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Frustration wave order in iron(II) oxide spinels

Giuditta Perversi¹, Angel M. Arevalo-Lopez¹,², Clemens Ritter³ & J. Paul Attfield⁴

Frustrated magnetic materials can show unconventional correlations such as quantum spin liquid states and monopole excitations in spin icles. These phenomena are observed on uniformly frustrated lattices such as triangular, kagome or pyrochlore types, where all nearest neighbour interactions are equivalent. Here we report incommensurate long-range spin amplitude waves in the spinels Fe₂GeO₄ and γ-Fe₂SiO₄ at low temperatures, which indicate that the degree of frustration may itself be a fluctuating quantity that can spontaneously order without a lattice distortion as a ‘frustration wave’. Fe₂GeO₄ with propagation vector (2/3 + δ 2/3 + δ 0) has ordered Fe²⁺ moments that vary between fully saturated 4 μB and 0 values, consistent with a frustration wave order. γ-Fe₂SiO₄ has a more complex (¾ + δ ¾ + δ 0) order that coexists with an ordered spin ice phase. Dynamic orbital fluctuations are proposed to give rise to locally correlated patterns of ferromagnetic and anti-ferromagnetic interactions consistent with the observed orders.

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Long-range spin order is sometimes avoided in frustrated magnetic materials, leading to unconventional correlations such as quantum spin liquids and ice states. Frustrated long-range spin orders are also observed and the degree of frustration for an individual spin or a larger grouping within the ordered lattice may be quantified by the function:

\[
F = \frac{1}{2} \left( 1 - \sum \mathbf{S}_i \mathbf{S}_j / \sum \mathbf{S}_i \mathbf{S}_j \right)
\]

where the exchange Hamiltonian for interacting spins \( \mathbf{S}_i \) and \( \mathbf{S}_j \) is given by \( -J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \). \( F \) varies between 0 for unfrustrated spins and 1 for complete frustration. For a collinear spin order on a simple lattice in which exchange couplings are equivalent and are either fully frustrated or unfrustrated, the degree of frustration simplifies to \( F = \frac{N_f}{N} \), where \( N_f \) is the number of frustrated interactions and \( N \) is the total number of interactions around each spin.

Conventional frustrated systems have constant \( F \) at all spins, for example, the canonical pyrochlore-type lattice of corner-sharing tetrahedra of antiferromagnetically interacting moments has \( F = 1/3 \) at all sites in the ordered ground states shown in Fig. 1(a, b). The related ‘2-in 2-out’ spin ice order shown in Fig. 1(c) is also uniformly frustrated. The physics of many investigated pyrochlores is thus predicated on the uniformity of the degree of frustration (\( F \)) throughout the lattice.

\( \text{Fe}_2\text{GeO}_4 \) and the high-pressure \( \gamma \)-form of \( \text{Fe}_2\text{SiO}_4 \) are cubic \( \text{B}_2\text{O}_3 \) spinels, where orbitally degenerate \( 3\text{d}^9 \) \( \text{Fe}^{2+} \) cations with \( S = 2 \) spins form a pyrochlore-type B-site lattice. \( \gamma \)-\( \text{Fe}_2\text{SiO}_4 \) is also of geophysical interest as one of the main constituents of the Earth's mantle. Previous studies have established that both materials have magnetic transitions near 10 K, but the low-temperature spin orders are not reported and preliminary abstracts have differing results. Our investigation of their magnetic structures has led to the discovery of frustration wave order as a class of ground states, where spin–spin interactions become spatially non-uniform within a structurally uniform lattice.

**Results**

**Spin order in \( \text{Fe}_2\text{GeO}_4 \).** Synthesis of the polycrystalline \( \text{Fe}_2\text{GeO}_4 \) sample and characterisation measurements are described in methods with further details in Supplementary Figs. 1, 5 and 6, Supplementary Tables 1, 3 and 4 and Supplementary Notes 1 and 2. Magnetic susceptibility measurements (Fig. 2a) for \( \text{Fe}_2\text{GeO}_4 \) reveal two magnetic transitions with a susceptibility maximum at \( T_{m1} \approx 9 \text{ K} \) and divergence of field and zero-field cooled susceptibilities at \( T_{m2} \approx 7 \text{ K} \), consistent with a previous report. Alternative Current (AC) measurements show no frequency dependence in the low-temperature features, indicating an absence of the spin–glass behaviour (Fig. 2b). A broad magnetic contribution to the low-temperature heat capacity appears to extend up to around 50 K (Fig. 2c), but the integrated entropy of the theoretical value of \( \text{Rhn}_5 \) for long-range order of \( S = 2 \) spins. Fits to synchrotron X-ray diffraction data at 5 K, as well as the neutron data below, show that the crystal structure remains cubic \( \text{Fd} \ 3 \text{ m} \) at low temperatures with no distortion observed (Fig. 2d). This is unusual as spin orders in oxide spinels usually lead to lattice distortions, e.g. \( \text{ZnV}_2\text{O}_4 \), \( \text{LiMn}_2\text{O}_4 \), \( \text{MgCr}_2\text{O}_4 \) and \( \text{Co}_2\text{GeO}_4 \) all distort from cubic to tetragonal symmetry at orbital or anti-ferromagnetic ordering transitions. Hence the measurements indicate that the orbital states and a large fraction of the \( \text{Fe}^{2+} \) spins remain dynamic below the two magnetic transitions.

Sharp magnetic diffraction peaks indicative of long-range spin order appear below the magnetic transition at \( T_{m1} \approx 9 \text{ K} \) with an additional weak peak observed below \( T_{m2} \approx 7 \text{ K} \), as shown in Fig. 3a. These peaks were indexed by very similar propagation vectors \( \mathbf{k}_i = (2\delta_i/3, 2\delta_i/3, 2\delta_i/3, 0) \) for peaks appearing below \( T_{m1} \) (\( i = 1 \) or 2). Representation analysis shows that the single Fe B lattice position is split into magnetically distinct Fe1 and Fe2 sites. The magnetic intensities from each transition are fitted by a double-\( \kappa \) model, in which different propagation vectors \( \mathbf{k}_i \) apply to different sites Fe\( j \) (\( j = 1 \) or 2), \( \mathbf{k}_{i1} = (2\delta_i/3 - 2\delta_j/3, 2\delta_j/3, 2\delta_j/3, 0) \) and \( \mathbf{k}_{i2} = (2\delta_i/3, 2\delta_j/3, 2\delta_j/3, 0) \). A good fit to the peaks that are observed below \( T_{m1} \), as shown in Fig. 3b where refined \( \delta_j = -0.025(1) \), can only be obtained using a model in which ordered moment amplitudes are modulated, as displayed in Fig. 3c. The sublattices of Fe1 and Fe2 spins are mutually perpendicular and each has collinear antiferromagnetic chains of spins pointing parallel to their propagation direction. The additional magnetic peak observed below \( T_{m2} \) is fitted by an additional order of small perpendicular moment components that describe a canting of the above...
region with discontinuities at $T_m = 9$ K and $T_n = 7$ K. The Curie-Weiss fit to points between 150 and 400 K gives an effective paramagnetic moment of $4.25 \mu_B$, consistent with high-spin 3$d^6$ Fe$^{2+}$ spins and a Weiss temperature of $\theta = -19.6$ K.

The maximum resultant amplitude is $0.92(7) \mu_B$ at 1.8 K. The maximum resultant amplitude is $4.05(8) \mu_B$, in agreement with the ideal value of $4 \mu_B$ for high-spin Fe$^{2+}$. Ordered moments are modulated between 0 (fully frustrated) and $4 \mu_B$ (unfrustrated) values. The average ordered moment magnitude is 64% of the ideal value, so the equivalent of approximately one-third of the spins remain dynamic below the magnetic ordering transitions, qualitatively consistent with the substantial reduction of magnetic entropy.

**Fig. 2** Magnetic and structural characterisation of Fe$_2$GeO$_4$. 

**a** Magnetic susceptibility in an applied field of 0.5 T with inset is showing the low-temperature region where magnetic transitions occur at $T_m = 9$ K and $T_n \approx 7$ K. The Curie-Weiss fit to points between 150 and 400 K gives an effective paramagnetic moment of $4.25 \mu_B$, consistent with high-spin 3$d^6$ Fe$^{2+}$ spins and a Weiss temperature of $\theta = -19.6$ K.

**b** Real part of the AC susceptibility in an oscillating field of 0.5 T with inset is showing the low-temperature region where magnetic transitions occur at $T_m = 9$ K and $T_n \approx 7$ K. The Curie-Weiss fit to points between 150 and 400 K gives an effective paramagnetic moment of $4.25 \mu_B$, consistent with high-spin 3$d^6$ Fe$^{2+}$ spins and a Weiss temperature of $\theta = -19.6$ K.

**c** Heat capacity variation with the lattice contribution to $C_T$ for high-spin Fe$^{2+}$.

**d** Fit of the cubic spinel model to the synchrotron X-ray diffraction profile ($\lambda = 0.1917$ Å) at 5 K with the region containing (400) and (440) reflections that are sensitive to a tetragonal lattice distortion shown in the inset. No peak splittings or broadenings that would evidence a lattice distortion are observed.

magnetic structure. Temperature variations of the moment amplitudes $\mu_i$ and propagation vector shifts $\delta_i$ are shown in Fig. 3d and the maximum amplitudes of the two modulated moment components are $\mu_1 = 3.94(3)$ and $\mu_2 = 0.92(7) \mu_B$ at 1.8 K. The maximum resultant amplitude is $\mu = 4.05(8) \mu_B$, in agreement with the ideal value of $4 \mu_B$ for high-spin Fe$^{2+}$. Ordered moments are modulated between 0 (fully frustrated) and $4 \mu_B$ (unfrustrated) values. The average ordered moment magnitude is 64% of the ideal value, so the equivalent of approximately one-third of the spins remain dynamic below the magnetic ordering transitions, qualitatively consistent with the substantial reduction of magnetic entropy.

**Frustration wave picture for Fe$_2$GeO$_4$.** Amplitude-modulated spin-density wave (SDW) order of local moments is relatively common in metallic magnets, where exchange couplings are coupled to the Fermi surface vectors, as described in RKKY theory. However, amplitude modulation of moments between zero and fully saturated values as observed in Fe$_2$GeO$_4$ is highly unusual in non-metallic materials, as even complex spin textures such as helimagnets, spin vortices or skyrmions have uniform moment amplitudes, while spin directions change. Elliptical spiral structures in frustrated systems can modulate moment amplitudes over part of the available range, e.g. in FeTe$_2$O$_5$Br$_2$ and ‘idlespin’ orders provide a special case where some spins remain disordered due to frustration of their interactions with surrounding uniformly ordered spins, an example is observed below 0.7 K in the pyrochlore Gd$_3$Ti$_2$O$_7$. The only close SDW analogue to Fe$_2$GeO$_4$ we are aware of is the spin order in Ca$_3$Co$_2$O$_6$, where chains of collinear moments are modulated between 0 and $5.0 \mu_B$ moments for $S = 2$ Co$^{3+}$ moments with a sizable orbital contribution.

Strongly frustrated systems based on orbitally non-degenerate ions such as $S = 5/2$ Fe$^{3+}$ in FeTe$_2$O$_5$Br and $S = 7/2$ Gd$^{3+}$ in Gd$_2$Ti$_2$O$_7$ can stabilise spin arrangements of varying amplitude to minimise exchange energy between unfavourably oriented moments and gain entropy from the thermally fluctuating components at non-zero temperatures. However, the observation
Fig. 3 Low-temperature neutron diffraction results for Fe₂GeO₄. a Magnetic scattering profiles obtained by subtracting the 25 K D02 data from profiles between 2.5 and 9.5 K, recorded in ~0.3 K steps and at 12 and 15 K. h k l labels correspond to magnetic satellite reflections at (hkl) + k, while the weak 000 peak indicated in pink appears below T_m = 6.6 K with vector k. b Fit of the crystal and magnetic structures at 2 K to high-resolution D20 data at 2 K (λ = 2.41 Å). Two weak impurity peaks are labelled with asterisks. Magnetic reflection markers are in violet (k0) and pink (k2), and the structural reflections are in green. c The k order below T_m with sinusoidal modulation of the Fe₁ (blue) and Fe₂ (red) moment amplitudes in the [100] direction. Only one of the two Fe interactions along its edges, and these have two distinct configurations as shown in Fig. 4b. The configuration where antiferromagnetic couplings are on adjacent (A) edges of the tetrahedron is notable, as the simplest collinear ground state for comparable interaction strengths J_A = −J_F is a 3 up/1 down configuration in which two spins are unfrustrated (F = 0), while
the other two are partially frustrated ($F = 1/3$). This demonstrates how large variations in $F$ between neighbouring spins may arise as a result of the local orbital ordering configuration. The alternative arrangement with antiferromagnetic couplings on opposite (O) tetrahedral edges has all spins equally frustrated ($F = 1/3$). There are 24 equivalent A-type configurations, but only six for O-types, hence (neglecting any long range orbital correlations) 80% of Fe$_4$ tetrahedra are A-type at any instant in the orbitally fluctuating state in the absence of longer-range orbital correlations and 16% of Fe$^{2+}$ spins are in a locally unfrustrated ($F = 0$) environment at the apices between two A-type tetrahedra. This shows that dynamically correlated orbital fluctuations (dynamic orbital order) can lead to large local fluctuations in $F$, and long-range magnetic and frustration wave order at low temperatures.

We propose that frustration wave order in Fe$_2$GeO$_4$ arises from exchange interactions between ordered spin components in one sublattice via the dynamic components of their neighbours in the other. This is illustrated using the ordered Fe1 spins, which are represented by a commensurate approximant ($\frac{1}{3} - \frac{1}{3} 0$) model for simplicity in Fig. 4c (the small incommensurability most likely results from next-nearest-neighbour Fe–O...O–Fe magnetic couplings that are neglected here). Ferromagnetic chains of fully ordered Fe1 up spins ($+S$) and partially fluctuating Fe1 down spins with ordered components of $-S/2$ are linked by Fe2 spins that are ordered in a perpendicular direction, so no Heisenberg exchange occurs. However, fluctuating components of Fe2 spins can couple to Fe1 spins as shown in Fig. 4d. The observed order is consistent with A-type tetrahedra leading to unfrustrated interactions around the Fe1 ($+S$) chain, while other tetrahedra fluctuate between A and O configurations leading to some frustrated interactions at the other Fe1 ($-S/2$) chains. The Fe2 spin components fluctuate between up and down states in the various configurations and have no static order parallel to Fe1 spins. The orbital states fluctuate in a highly correlated manner but without leading to localisation and orbital order. Similar orbital pictures can be drawn for any sampled region in the full incommensurate structure (Fig. 3c). The modulation of the $F$ consistent with the commensurate approximant ($\frac{1}{3} - \frac{1}{3} 0$) model for Fe$_2$GeO$_4$ is shown in Fig. 4c. The Fe1 ($+S$) spins are always unfrustrated while those at Fe2 sites are highly frustrated with pyrochlore-like $F = 1/3$ values, and the partly frustrated Fe1 ($-S/2$) spins have intermediate values, shown as $F = 1/6$ on the assumption of equal fluctuations between A and O configurations of their local spin tetrahedra.

Spin Order in γ-Fe$_2$SiO$_4$. The high-pressure spinel γ-Fe$_2$SiO$_4$ was also studied to investigate the chemical pressure effects of replacing Ge in Fe$_2$GeO$_4$ by smaller Si. High-pressure synthesis of the polycrystalline γ-Fe$_2$SiO$_4$ sample and characterisation measurements are described in methods with further details in Supplementary Figs. 2, 3, 4 and 7, Supplementary Tables 2, 5, 6 and 7 and Supplementary Notes 1 and 3. Two magnetic ordering transitions are observed in low-temperature neutron diffraction profiles of γ-Fe$_2$SiO$_4$, as shown in Fig. 5a and b. Magnetic diffraction peaks appearing below $T_m = 12$ K are indexed by propagation vector $k = (\frac{1}{4} + \frac{1}{4} + \frac{1}{4} 0)$, and are fitted by double-$k$ magnetic structures, similar to that of K$_1$-Fe$_2$GeO$_4$. Two modulated spin components are present and their combinations can describe a canted arrangement (Fig. 5c) or an elliptical helical order (Fig. 5d). These fit the magnetic intensities equally well, and the ordered moment amplitudes are modulated in both cases, so it is not clear whether this is a frustration wave or a more conventional elliptical spin order.

\[ J_{\text{AF}} \approx 3 0 \]
Further magnetic peaks that emerge below $T_{m2} = 8 \text{ K}$ for $\gamma$-Fe$_2$SiO$_4$ are indexed on a commensurate $k_2 = (1 \ 0 \ 0)$ vector and are fitted by an ordered spin ice model (Fig. 1c, 5e), in which all moment amplitudes are equal. Spin ice ordering is very rare in transition metal oxide spinels, but is reported in the V$^{3+}$ sublattice of FeV$_2$O$_4$, although this phase is tetragonally distorted with both Fe$^{2+}$–V$^{3+}$ and V$^{3+}$–V$^{3+}$ magnetic interactions operating$^{28}$. The observation of a spin ice phase competing with the modulated wave state reveals a fine energy balance between these two classes of ground state in $\gamma$-Fe$_2$SiO$_4$. Long-range spin ice orders in pyrochlore oxides such as Sm$_2$Mo$_2$O$_7$ and Nd$_2$Mo$_2$O$_7$ result from weak exchange coupling and large dipolar interactions coupled with local anisotropy$^{29}$. Local variations of ferromagnetic and antiferromagnetic couplings driven by the correlated orbital fluctuations may also help to stabilise the spin ice phase of $\gamma$-Fe$_2$SiO$_4$. 

Discussion

In conclusion, the unusual magnetic structure of Fe$_2$GeO$_4$ evidences a previously unrecognised class of ground states for orbitally degenerate spins on frustrated lattices, in which the degree of frustration orders spatially across structurally equivalent sites, resulting in large amplitude modulations of the moment in the magnetically ordered phases. This arises because the exchange interactions depend on the d-orbital occupancy, so that a coupling of spins and orbitals can give rise to a long-range modulation of the exchange interactions and hence the frustration function. Weak coupling of Fe$^{2+}$ orbital states to the lattice appears to be important for avoiding structural distortions that probably destabilise frustration wave orders in other orbitally degenerate materials. The $\gamma$-Fe$_2$SiO$_4$ analogue has a more complex modulated order that may be frustration wave driven, competing with a spin ice phase. Frustration waves lead to spatial organisation of statically ordered and highly correlated, but dynamic orbital and spin components that may give rise to novel excitations and quantum phenomena in these and other materials. Further exploration of the complex spin orders in Fe$_2$GeO$_4$ and $\gamma$-Fe$_2$SiO$_4$ using single crystals and of their excitations by inelastic neutron scattering and other spectroscopies will thus be worthwhile.

Methods

Sample synthesis and characterisation. Fe$_2$GeO$_4$ and olivine-type $\alpha$-Fe$_2$SiO$_4$ were synthesised as polycrystalline powders by grinding stoichiometric quantities of Fe (-22 mesh, 99.998%, Alfa Aesar), GeO$_2$ / SiO$_2$ (99.999% Alfa Aesar) and Fe$_3$O$_4$ (99.999% Sigma Aldrich) powders and pressing them into a pellet. The reactions were carried out in evacuated silica tubes, heating in a...
box furnace at 900 °C for 60 h and then slow-cooling for 12 h. α-Fe$_2$SiO$_4$ was transformed to spinel-type γ-Fe$_2$SiO$_4$ in a Walker-type multi-anvil press in BN capsule, pressurizing at 6 GPa at 900 °C for 20 min before quenching. Laboratory X-ray diffraction using a Bruker D2 diffractometer confirmed the formation of cubic Fe$_3$Si normal spinels with Fe$^{2+}$ only at the octahedral B-sites. Physical measurements were performed using a Quantum Design MPMS XL7 SQUID magnetometer for DC susceptibility and a Quantum Design PPMS for AC susceptibility and heat capacity measurements.

**Powder neutron diffraction.** Powder neutron diffraction (PND) data were collected at the ILL facility in Grenoble. High-resolution profiles for a 3 g sample of Fe$_2$GeO$_4$ were collected on instrument D2B at wavelength λ = 1.59475 Å with 10° collimation at 2 K and at full flux at 2, 6, 10, 50, 100, 200 and 300 K. Measurements were performed on high-resolution integrated data from the central region of the detector. Additional PND data were collected from D20 with λ = 2.41 Å at 1.8, 2.5, 12, 15 and 25 K; ramp collection between 2.5 and 9.5 K in ~ 0.3 K steps was used to follow the evolution of the magnetic structure. PND data for γ-Fe$_2$SiO$_4$ were collected between 2 and 300 K from D20 (λ = 2.41) on 120 mg sample. Data acquired with high takeoff angle (90°) were used for crystal structure refinement to confirm cubic symmetry, whereas low takeoff angle (42°) data were used for magnetic structure determination.

The structural and magnetic refinements were performed with the Rietveld refinement routines implemented in FullProf, using the k-search and the Basreps software for magnetic symmetry determination and analyses. Crystal and magnetic structures were visualised with FPStudio in the FullProf suite and with the VESTA software. Representation analysis shows that the single Fe B lattice positions for the second phase correctly and re-rst order is its nature. The order appears to be commensurate with 12 K is similar to that of Fe$_2$GeO$_4$; for the elliptical helical model for the spinel LiMn$_2$O$_4$: a frustrated antiferromagnet and cathode material. Chem. Mater. 11, 1510–1518 (1999).

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Author contributions
G.P. and J.P.A. designed the concept for this study. G.P., A.M.A.-L. and C.R. performed the experimental work and data analysis. G.P. and J.P.A. wrote the manuscript with inputs from all authors.

Additional information
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