Spin Hamiltonian, Emergence of Order Out of a Coulomb Phase and Fake Criticality in the Highly Frustrated Pyrochlore Heisenberg Antiferromagnet FeF$_3$

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FeF$_3$, with its half-filled Fe$^{3+}$ 3d orbital, hence zero orbital angular momentum and $S = 5/2$, is often put forward as a prototypical highly-frustrated classical Heisenberg pyrochlore antiferromagnet. By employing ab initio density functional theory (DFT), we obtain the spin Hamiltonian for this material. This Hamiltonian contains nearest-neighbor antiferromagnetic Heisenberg, bi-quadratic and Dzyaloshinsky-Moriya interactions as dominant terms. We use Monte Carlo simulations to investigate the critical properties of the system. We find that upon decreasing the temperature, the system passes through a Coulomb phase, predominantly composed of coplanar states, before transforming into an “all-in/all-out” (AIAO) state via a very weakly first order transition at a critical temperature $T_c \approx 22$ K in reasonable agreement with the experimental value. Despite the transition being first order, the AIAO order parameter evolves below $T_c$ with a power-law behavior characterized by a pseudo “critical exponent” $\beta \approx 0.18$ in accord with experiment.

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Systems with magnetic moments on the vertices of two- and three-dimensional networks of corner-sharing triangles or tetrahedra and with predominant effective antiferromagnetic nearest-neighbor (n.n.) interactions have tenuous tendency towards conventional long-range magnetic order [1,2]. As a result, the low-temperature properties of materials with such a magnetic moment architecture are ultimately dictated by the mutual competition of perturbations beyond n.n. interactions. This vying at the low-energy scale is at the origin of the plethora of collective and thermodynamic phenomena found in such highly-frustrated magnetic systems [2].

On the theoretical front, one expects highly-frustrated magnets to ubiquitously display a Coulomb phase [3]. This is an emergent state with local constraints described by a divergence-free “spin field” and whose defects, where the constraints are violated, behave as effective charges with Coulombic interactions. The Coulomb phase and its underlying gauge theory description provides an elegant field-theoretic setting to study the effect of various perturbations beyond n.n. interactions. This vying at the low-energy scale is at the origin of the plethora of collective and thermodynamic phenomena found in such highly-frustrated magnetic systems [2].

There is good evidence that the classical spin liquid state of spin ice materials with discrete Ising spins may be described by a Coulomb phase [3,4]. Unfortunately, there are few, if any, materials with continuous symmetry spins that cleanly display a Coulomb phase, as may be signalled by pinch points. For example, in Y$_3$Mo$_2$O$_7$ complex orbital effects [6,7] and spin glass behavior [8,9] irradicate the Coulomb phase. In the ZnCr$_2$O$_4$ spinel, pinch points are not observed [10], possibly because the perturbations beyond n.n. interactions and spin-lattice coupling eliminate them already at high temperature in the paramagnetic state [11]. In this letter, we propose that FeF$_3$, with magnetic Fe$^{3+}$ ions on a pyrochlore network of corner-sharing tetrahedra, may be a good candidate for a Coulomb phase with Heisenberg spins.

With Fe$^{3+}$ being a 3d S-state (spin-only) S = 5/2 ion, single-ion anisotropy and anisotropic spin-spin interactions should be negligible in FeF$_3$, making it a good candidate material with predominant antiferromagnetic n.n. Heisenberg exchange. Neutron scattering and Mössbauer experiments find long-range magnetic order below $T_c \approx 20^{\pm 2}$ K [12,16]. The static magnetic susceptibility shows a deviation from the Curie-Weiss law, even at 300 K, implying the existence of strong antiferromagnetic exchange and short-range correlations extending up to temperatures much higher than $T_c$ [12]. The ordered phase is an “all-in/all-out” (AIAO) state in which the Fe$^{3+}$ magnetic moments point from the corners to the centers (or vice versa) of each tetrahedron (see Fig. 4). Notably, neutron diffraction experiments find a power-law growth of the AIAO order parameter characterized by a “critical exponent” $\beta \sim 0.18$ [16]. Such a value differs significantly from standard order-parameter exponents $\beta \sim 1/3$ for three-dimensional systems, the observation of which has prompted the suggestion of an underlying “new” universality class [16]. To the best of our knowledge, there has been no attempt to determine quantitatively the spin Hamiltonian of FeF$_3$ and to relate the experimentally observed unusual critical behavior to its Hamiltonian. With the hope of reviving interest in

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this material, which could be viewed as a paradigmatic semi-classical pyrochlore Heisenberg antiferromagnet, we employ density-functional theory (DFT) to flesh out its spin Hamiltonian, \( \mathcal{H} \). By computing the energy of various spin configurations and performing Monte Carlo simulations, we expose a highly entropic coplanar (Coulombic) state above \( T_c \) and its demise at \( T \leq T_c \) against an energetically selected AIAO state. Interestingly, we replicate in our Monte Carlo (MC) simulations the aforementioned unusual \( \beta \sim 0.18 \) exponent.

**FIG. 1:** (Color online): The structure of pyr-FeF\(_3\). Red (dark grey) spheres denote the Fe\(^{3+}\) ions. The F\(^-\) ions (not shown) are located at the (shown) bent where bonds merge. (a) The all-in (all-out) state. (b) A coplanar spin configuration (for clarity, a long-range coplanar state is shown).

**Spin Hamiltonian and DFT calculations** — The classical spin Hamiltonian for FeF\(_3\) can be written as

\[
\mathcal{H} = \mathcal{H}_{\text{Heis}} + \mathcal{H}_{\text{bi-qu}} + \mathcal{H}_{\text{ring}} + \mathcal{H}_{\text{DM}} + \mathcal{H}_{\text{single-ion}}.
\]

Here, \( \mathcal{H}_{\text{Heis}} \) denotes the isotropic Heisenberg Hamiltonian with bilinear exchange interactions:

\[
\mathcal{H}_{\text{Heisenberg}} = \sum_{i \neq j} J_{ij} \mathbf{n}_i \cdot \mathbf{n}_j.
\]

The third term is the 4-spin ring-exchange interaction:

\[
\mathcal{H}_{\text{ring}} = \sum_{ijkl} K_{ijkl} \left[ (\mathbf{n}_i \cdot \mathbf{n}_j)(\mathbf{n}_k \cdot \mathbf{n}_l) + (\mathbf{n}_i \cdot \mathbf{n}_k)(\mathbf{n}_j \cdot \mathbf{n}_l) - (\mathbf{n}_i \cdot \mathbf{n}_l)(\mathbf{n}_j \cdot \mathbf{n}_k) \right].
\]

The last two terms, originating from relativistic spin-orbit coupling (SOC), denote the Dzyaloshinsky-Moriya (DM) and single-ion anisotropic interactions, respectively.

\[
\mathcal{H}_{\text{DM}} = D \sum_{(i,j)} \mathbf{D}_{ij} \cdot (\mathbf{n}_i \times \mathbf{n}_j)
\]

\[
\mathcal{H}_{\text{single-ion}} = \Delta \sum_i (\mathbf{n}_i \cdot \mathbf{d}_i)^2.
\]

\( \hat{D}_{ij} \) are the DM (unit) vectors (determined according to the Moriya rules) \(^{[12]}\) and \(^{[13]}\), and the unit vector \( \mathbf{d}_i \) denotes the single-ion easy-axis (local cubic [111]) direction at site \( i \).

We next use DFT to investigate the properties of FeF\(_3\). For all computations, the experimental data for the conventional cubic unit cell lattice parameter (10.325 Å) and the position of the ions were used \(^{[13]}\). The DFT calculations were carried out with the full-potential linearized augmented plane wave (FLAPW) method, employing the Fleur code \(^{[10]}\). To account for the electron-exchange-correlation, we used the local density approximation (LDA). Further correction to the electron-electron interactions was implemented by considering the on-site electron repulsion using the LDA+U method. The effective on-site Coulomb interaction, \( U_{\text{eff}} \), is defined as \( U_{\text{eff}} = U - J_H \), where \( U \) is the bare Coulomb repulsion and \( J_H \) is the on-site ferromagnetic Hund’s exchange, which we set to 1.0 eV, a rather conventional value in such DFT calculations. Using a linear response approach \(^{[20]}\), we obtain \( U_{\text{eff}} \approx 2.8 \) eV from the Quantum-ESPRESSO code \(^{[21]}\).

The minimum energy states have a continuous \( O(3) \) degeneracy within LDA+\( U \). However, incorporating the effect of SOC within the LDA+\( U \)+SOC scheme, leads to an AIAO configuration with spins along \langle 111 \rangle as the state of minimum energy. We find FeF\(_3\) to be an insulator with a 1.0 eV band gap within the LDA+SOC calculations. The band gap rises to 2.5 eV in LDA+U+SOC with \( U_{\text{eff}} = 2.8 \) eV. The hybridization between iron \( d \)-orbitals and fluorine \( p \)-orbitals changes the formal ionization state of the Fe and F atoms. This induces a weak magnetic moment for F (\( \mu_F \approx 0.1 \mu_B \) within the muffin-tin sphere) along with a magnetic moment smaller than the theoretical \( 5 \mu_B \) value for Fe (\( \mu_F \approx 4.2 \mu_B \) in the muffin-tin sphere).

We next determine the coupling constants of \( \mathcal{H} \) in Eq. 1 using spin-polarized DFT calculations. For the first three (isotropic) terms of Eq. 1, we calculate using LDA+\( U \) the total energy difference between various magnetic configurations \(^{[18]}\). We assume that \( J_{ab} \) \(^{[22]}\) as well as farther Heisenberg exchanges \( (J_m, m > 4) \), and bi-quadratic terms farther than first n.n. \( (B_m, m > 1) \) are negligible. Then, by matching the energy differences for spin-polarized states, with that of \( \mathcal{H} \), we determine \( J_1, J_2, J_3 \) and \( B_1 \) \(^{[18]}\). To compute the anisotropic DM (\( D \)) and single-ion (\( \Delta \)) couplings, arising from SOC effects, we performed calculations within the LDA+\( U \)+SOC framework. To do so, we considered non-collinear spin-polarized configurations \(^{[18]}\), keeping the isotropic terms of \( \mathcal{H} \) unchanged \(^{[18]}\). The values of the most significant couplings within LDA+\( U \)+SOC are (all in meV):

\[ J_1 = 32.7, J_2 = 0.6, J_3 = 0.5, B_1 = 1.0, D = 0.6. \] (7)

The ring-exchange \( K \) as well as the single-ion coupling \( \Delta \), were found to be smaller than 0.1 meV \(^{[18]}\), so we henceforth ignore them. The Curie-Weiss temperature,
\( \theta_{CW} \), can be thus estimated by \( \theta_{CW} \sim q J_1 / 3 \sim 760 \) K, where \( q = 6 \) is the number of nearest neighbors.

**Ground states and MC simulations** — Following Refs. \(^{23, 24}\), we find that Gaussian mean-field theory predicts an AIAO ordering for \( \mathcal{H} \) with the above \( \{J_1, J_2, J_{3a}, D\} \) values and with \( B_1 = 0 \). This is confirmed by MC simulations, remaining as such when \( B_1 = 1.0 \text{ meV} \) is included since \( B_1 > 0 \) stabilizes an \( O(3) \) symmetric AIAO state (see discussion below). The magnitude of the \( J_2 \) and \( J_{3a} \) DFT values are sufficiently small that they do not destabilize the AIAO state selected by \( B_1 \) and \( D \). Given the accuracy limitations of DFT, we do not wish to overstate this point. Rather, we shall argue that DFT returns \( J_2 \) and \( J_{3a} \) values that, in agreement with experiments, do not destabilize the AIAO ground state produced by \( J_1, B_1 \) and \( D \). We thus henceforth ignore the \( J_2 \) and \( J_{3a} \) couplings and consider a minimal Hamiltonian, \( \mathcal{H}_{\text{min}} \), for FeF\(_3\) with \( \mathcal{H}_{\text{min}} = \mathcal{H}(J_1, B_1, D, J_2 = 0, J_{3a} = 0) \) with the above LDA+U+SOC \( J_1 = 32.7, B_1 = 1.0 \) and \( D = 0.6 \) (all in meV) values.

The ground state of the first term of \( \mathcal{H}_{\text{min}} \) with \( J_1 > 0 \) and \( B_1 = D = 0 \), the n.n. antiferromagnetic Heisenberg model, is highly degenerate on the pyrochlore lattice \(^{23, 24}\). Its ground state manifold consists of spin configurations with vanishing total spin on each tetrahedron, hence leaving two continuous internal degrees of freedom per tetrahedron \(^{18, 23, 25, 26}\). One finds that the minimum energy of \( \mathcal{H}_{\text{min}} \) with \( J_1 \neq 0, B_1 \neq 0 \) and \( D = 0 \) is achieved with a globally \( O(3) \) degenerate non-coplanar AIAO spin configuration with an angle 109.47° between each pair of spins on a tetrahedron \(^{18}\). Finally, including \( D \neq 0 \) fixes the spin directions within this configuration to a single AIAO state, that is reducing the \( O_3 \) global symmetry of the ground state of \( \mathcal{H}_{\text{min}}(J_1, B_1, 0) \) to a global \( Z_2 \) symmetry for \( \mathcal{H}_{\text{min}}(J_1, B_1, D) \)^\(^{18}\). With \( B_1 = 0 \), the direct DM interactions with \( D \neq 0 \) also dictates an AIAO state \(^{17}\). The ground state energy per spin \(^{18}\) for the coplanar and AIAO state is, respectively, \( \epsilon_{\text{coplanar}} = -J_1 + B_1 - \sqrt{2}D \) and \( \epsilon_{\text{AIAO}} = -J_1 + B_1 / 3 - 2\sqrt{2}D \), showing that the ground state is AIAO for all \( B_1 > 0 \) and \( D > 0 \) values, consistent with experiments \(^{12}\).

Quite interestingly, with \( J_1 \neq 0, B_1 \neq 0 \) and \( D = 0 \), \( \mathcal{H}_{\text{min}} \) displays a saddle point in its energy landscape, which corresponds to coplanar states \(^{18}\). In such a coplanar state, two out of four spins on a tetrahedron are antiparallel along a given axis and perpendicular to the other axis along which the two remaining spins are themselves aligned mutually antiparallel. The addition of \( D \neq 0 \) restricts the orientation of the “coplanes” to be along the \( xx, xy \) or \( yz \) planes of the cubic unit cell, depending on which pairs of spins are chosen to be colinear \(^{18}\). A possible spin arrangement in such a coplanar state within the \( xx \) plane is depicted in Fig. \(^{4}\). The manifold of such coplanar states counts an exponentially large number of them, giving an extensive entropy.

We next perform Monte Carlo simulations to gain further insight into the finite temperature properties of \( \mathcal{H}_{\text{min}} \). We use standard single-spin Metropolis algorithm on lattices consisting of \( N = 4 \times L^3 \) spins. To ensure thermal equilibrium, \( 1 \times 10^6 \) Monte Carlo steps (MCSs) per spin were used for each temperature and also \( 1 \times 10^6 \) for the data collection. To reduce the correlation between the measurements, 10 to 20 MC sweeps were discarded between successive data collections.

Quantities of interests are the AIAO order parameter \( m \), defined as \( m = \sum_a \mathbf{S}^a \cdot \mathbf{d}^a / N \) (\( \mathbf{d}^a \) is the local cubic \([111] \) direction at sublattice \( a \)) and the Binder fourth order cumulant for both \( m \) and energy \( E \), defined respectively as

\[
U_m(T) = 1 - \frac{1}{3} \frac{m^4}{\langle m^2 \rangle^2}, \quad U_E(T) = 1 - \frac{1}{3} \frac{\langle E^2 \rangle}{\langle E \rangle^2}.
\] (8)

\( U_m \) vanishes in the paramagnetic phase, where the probability density function of \( m \) is Gaussian, approaching 2/3 in the ordered phase \(^{27, 29}\). However, \( U_E \) tends asymptotically to 2/3 in both the ordered and paramagnetic phase while reaching a minimum, \( U_{m_{\text{min}}} \), in the region near the transition point.

The temperature dependence of \( m \) and \( U_m \) is shown in the main panel and top inset of Fig. \(^{2}\), respectively, for lattices of linear size \( L = 4, 6, 8, 10 \). Both plots indicate a narrow critical region around \( T \approx 0.06 J_1 \). The bottom inset in Fig. \(^{2}\) shows the finite size scaling of \( m \) for different \( L \) according to the finite-size scaling behavior

\[
m = L^{-\beta/\nu} \mathcal{M}(tL^{1/\nu}),
\] (9)

where \( t \equiv (T - T_c) / T_c \) is the reduced temperature, \( \beta \) is the order parameter exponent, \( \nu \) is the correlation length exponent and \( \mathcal{M} \) is the scaling function. This analysis yields \( T_c / J_1 = 0.060(1) \), \( \beta = 0.18(2) \) and \( \nu = 0.60(2) \). With \( J_1 = 32.7 \text{ meV} = 379.47 \text{ K} \), we get \( T_c \approx 22 \text{ K} \), in

FIG. 2: (Color online) main panel: variation of the AIAO order parameter \( m \) versus temperature (in units of \( J_1 \)), for lattices of linear size \( L = 4, 6, 8, 10 \). Top inset: Fourth order Binder cumulant of \( m \) versus temperature \( T \) for the same lattice sizes. Bottom inset: Finite size scaling of \( m \) according to Eq. (4) with \( \beta = 0.18(2) \) and \( \nu = 0.60(2) \).
Figures 3a and 3b show each tetrahedron, distribution function of the four-spin correlation within temperature, hence very close to 2.

In order to shed more light on the order of the transition, we compute the probability distribution function, which might actually be extremely weakly first order. Perhaps most noteworthy, the exponent $\beta \approx 2$ for any two neighboring spins on a tetrahedron, while the latter corresponds to the aforementioned coplanar spin states for which one easily sees that the four-spin correlation in Eq. (11) has $R = 1$. The inset in Fig. 3a, shows the $T$ dependence of the thermal average of this correlation, $\langle R \rangle$, which displays a sharp drop at the transition, a further indication for the discontinuous nature of the transition. Interestingly, the non-Gaussian behavior and non-zero centering of $P(R)$ extends to temperatures as high as $T \sim J_1 \sim 330$ K.

### Conclusion

From DFT calculations, we have determined the predominant couplings of the spin Hamiltonian of the FeF$_3$ pyrochlore Heisenberg antiferromagnet. We find that bi-quadratic exchange and anisotropic direct Dzyaloshinskii-Moriya interactions conspire to select an all-in/all-out ground state. Monte Carlo simulations find a transition to that state at a critical temperature $T_c \approx 22$ K, in good agreement with experiments. The transition is found to be characterized by an order parameter pseudo “critical exponent” $\beta \approx 0.18$, also in agreement with that found in experiment. We view this exponent not as signaling an unusual universality class, but rather as an effective power-law parametrization near the very weakly first order transition, perhaps near a mean-field tricritical point for which $\beta = 1/4$ (up to logarithmic correction because three-dimensions is the upper critical dimension for tricritical behavior [31]). Indeed, for $D/J_1 \lesssim 0.01$, the transition is found to be strongly first order while it is second order and in the threedimensional Ising universality class for $D/J_1 \gtrsim 0.1$ [31].

We find the state above $T_c$ to be composed of entropically favored coplanar states without long-range magnetic order. In conclusion, we hope that the present study will anticipate on the basis of work to display rather fascinating properties hitherto unexplored in highly frustrated Heisenberg pyrochlore antiferromagnets.

$$U_{\text{min}}^E(L) = U^* + AL^{-d} + O(L^{-2d}), \quad (10)$$

with $U^* < 2/3$ and $d$ the space dimension. The precise linear fit of $U_{\text{min}}^E(L)$ versus $L^{-3}$, with $U^* = 0.666664(1)$, hence very close to 2/3, that we observe (see Fig. 8 in the Supplemental Material [18]) suggests that the transition might actually be extremely weakly first order.

In order to shed more light on the order of the transition, we compute the probability distribution function of the order parameter per tetrahedron, $P(m_n)$, with $m_n = \sum_{i=1}^{4} \mathbf{S}_i \cdot \mathbf{d}^i$. We also compute the probability distribution function of the four-spin correlation within each tetrahedron, $P(R)$, with

$$R \equiv (\mathbf{S}_1 \cdot \mathbf{S}_2)(\mathbf{S}_3 \cdot \mathbf{S}_4) + (\mathbf{S}_1 \cdot \mathbf{S}_3)(\mathbf{S}_2 \cdot \mathbf{S}_4) + (\mathbf{S}_1 \cdot \mathbf{S}_4)(\mathbf{S}_2 \cdot \mathbf{S}_3). \quad (11)$$

Figures 3a and 3b show $P(m_n)$ and $P(R)$ versus temperature $T$ for a lattice of linear size $L = 10$. $P(m_n)$ is a Gaussian function centered at $m_n = 0$ for $T \gg T_c$. Decreasing $T$, $P(m_n)$ deviates from a Gaussian form near $T_c$, developing four peaks with $m_n \neq 0$ for $T \lesssim T_c$. Well below the transition, only two peaks at $|m_n| \approx 4$ remain, corresponding to almost perfect AIAO order. The peculiar temperature evolution of $P(m_n)$ leads us to speculate that another state coexists or competes with the AIAO state near $T_c$. The nature of this other state can be clarified by considering the density probability $P(R)$. As seen in Fig. 3b, two peaks arise in $P(R)$ close to the transition temperature; one at $R = \frac{1}{3}$ and the other at $R = 1$. The former corresponds to an AIAO spin configuration, for which $(\mathbf{S}_a \cdot \mathbf{S}_b) = -\frac{1}{3}$ for any two neighboring spins on a tetrahedron, while the latter corresponds to the aforementioned coplanar spin states for which one easily sees that the four-spin correlation in Eq. (11) has $R = 1$. The inset in Fig. 3b, shows the $T$ dependence of the thermal average of this correlation, $\langle R \rangle$, which displays a sharp drop at the transition, a further indication for the discontinuous nature of the transition. Interestingly, the non-Gaussian behavior and non-zero centering of $P(R)$ extends to temperatures as high as $T \sim J_1 \sim 330$ K. This indicates that the state above $T_c$ fulfills the above “coplanarity rule”, is divergence-free in the “spin field” and should be viewed as a Coulomb phase [3].
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Supplemental Material

In this Supplemental Material, we present details to assist the reader with the main part of the paper. Section I provides detailed information as to how the interaction parameters of the spin Hamiltonian $\mathcal{H}$ were determined from the density functional theory (DFT) calculations. Section II discusses the nature of the energy landscape of the bi-quadratic part of the spin Hamiltonian and how it displays a saddle point. Section III discusses the orientation of the Dzyaloshinsky-Moriya (DM) vectors. Finally, Section IV shows the finite-size evolution of the energy Binder cumulant, $U_E$, referred to in the main text.
I. AB INITIO DERIVATION OF THE SPIN HAMILTONIAN FOR THE PYROCHLOR-E-FeF₃

To derive the spin Hamiltonian, we compute the energy difference between some chosen magnetic configurations, using LDA and LDA+U. In the following, we illustrate the method for the derivation of the isotropic, i.e. Heisenberg, 4-spin ring and the bi-quadratic exchanges, as well as the anisotropic terms such as the DM and the single-ion interactions.

A. Technical Details

To calculate the Heisenberg exchange couplings, we use a super-cell containing 16 Fe atoms (see Fig. 3), while for the 4-spin ring, bi-quadratic, single-ion and the DM coupling constants, we use the primitive cell of pyrochlore-FeF₃, which contains 4 Fe atoms.

The muffin-tin radius of 2.2(au) and 1.35(au) are used for Fe and F ions, respectively. The cut-off wave-vector $k_{\text{max}} = 3.8\,\text{au}^{-1}$ is taken for the expansion of wave function in the interstitial region while 64 $k$-points are picked up for performing the Brillouin zone integration. Although, the magnetic moment of F is much less than Fe, choosing the direction of the fluorine magnetic moments, plays a crucial role in the minimization of the total energy. Our calculations show that for a fixed direction of Fe magnetic moments, the direction of a given fluorine moment in a Fe-F-Fe bond is uniquely determined as $\mu_F \parallel (\mu_{Fe_1} + \mu_{Fe_2})$, where $\mu_{Fe_1}$, $\mu_{Fe_2}$ are the magnetic moment directors of the nearby Fe ions. As an example, choosing a direction perpendicular to the optimized direction, tends to increase the total energy by about 14 meV per Fe ion.

B. Spin Hamiltonian parameters

1. 4-spin ring exchange

We begin with the calculation of the 4-spin ring exchange ($K$). To proceed, we compare the energies of three colinear configurations within each tetrahedron. We use $n_i = \pm 1$ to show the direction of the magnetic moment of the ion at site $i$, along an arbitrary direction (say the z-axis). The configurations are chosen as $C_1 = \{n_1 = n_2 = n_3 = n_4 = 1\}, C_2 = \{n_1 = n_2 = 1, n_3 = n_4 = -1\}, C_3 = \{n_1 = -1, n_2 = n_3 = n_4 = 1\}$. It can be seen that the energy differences between these configurations are

$$E_1 - E_2 = 16J_1 + 32J_2$$
$$E_1 - E_3 = 12J_1 + 24J_2 + 9K,$$  \hspace{1cm} (12)

FIG. 4: The Heisenberg interactions $J_1$, $J_2$, $J_{3a}$ and $J_{3b}$ in pyrochlore FeF₃. Red (Dark grey)spheres denote the Fe³⁺ ions. The F⁻ ions (not shown) are located at the crossing of the bonds.

where $E_1$, $E_2$ and $E_3$ is the total energy of $C_1$, $C_2$ and $C_3$ configuration, respectively. These equations yield

$$(E_1 - E_2) - \frac{4}{3}(E_1 - E_3) = -12K. \hspace{1cm} (13)$$

Our calculation within LDA results in $K \sim 0.1$ meV. However, LDA+U with $U_{\text{eff}} = 2.8$ eV, gives even smaller value for $K$. We therefore ignore the 4-spin ring exchange term in the rest of our calculations.

2. Heisenberg exchange parameters

The Heisenberg couplings $J_1$, $J_2$, $J_{3a}$ and $J_{3b}$ are represented in Fig. 3. Taking the colinear spin configurations, A, B, C and D as illustrated in Fig. 3, one can show that the bi-quadratic term does not affect the energy differences, and therefore the only contributions to the total energy differences between these configurations come solely from the Heisenberg terms. According to Fig. 5 we obtain the following expressions for the energy of each configuration:

$$E_A = 48J_1 + 96J_2 + 48J_{3a} + 48J_{3b} \hspace{1cm} (14)$$
$$E_B = 24J_1$$
$$E_C = 48J_{3a} + 48J_{3b}$$
$$E_D = 12J_1 - 16J_2 - 8J_{3a} - 8J_{3b}$$

LDA+U calculation with $U_{\text{eff}} = 2.8$ eV, results in the energy differences $E_A - E_B = 866.4$ meV, $E_A - E_C = 1627.9$ meV, and $E_A - E_D = 1274.9$ meV, from which, assuming $J_{3b} \ll J_{3a}$, we get $J_1 = 32.7$ meV, $J_2 = 0.6$ meV and $J_{3a} = 0.5$ meV.
FIG. 5: The four colinear magnetic moment configurations (A, B, C and D) to derive the Heisenberg exchange interactions $J_1$, $J_2$, $J_3$. The direction of magnetic moment are shown by green arrows.

3. bi-quadratic term

To calculate the nearest-neighbor bi-quadratic coupling $B_1$, we seek magnetic configurations that are energetically degenerate in terms of the Heisenberg interactions, in the absence of spin-orbit correction. A systematic way of generating such configurations is as follows. The direction of the magnetic moments can be characterized by polar and azimuthal angles $\theta$ and $\phi$, respectively. Starting from an all-in/all-out configuration, we choose two Fe ions in a tetrahedron and rotate the direction of their magnetic moment according to $\theta'_{1,2} = \theta_{1,2} + \delta$, $\phi'_{1,2} = \phi_{1,2} - 2\delta$. For the remaining two Fe ions, we do the same but change the sign of $\delta$, $\theta'_{3,4} = \theta_{3,4} + \delta$, $\phi'_{3,4} = \phi_{3,4} - 2\delta$. This way, the vector sum of the magnetic moments remains equal to zero under this rotation. The contribution from the Heisenberg terms remaining unchanged by this rotation, the only contributions to the variation of the total energy come from the other isotropic terms within LDA and LDA+$U$ (the anisotropic terms do not play any role because the spin-orbit coupling is not considered at this point). Ignoring the ring-exchange, and fitting the energy variations (obtained by LDA+$U$ with $U = 2.8$ eV), versus $\delta$ (shown in Fig.6), we find the nearest-neighbor bi-quadratic coupling $B_1 = 1.0$ meV.

FIG. 6: Total energy difference (within LDA+$U$) between all-in configuration and the configuration with the condition of zero total zero spin, $S_{tot} = 0$, on each tetrahedron. The dash line shows the fitting to the data using the bi-quadratic term of the Hamiltonian $H_{bi-qu}$.

FIG. 7: Total energy difference (within LDA+$U$) between the all-in configuration and the corresponding rotated one by the azimuthal angle $\phi$. The dash line shows the fitting to the data using the DM term in the Hamiltonian, $H_{DM}$.

4. Single-ion and Dzyaloshinsky-Moriya term

To derive the DM interaction, we require magnetic configurations for which the full $O(3)$ isotropic part of the Hamiltonian, $H_{Heis} + H_{bi-qu} + H_{ring}$, remains unchanged.

In the absence of spin-orbit coupling (SOC), a uniform rotation of all magnetic moments does not change the total energy due to the $O(3)$-symmetry of the non-relativistic part (see main text). However, including the spin-orbit correction to the ab initio calculations (LDA+$U$+SOC), would lift the rotational symmetry. We start from an all-in (all-out) configuration and rotate all the magnetic moments uniformly by an angle $\phi$ around the global z-axis. Fitting the symmetry breaking relativistic corrections, $H_{DM} + H_{single-ion}$, to the computational total DFT energy (taking $U_{eff} = 2.8$ eV) versus $\phi$ (Fig.7), enables us to obtain $D = 0.6$ meV and $\Delta \sim 0.0$ for the DM and single-ion couplings, respectively.
II. ENERGY LANDSCAPE FOR A SINGLE TETRAHEDRON

Consider four classical spins residing on the corners of a single tetrahedron, interacting via a Hamiltonian containing the antiferromagnetic Heisenberg, bi-quadratic and DM interactions.

\[ \mathcal{H} = \mathcal{H}_{\text{Heis}} + \mathcal{H}_{\text{bi-qu}} + \mathcal{H}_{\text{DM}}. \] (15)

The first term has a highly degenerate ground state manifold characterized by the two angles \( \theta \) and \( \phi \), shown in Fig. 5. Choosing the z-axis along \( \mathbf{S}_1 + \mathbf{S}_4 \) (the dashed line in Fig. 5), we can parametrize the spins within a tetrahedron by \( \theta \) and \( \phi \)

\[
\begin{align*}
\mathbf{S}_1 &= (-\cos \frac{\theta}{2}, 0, \sin \frac{\theta}{2}) \\
\mathbf{S}_2 &= (\cos \frac{\theta}{2}, 0, \sin \frac{\theta}{2}) \\
\mathbf{S}_3 &= (\cos \frac{\theta}{2} \cos \phi, \cos \frac{\theta}{2} \sin \phi, -\sin \frac{\theta}{2}) \\
\mathbf{S}_4 &= (-\cos \frac{\theta}{2} \cos \phi, -\cos \frac{\theta}{2} \sin \phi, -\sin \frac{\theta}{2}).
\end{align*}
\] (16)

The above relations enable us to write the bi-quadratic term as follows:

\[ \mathcal{H}_{\text{bi-qu}} = B_1 Q, \] (17)

in which

\[ Q = 1 - 2 \sin^2 \phi \cos \theta + (3 + \cos^2 \phi) \cos^2 \theta + \cos^2 \phi. \] (18)

\( Q \) as a function of \( \theta \) and \( \phi \), depicted in Fig. 4, displaying the rescaled energy landscape of bi-quadratic term, shows a minimum at \( \phi = \frac{\pi}{2} \), \( \theta = \cos^{-1}(1/3) \) with the value \( \frac{2D}{\phi} \). This means that the ground state configuration corresponds to a non-coplanar state with an angle of 109.47° between each pair of spins. In this configuration, the plane of each pair is perpendicular to the plane of the other two spins. The \( O_3 \) symmetry of bi-quadratic interaction offers the freedom to rotate this configuration by any arbitrary angle. However, it can be easily seen that the DM interaction selects the orientation by which the spins are aligned along the vectors connecting the corners to the center of the tetrahedron, the so called all-in/all-out (AIAO) configuration.

Crucially, Fig. 9 shows a saddle point for \( \mathcal{H}_{\text{bi-qu}} \) at \( \phi = \pi \) and \( \theta = \frac{\pi}{2} \). This corresponds to the coplanar state discussed in the main body of the paper. There are three independent choices for constructing such a state. Depending on which two spins are considered to be coplanar, the DM interaction restricts the spins to be in one of the \( xy \), \( xz \) or \( yz \) planes. To show this, first assume \( \mathbf{S}_1 = -\mathbf{S}_4 \), \( \mathbf{S}_3 = -\mathbf{S}_4 \) and \( \mathbf{S}_1 \perp \mathbf{S}_2 \). Then, using Eqs. (25), we find for the DM term

\[ \sum_{ij} D_{ij} (\mathbf{S}_i \times \mathbf{S}_j) = (\mathbf{D}_{13} + \mathbf{D}_{24} - \mathbf{D}_{14} - \mathbf{D}_{23}) \cdot (\mathbf{S}_1 \times \mathbf{S}_3) = -2\sqrt{2} \mathbf{e}_x \cdot (\mathbf{S}_1 \times \mathbf{S}_3). \] (19)

From this, the minimum energy condition requires that \( \mathbf{S}_1 \) and \( \mathbf{S}_4 \) lay in the \( yz \)-plane in such a way that their cross product gives \( \mathbf{e}_x \). If we choose \( \mathbf{S}_1 = -\mathbf{S}_3 \), \( \mathbf{S}_2 = -\mathbf{S}_4 \) and \( \mathbf{S}_1 \perp \mathbf{S}_2 \), we find

\[ \sum_{ij} D_{ij} (\mathbf{S}_i \times \mathbf{S}_j) = (\mathbf{D}_{12} + \mathbf{D}_{14} + \mathbf{D}_{23} + \mathbf{D}_{34}) \cdot (\mathbf{S}_1 \times \mathbf{S}_2) = 2\sqrt{2} \mathbf{e}_y \cdot (\mathbf{S}_1 \times \mathbf{S}_2). \] (20)

From this, we find that \( \mathbf{S}_1 \) and \( \mathbf{S}_2 \) lay in the \( xz \)-plane in such a way that their cross product gives \( -\mathbf{e}_y \). Finally, taking \( \mathbf{S}_1 = -\mathbf{S}_4 \), \( \mathbf{S}_2 = -\mathbf{S}_3 \) and \( \mathbf{S}_1 \perp \mathbf{S}_2 \), we get

\[ \sum_{ij} D_{ij} (\mathbf{S}_i \times \mathbf{S}_j) = (\mathbf{D}_{12} - \mathbf{D}_{13} + \mathbf{D}_{24} - \mathbf{D}_{34}) \cdot (\mathbf{S}_1 \times \mathbf{S}_2) = 2\sqrt{2} \mathbf{e}_z \cdot (\mathbf{S}_1 \times \mathbf{S}_2). \] (21)
which implies that $\mathbf{S}_1$ and $\mathbf{S}_2$ lay in the $xy$-plane in such a way that their cross product gives $-\mathbf{e}_z$.

The above arguments lead us to the following expressions for the energy of the coplanar and all-in/all-out states, for each tetrahedron

$$E_{\text{co-planar}} = -2J_1 + 2B_1 - 2\sqrt{2}D$$
$$E_{\text{all-in}} = -2J_1 + 2B_1/3 - 4\sqrt{2}D. \quad (23)$$

III. MORIYA DM VECTORS

The following minimal spin Hamiltonian, $\mathcal{H}_{\text{min}}$, is used for FeF$_3$

$$\mathcal{H}_{\text{min}} = J_1 \sum_{\langle i,j \rangle} \sum_{a,b} \mathbf{S}_i^a \cdot \mathbf{S}_j^b + B_1 \sum_{\langle i,j \rangle} \sum_{a,b} (\mathbf{S}_i^a \cdot \mathbf{S}_j^b)^2 + D \sum_{\langle i,j \rangle} D_{ij}^{ab} \cdot (\mathbf{S}_i^a \times \mathbf{S}_j^b), \quad (24)$$

in which $\mathbf{S}$ is unit vector, $J_1 > 0$ is the nearest-neighbor antiferromagnetic exchange interaction, $B_1 > 0$ is the nearest neighbor bi-quadratic interaction while the last term is the anisotropic DM interaction. $i,j = 1 \cdots N$ and $a,b = 1, 2, 3, 4$ denote the Bravais lattice and sub-lattice indices, respectively and $\langle i,j \rangle$ means the nearest neighbor lattice points. Considering a single tetrahedron, the plane which contains two neighboring lattice points and the middle point of the opposite bond in the tetrahedron is a mirror plane. Applying Moriya’s rules [32] implies that the $\mathbf{D}$ vector can only be perpendicular to this mirror plane or, equivalently, parallel to the opposite bond. Therefore, $D_{ij}^{ab}$’s represent the vectors along the six directions given by:

$$D_{12} = \frac{D}{\sqrt{2}}(0, 1, 1), \quad D_{13} = \frac{D}{\sqrt{2}}(-1, 0, -1)$$

IV. ENERGY BINDER RATIO

The energy Binder ratio, $U_E(T)$ is defined as

$$U_E(T) \equiv 1 - \frac{1}{3} \frac{\langle E^4 \rangle}{\langle E^2 \rangle^2}. \quad (26)$$

$U_E$ tends asymptotically to 2/3 in both the ordered and paramagnetic phase while reaching a minimum, $U_{E \text{min}}$, in the region near the transition point. For a first order transition, the finite-size scaling of $U_{E \text{min}}$ is given by [29]

$$U_{E \text{min}}(L) = U^* + AL^{-d} + \mathcal{O}(L^{-2d}), \quad (27)$$

with $U^* < 2/3$ and $d$ the space dimension. Fig. 11 illustrating the precise linear fit of $U_{E \text{min}}(L)$ versus $L^{-d}$, with $U^* = 0.666664(1)$, hence very close to 2/3, suggests that the transition might actually be extremely weakly first order.