_{33}$ bond to be used simultaneously, in order to eliminate contributions of Dzyaloshinsky-Moriya couplings on the bonds $J_{43}$ and $J'_{43}$. All calculations were performed on the DFT+U+SO level in VASP, hence we chose $U_d = 7$ eV for the octahedrally coordinated Fe and $U_d = 9$ eV for the tetrahedrally coordinated Fe.

Total energies as a function of the polar angle $\varphi$ (Fig. 6 of the manuscript) were parametrized as follows,

$$E = A (1 - \cos[2 (\varphi - \varphi_0)])$$,

where $A$ is the magnitude of the single-ion anisotropy, and $\varphi_0$ defines preferred spin direction in the $ab$ plane.
FIG. S3. The unit cell of Bi$_4$Fe$_5$O$_{13}$F, along with the notation of the different sites and the connectivity of the isotropic exchange couplings. There is a pair of Fe1 sites, \{1,2\} or \{3,4\}, sitting on each of the four-fold sites of the Cairo lattice, one above and the other below the plane. Each of the spins of the pair couples with $J_{43}$ or $J'_{43}$, respectively, to the Fe2 sites with \{5,6,7,8\}. The Fe3 sites \{9,10\} sit right below and above the Fe1 sites, connecting neighboring planes to each other via $J_{\perp}$. The coupling $J_{44}$ (not shown) connects 1 with 2, and 3 with 4.

Absolute values of the anisotropy are relatively small, given the $d^5$ nature of the Fe$^{3+}$ ions. The much larger value of $A$ for Fe3 compared to Fe1 can be related to the strongly distorted nature of the Fe$_3$O$_6$ octahedra. Remarkably, the calculated single-ion anisotropy with $\varphi_0 = 90^\circ$ for Fe3 favors model B and disfavors model A for the magnetic structure of phase I, in agreement with the experiment.

For the sake of completeness, we also compared single-ion energies for in-plane and out-of-plane spin directions and obtained 2.7 K for Fe1, −0.55 K for Fe2, and −2.9 K for Fe3, where positive sign implies easy-plane anisotropy (ab plane) and negative sign implies easy-axis anisotropy (c direction). Although the easy-axis anisotropy of Fe3 is slightly stronger than the easy-plane anisotropy of Fe1, the easy-plane nature of Fe1 spins prevails, because the Fe1 atoms are twice more abundant compared to Fe3.

S3. CLASSICAL PHASE DIAGRAM OF THE MODEL

Figure S3 shows the topology of the Heisenberg interactions within one unit cell of Bi$_4$Fe$_5$O$_{13}$F. The system has a square Bravais lattice, defined by the primitive translations $t_1$ and $t_2$ (the ones spanning the shaded region of the figure). There are ten sites per unit cell labeled by the numbers 1-10. Among these, \{1, 2, 3, 4\} are Fe1 sites, \{5, 6, 7, 8\} are Fe2 sites, and \{9,10\} are Fe3 sites. Sites 1, 2 and 9 sit on top of each other, and the same is true for sites 3,4, and 10, see figure. In the following we shall denote the spins by $S_{r,\nu}$, with $r$ labeling the primitive position of the unit cell and $\nu = 1-10$. The isotropic Heisenberg Hamiltonian reads:

$$
\mathcal{H} = \sum_r \left\{ J_{44} (S_{r,1} \cdot S_{r,2} + S_{r,3} \cdot S_{r,4}) + J_{\perp} (S_{r,1} \cdot S_{r+e,9} + S_{r,2} \cdot S_{r,0} + S_{r,3} \cdot S_{r+e,10} + S_{r,4} \cdot S_{r,10}) \\
+ J_{43} [ (S_{r,1} + S_{r,2}) \cdot (S_{r,5} + S_{r,7}) + (S_{r,3} + S_{r,4}) \cdot (S_{r,6} + S_{r-t_1+t_2,8}) ] \\
+ J'_{43} [ (S_{r,1} + S_{r,2}) \cdot (S_{r,6} + S_{r,8}) + (S_{r,3} + S_{r,4}) \cdot (S_{r-t_1,5} + S_{r+t_2,7}) ] \\
+ J_{33} (S_{r,5} \cdot S_{r+t_2,7} + S_{r,6} \cdot S_{r-t_1,8}) \right\},
$$

where all couplings are antiferromagnetic (positive).

Before we establish the classical ground state phase diagram of the model we list a number of states that are of main interest.
and the energy is given by
\[ E_{\text{ortho}} = 2J_{44} - 4J_{J_{43}} - 2|\cos \phi_3|J_3| - 8|\sin \phi_3|J_{43}' . \]
where \( N_{uc} \) is the number of unit cells.

### B. Ferrimagnetic state

Next we examine the ferrimagnetic state, which has ordering wavevector \( \mathbf{Q} = 0 \). In this state, the Fe1 spins point in one direction and the Fe2 and Fe3 spins point in the opposite direction, see Fig. S4 (c). Here, the local fields are given by:
\[ h_1 = h_2 = h_3 = h_4 = (J_{44} - J_{43} - 2J_{43} - 2|\cos \phi_3|J_3| - 2|\sin \phi_3|J_{43}')S \]
\[ h_5 = h_6 = h_7 = h_8 = (J_{33} - 2|\cos \phi_3|J_{43} - 2|\sin \phi_3|J_{43}')S \]
\[ h_9 = h_{10} = -2J_{43}' S , \]
and the energy is
\[ E_{\text{ferrim}} = 2J_{44} - 4J_{43} + 2J_{33} - 8(J_{43} + J_{43}') . \]
C. Mixed state

Let us also examine the mixed state of Ref. [24], which has ordering wavevector \( \mathbf{Q} = (\pi, \pi, 0) \). This state combines the orthogonal state in the plane and the ferrimagnetic state perpendicular to the plane. Specifically, this state can be obtained by starting from the orthogonal state, say in the \( xy \) plane, and then tilting the spins out of the plane as follows: the spins 1, 2, 3, 4 tilt above the \( xy \) plane by an angle \( \theta \), the spins 9, 10 tilt below the plane by the same angle \( \theta \), and finally the spins 5, 6, 7, 8 tilt below the plane by an angle \( \theta' \). The total energy can be found by combining the energies from the orthogonal and the ferrimagnetic state:

\[
\frac{E_{\text{tot}}}{N_{\text{uc}}S^2} = 2J_{44} - 4J_\perp - 2J_{43} \cos(2\theta') - 8J_{43} \sqrt{1 + x^2} \cos \theta \cos \theta' - 8(J_{43} + J'_{43}) \sin \theta \sin \theta'.
\]  

(9)

Minimizing with respect to \( \theta \) and \( \theta' \) gives:

\[
\tan \theta' = \frac{\sqrt{1 + x^2}}{1 + x} \tan \theta, \quad \cos \theta' = \frac{2J_{43}J'_{43}}{J_{12}J_{43}} \cos \theta,
\]

(10)

and combining the two equations gives

\[
\sin \theta' = \frac{2J_{43}J'_{43}}{(J_{43} + J'_{43})J_{33}} \sin \theta, \quad \sin^2 \theta = \frac{(J_{43} + J'_{43})^2[(2J_{43}J'_{43})^2 - J_{33}^2(J_{43}^2 + J'_{43}^2)]}{(2J_{43}J'_{43})^3}.
\]

(11)

Note that the corresponding relations for the angles \( \theta \) and \( \theta' \) given in Ref. [24] for the special case of \( J_{43} = J'_{43} \) can be recovered from the above relations by setting \( J'_{43} = J_{43} \) and \( J_{43} \to J_{43}/2 \). The extra factor of two must be inserted to take into account that in the present model we have two Fe1 sites sitting at each four-fold site of the Cairo lattice, and not one spin as in Ref. [24].

Finally, let us rewrite the energy of the mixed phase using the solutions for the angles \( \theta \) and \( \theta' \):

\[
\frac{E_{\text{mixed}}}{N_{\text{uc}}S^2} = 2J_{44} - 4J_\perp - 8\frac{J_{43}J'_{43}}{J_{33}} - 2J_{33} - 2\frac{J_{43}J_{33}}{J_{33}} - 2\frac{J'_{43}J_{33}}{J_{33}}.
\]

(12)

D. Collinear phases A

Next we discuss the collinear state A that is mentioned in Fig. 7 of the main text. This state has ordering wavevector \( \mathbf{Q} = (\pi, \pi, 0) \) and is written as in Eq. (3) but with:

\[
\phi_5 = \pi, \quad \phi_3 = \phi_6 + \pi, \quad \phi_6 = \{0, \pi\}.
\]

(13)

In this state all \( J_{43} \) are satisfied, and only half of \( J'_{43} \) are satisfied, and the two choices of \( \phi_6 \) fix which of the two halves are satisfied. The choice with \( \phi_6 = 0 \) is shown in Fig. S4 (d). The energy corresponding to this solution is

\[
\frac{E_A}{N_{\text{uc}}S^2} = 2J_{44} - 4J_\perp - 2J_{33} - 8J_{43}.
\]

(14)

Finally, the expressions for the local fields are:

\[
\begin{align*}
    h_1 &= h_2 = (J_{44} - 2J_{43} \pm 2J'_{43} - J_\perp)S, \\
    h_3 &= h_4 = (J_{44} - 2J_{43} \mp 2J'_{43} - J_\perp)S, \\
    h_5 &= h_7 = (-2J_{43} \mp 2J'_{43} - J_{33})S, \\
    h_6 &= h_8 = (-2J_{43} \pm 2J'_{43} - J_{33})S, \\
    h_9 &= h_{10} = -2J_\perp S,
\end{align*}
\]

(15)

where \( \pm \) corresponds to \( \phi_6 = 0 \) or \( \pi \). So here we have two types of Fe1 and two types of Fe2 spins.

E. Collinear phases B

Let us also discuss the collinear state B that is mentioned in Fig. 7 of the main text. This state has again ordering wavevector \( \mathbf{Q} = (\pi, \pi, 0) \) and is written as in Eq. (3) but with:

\[
\phi_6 = \pi, \quad \phi_3 = \phi_5 = \{0, \pi\}.
\]

(16)
In this state all $J_{43}'$ are satisfied, and only half of $J_{43}$ are satisfied, and the choice of $\phi_5 = \{0, \pi\}$ gives which of the two halves are satisfied. The choice with $\phi_5 = 0$ is shown in Fig. S4(e). The energy corresponding to this solution is

$$
\frac{E_B}{N_{uc} S^2} = 2J_{44} - 4J_{\perp} - 2J_{33} - 8J_{43}'.
$$

(17)

Finally, the expressions for the local fields are now:

$$
\begin{align*}
    h_1 &= h_2 = (J_{44} \pm 2J_{43} - 2J_{43}' - J_{\perp})S, \\
    h_3 &= h_4 = J_{44} \mp 2J_{43} - 2J_{43}' - J_{\perp})S, \\
    h_5 &= h_7 = 2J_{43} - 2J_{43}' - J_{33})S, \\
    h_6 &= h_8 = \mp 2J_{43} - 2J_{43}' - J_{33})S, \\
    h_9 &= h_{10} = -2J_{\perp} S,
\end{align*}
$$

(18)

where $\pm$ corresponds to $\phi_5 = 0$ or $\pi$. So we again have two types of Fe1 and two types of Fe2 sites.

F. Boundaries between different phases

Let us now establish the boundaries between the five phases discussed above. First of all, the orthogonal state is degenerate with the collinear phase A (B) when $J_{43}' = 0$ ($J_{43} = 0$). In these limits the classical degeneracy is actually much larger since we have decoupled chains, and each chain forms a Néel order along an independent spin direction. The collinear states A and B (as well as the orthogonal states A and B) are just two special members of this manifold. They are discussed here because they are the only collinear states in the phase diagram, together with the partly disordered, collinear phase that is stabilized by quantum fluctuations in the corner $J_{43} = J_{43}' = 0$ [24].

Next, the boundary between the orthogonal and the mixed phase is determined by the line

$$
x_2 = \frac{x_1}{\sqrt{4x_1^2 - 1}}
$$

(19)

where $x_1 \equiv J_{43}/J_{33}$ and $x_2 \equiv J_{43}'/J_{33}$. This is the brown line in Fig. 7 of the main text. Next, the boundary between the mixed and the ferrimagnetic phase is determined by the line

$$
x_2 = \frac{x_1}{2x_1 - 1}
$$

(20)

which is where the two canting angles $\theta = \theta' = \pi/2$. This is the blue line in Fig. 7 of the main text.

G. Generalized Luttinger-Tisza method of Lyons and Kaplan

So far, we have only compared the energies of five possible configurations, but we have not proved which ones are the global ground states and where in the phase diagram. To this end, we will use Lyons and Kaplan’s generalization [54] of the Luttinger-Tisza method [55]. We first rewrite the energy in momentum space

$$
\mathcal{H} = \sum_{k} \sum_{\nu,\mu=1}^{10} \Lambda_{\nu,\mu}(k) S_{k,\nu} \cdot S_{k,\mu}
$$

(21)

where $S_{k,\nu} = \frac{1}{\sqrt{N_{uc}}} \sum_{r,\nu} e^{-ikr} S_{r,\nu}$, and the 10\times10 interaction matrix $\Lambda$ is given by:

$$
\Lambda(k) = \frac{1}{2} \begin{pmatrix}
    0 & J_{44} & 0 & 0 & J_{43} & J_{43}' & J_{43} & J_{43}' & J_{\perp} e^{-ik} c & 0 \\
    J_{44} & 0 & 0 & 0 & J_{43} & J_{43}' & J_{43} & J_{43}' & J_{\perp} & 0 \\
    0 & 0 & 0 & J_{44} & J_{33} e^{ik t_1} & J_{43} & J_{43}' e^{-ik} t_2 & J_{43} e^{-ik} (t_1 - t_2) & 0 & J_{\perp} e^{-ik} c \\
    0 & 0 & 0 & J_{44} & J_{33} e^{-ik} t_1 & J_{43} & J_{43}' e^{ik t_2} & J_{43} e^{ik} (t_1 - t_2) & 0 & J_{\perp} e^{ik} c \\
    J_{43} & J_{43} & J_{43}' e^{-ik} t_2 & J_{33} e^{-ik} t_1 & 0 & 0 & J_{33} e^{-ik} t_2 & 0 & 0 & 0 \\
    J_{43} & J_{43} & J_{43}' e^{ik t_2} & J_{33} e^{ik t_1} & 0 & 0 & 0 & J_{33} e^{ik} t_1 & 0 & 0 \\
    J_{43} & J_{43} & J_{43}' e^{-ik} (t_1 - t_2) & J_{33} e^{-ik} (t_1 - t_2) & 0 & 0 & 0 & 0 & J_{\perp} e^{-ik} c & 0 \\
    J_{43} & J_{43} & J_{43}' e^{ik} (t_1 - t_2) & J_{33} e^{ik} (t_1 - t_2) & 0 & 0 & 0 & 0 & J_{\perp} & 0 \\
    J_{\perp} e^{ik} c & J_{\perp} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & J_{\perp} e^{ik} c & J_{\perp} & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
$$
Next we replace the strong constraints $S^2_{r,\nu} = S^2$, with the 'generalized weak constraint' of Lyons and Kaplan [54],

$$\sum_{r,\nu} \alpha_{\nu} S^2_{r,\nu} = S^2 N_{uc} \sum_{\nu} \alpha_{\nu},$$  \hfill (22)

where the set $\{\alpha_{\nu}\}$ is a fixed set of numbers. Minimizing the associated Langrange multiplier problem leads to the equations:

$$\sum_{\nu} \Lambda_{\mu,\nu}(-q)S_{q,\nu} = \lambda \alpha_{\mu} S_{q,\mu} \Rightarrow \sum_{\nu} \tilde{\Lambda}_{\mu,\nu}(-q)\tilde{S}_{q,\nu} = \lambda \tilde{S}_{q,\mu},$$  \hfill (23)

where $\lambda$ is the Langrange multiplier,

$$\tilde{\Lambda}_{\mu,\nu} = \frac{\Lambda_{\mu,\nu}}{\sqrt{\alpha_{\mu} \alpha_{\nu}}}, \quad \tilde{S}_{k,\mu} = \sqrt{\alpha_{\mu}} S_{r,\mu}. \hfill (24)$$

The total ground state energy can be expressed as

$$E = N_{uc} S^2 \sum_{\nu=1}^{10} \alpha_{\nu},$$  \hfill (25)

and since the set $\{\alpha_{\mu}\}$ is fixed, the minimum energy of this ‘generalized soft constraint problem’ is obtained by minimizing $\lambda$, i.e. by choosing the minimum eigenvalue of the matrix $\tilde{\Lambda}$ over the whole Brilouin zone. Now the key point is the following [54]: All solutions of the original ‘hard constraint problem’ satisfy the ‘generalized soft constraint’. So all solutions of the former problem are enclosed within the domain of solutions of the latter problem. So if we find the minimum solution over the latter domain, then this must be the minimum solution of the ‘hard constraint problem’ as well.

The main problem then reduces to ‘guessing’ the right set $\{\alpha_{\mu}\}$. To this end we go back and identify

$$\lambda \alpha_{\mu} \rightarrow h_{\mu}/(2S),$$  \hfill (26)

where $h_{\mu}$ is the strength of the local mean field at site $\mu$. And for the latter we can just try out the local fields from some of the above five configurations. Accordingly, we have checked numerically the eigenspectrum of the matrices $\tilde{\Lambda}_{\text{ortho}}$ and $\tilde{\Lambda}_{\text{ferri}}$, obtained from Eq. (24) with the local fields associated with the orthogonal and the ferrimagnetic state, respectively. We find the following numerically:

1. Within the ‘orthogonal’ region of Fig. 7 of the main text, the minimum eigenvalue of the matrix $\tilde{\Lambda}_{\text{ortho}}$, sits at the wavevector $Q = (\pi, \pi, 0)$, it is two-fold degenerate, and the associated eigenvectors can be combined to give precisely the two orthogonal states. This proves that the two orthogonal states are the absolute minima of the energy in this region of the phase diagram.

2. Within the ‘ferrimagnetic’ region of Fig. 7 of the main text, the minimum eigenvalue of the matrix $\tilde{\Lambda}_{\text{ferri}}$, sits at the wavevector $Q = (0, 0, 0)$, it is not degenerate, and the associated eigenvector gives precisely the ferrimagnetic state. This proves that the ferrimagnetic state is the absolute minimum of the energy in this region of the phase diagram.

3. Within the ‘mixed’ region of Fig. 7 of the main text, the minimum eigenvalue of the matrix $\tilde{\Lambda}_{\text{ferri}}$, sits at the wavevector $Q = (\pi, \pi, 0)$, and it is two-fold degenerate, and the two solutions correspond to the orthogonal states. Likewise the minimum eigenvalue of the matrix $\tilde{\Lambda}_{\text{ortho}}$, sits at the wavevector $Q = (0, 0, 0)$, it is not degenerate and corresponds to the ferrimagnetic solution. This proves that neither the ferrimagnetic nor the orthogonal states are the absolute minima in this region of the phase diagram, and reveals that the absolute minimum should be searched in the form of a linear combination of the two states instead.

 Altogether, we have proved that the phases shown in Fig. 7 of the main text correspond to the absolute minima configurations.

S4. QUALITATIVE BEHAVIOR OF THE LOCAL SPIN LENGTHS IN THE ISOTROPIC SPIN MODEL

Here we would like to briefly show the qualitative difference between the $T$-dependence of the interlayer Fe3 spins with that of the Fe1 and Fe2 sites. Figure S5 shows the $T$-dependence of the local spin lengths as obtained from a
FIG. S5. $T$-dependence of the local moments as obtained from a hybrid self-consistent quantum mean-field theory (left) and a single-site quantum mean-field theory (right). The exchange parameters used are the ones reported in the main text.

hybrid, quantum-mechanical mean-field approach. In this approach, the Fe1 and Fe3 sites are treated within single-site quantum mean-field theory, while the Fe2 spins are treated in pairs, by solving the problem of spin-$5/2$ dimers in some external self-consistent mean field. In this calculation we have used the exchange parameters reported in the main text.

As expected, the results overestimate the ordering temperature (which is in fact also determined by $J_\perp$, see e.g. Ref. [44]), but the qualitative behavior for the spin lengths is already captured by this mean-field approach. Specifically, we see that the Fe3 moments grow far more slowly with decreasing $T$ below the ordering temperature. This is a key aspect for the reorientation transition discussed in the main text.

Another noteworthy feature is the value of the Fe2 moments at zero temperature, which unlike the Fe1 spins, does not go to the maximum possible value of $5/2$, but is slightly reduced. This reduction is related to the fact that the ground state wavefunction of the dimer mean-field problem has a finite singlet component due to the finite $J_{33}$ coupling. Specifically, the local exchange field exerted on the two sites of the Fe2 dimer has a large staggered component (it has no uniform component at all when $J_{43} = J'_{43}$, see Ref. [24]). As a result, the ground state wavefunction of the dimer mean-field problem is a combination of the singlet (as in the absence of exchange field), the triplet, etc (up to $S = 5$). This admixture is responsible for the finite staggered polarization on the dimer.

For comparison we also show the results from a quantum, single-site mean-field theory on all sites, where all spin lengths go to $5/2$ at zero temperature.