Magnetic nano-fluctuations in a frustrated magnet

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Frustrated systems exhibit remarkable properties due to the high degeneracy of their ground states. Stabilised by competing interactions, a rich diversity of typically nanometre–sized phase structures appear in polymer and colloidal systems, while the surface of ice pre-melts due to geometrically frustrated interactions. Atomic spin systems where magnetic interactions are frustrated by lattice geometry provide a fruitful source of emergent phenomena, such as fractionalised excitations analogous to magnetic monopoles. The degeneracy inherent in frustrated systems may prevail all the way down to absolute zero temperatures, or it may be lifted by small perturbations or entropic effects. In the geometrically frustrated Ising–like magnet Ca₃Co₂O₆, we follow the temporal and spatial evolution of nanoscale magnetic fluctuations firmly embedded inside the spin–density–wave magnetic structure. These fluctuations are a signature of a competing ferrimagnetic phase with an incommensurability that is different from, but determined by the host. As the temperature is lowered, the fluctuations slow down into a super-paramagnetic regime of stable spatiotemporal nano-structures.

The Ising model on a two-dimensional (2D) triangular lattice with antiferromagnetic nearest-neighbour interactions \( J_{ab} > 0 \) has long embodied the archetype of a geometrically frustrated spin system. It is convenient to divide the triangular lattice into three sublattices, whereby every elementary triangle contains one site of each sublattice connected by three antiferromagnetic bonds that cannot be simultaneously satisfied. One bond per triangle remains frustrated at the minimum energy. The extensive ground-state degeneracy, equal to \( \exp(0.323N) \) as the number of spins \( N \to \infty \), means that the system is a spin liquid at finite temperatures above the \( T = 0 \) critical point. The residual entropy can be lifted by increasing the dimensionality through the stacking of layers of triangular lattices on top of each other.

Since the interaction \( J_c \) along the stacking direction \( c \)
FIG. 1: Nano-fluctuations imaged by small-angle neutron scattering in Ca$_3$Co$_2$O$_6$. a, The large central schematic illustrates the experimental setup and scattering observed on the small-angle multidetector from the nano-fluctuations embedded in the modulated PDA background. For $T < T_N \approx 25$ K, streaks are observed when the $c$-axis of the single crystal Ca$_3$Co$_2$O$_6$ is in the plane of the detector. b, The scattering volume in three dimensions measured by rotating a single crystal about the $c$-axis reveals isotropic scattering in the $ab$ plane. The sample region in the centre of the figure shows the arrangement of magnetic Co$^{3+}$ ions in Ca$_3$Co$_2$O$_6$, which lie in chains along the $c$-axis made up of face-sharing CoO$_6$ polyhedra alternating between blue low-spin ($S = 0$) octahedra and red high-spin ($S = 2$) trigonal prisms. c, A projection along the $c$-axis showing that the chains form a triangular lattice in the $ab$ plane. d, The magnetic structure along the $c$-axis consists of phase-shifted spin-density waves. We propose that the objects seen in SANS originate from areas of enhanced PDA fluctuations originating at nodal points of the three spin-density waves. e, In the $ab$-plane these nano-fluctuations are ferrimagnetic and have dimensions spanning several unit cells.

is unfrustrated, the ground state degeneracy reduces to $\exp(0.323N^{2/3})$. The result is a transition at $T > 0$ to a partially disordered antiferromagnetic (PDA) state. This state has long-range order along $c$ but only two out of three sublattices are ordered within the $ab$ plane, while the third fluctuates. The competing ferrimagnetic state, with the third sublattice direction fixed, has equal energy to the PDA, but the PDA is favoured for entropic reasons.$^{12}$

Small angle neutron scattering (SANS) experiments were performed on Ca$_3$Co$_2$O$_6$ to investigate the small $Q$ reciprocal space structure (Fig.1, central schematic and a). In the frustrated magnet Ca$_3$Co$_2$O$_6$, the magnetic Co$^{3+}$ ions form structural chains along the $c$-axis, with a buckled triangular arrangement in the $ab$ plane (Fig. 1c) resembling the stacked triangular model. The moments point along the chains with an Ising–like anisotropy$^{14,15}$, but below the ordering temperature at $T = T_N \approx 25$ K are amplitude–modulated by an incommensurate longitudinal spin density wave (SDW) propagating along the $c$-axis, with a phase shift of $120^\circ$ between adjacent chains$^{16,17}$ (Fig. 1d). Every one-sixth of the modulation period, a rigorous PDA condition (an “up”–“down”–“zero” expectation value for the sublattice magnetizations) holds, presumably accompanied by a strong fluctuation of the Ising–like spins. This modulation is thought to be stabilised by interchain interaction pathways$^{18–20}$.

Here, we uncover ferrimagnetic nanoscale fluctuations forming within the SDW ordered state at all $T < T_N$ in Ca$_3$Co$_2$O$_6$ (Fig. 1a). To scatter neutrons through small angles by reciprocal vectors $Q$ in the vicinity of the $Q = 0$ position, a local ferromagnetic component of spin correlations suffices. These dynamic objects produce two parallel streaks at incommensurate positions on the 2D SANS detector (Figs. 2a-b) running perpendicular to the $c$-axis which is aligned in the plane of the detector. This incommensurability is connected with a third of the real-space periodicity $d/3$ of the SDW modulation along $c$, reflecting the strong PDA-like fluctuation points in the ground state of the material (Fig. 1c). The scattering pattern does not change when the sample is rotated about the $c$-axis (Fig. 1b, also see Suppl. Info), implying that correlations are isotropic in the $ab$ plane. Accordingly, we can separate the along-chain ($Q_c$) and the isotropic in-plane ($Q_{ab}$) components, and the scattered neutron intensity
I(Q) is then described by

\[ I(Q) \propto \delta \left( Q_c \pm \frac{2\pi}{d} \right) \frac{Q_{ab}^2}{Q_c^2} \int_0^\infty C_{ab}(r) J_0(Q_{ab}r) r^2 dr, \]

where \( C_{ab}(r) \) is the spin-spin correlation in the \( ab \)-plane.

Spin correlations are further studied by looking at the \( Q_{ab} \) dependence of the scattering along the streaks (Fig. 2c). From Eq. (1), such profiles are Hankel transforms of the in-plane spin-spin correlation function \( C_{ab}(r) \) multiplied by \( Q_{ab}^2/Q_c^2 \). This multiplicative factor is a consequence of the dipolar interaction between neutrons and the atomic moments aligned along \( c \). In Fig. 2c, we show the measured profile compared to two model spin-spin correlation functions (more are compared in the Supplementary Information): (i) the finite-temperature expression for the 2D triangular lattice antiferromagnet (TLA), \( C_{ab}(r) \sim r^{-\frac{2}{3}} \exp(-r/\xi_{ab}) \), where we have ignored the antiferromagnetic \( \cos(2\pi r/3) \) modulation and (ii) a purely exponentially decaying correlation, \( C_{ab}(r) \sim \exp(-r/\xi_{ab}) \). For both models \( \xi_{ab} \) is temperature dependent. The intensity scale and correlation length \( \xi_{ab} \) are considered as fit parameters to the measured data-set. Model (i) might be anticipated to describe ferromagnetic correlations arising as perturbations of the PDA state, and for a 2D TLA we would expect \( \xi_{ab} \sim 1/|\ln \tanh(1/T)| \) to increase as \( T \) (here in units of the model’s coupling constant) decreases. However, the measured \( Q_{ab} \) profiles are seen to flatten as \( T \) decreases, implying a decreasing \( \xi_{ab} \). The form of the curves of all the measured datasets (c.f. Supplementary Information) are best described by the exponentially decaying correlations of model (ii). Fitting the data of Fig. 2a to model (ii) gives the correlation length \( \xi_{ab} \) as a function of temperature (Fig. 3a) — indeed showing a decrease of \( \xi_{ab} \) with decreasing temperature.

Characteristic scattering profiles from ferromagnetic nanophases. a, SANS detector images at different temperatures. b, Variation in direction normal to the streaks. The absence of higher-order peaks is demonstrative of the sinusoidal amplitude-modulation of nanofluctuations. c, Variation of scattered intensity along the streaks. This profile is a transform of the spin-spin correlation function in the triangular lattice plane, see Eq. (1). The nano-fluctuations originate from, but are distinct from the PDA background. The latter phase is well ordered over large length-scales \( > 0.5 \mu m \) at \( T \lesssim 25 \text{ K} \), producing resolution-limited antiferromagnetic Bragg peaks in our neutron diffraction data (Fig. 3b). Here the nano-fluctuations generate broad features superimposed on the sharp antiferromagnetic peaks \( Q_0 \) that are seen to share a common temperature dependence with the SANS signal (Fig. 3c). This is a signature of ferromagnetic nano-scale objects, which would give broad anti-ferromagnetic and \( Q = 0 \) peaks. The temperature dependences of the integrated intensities reveal a competition between the two components, since the embedded nano-structures exist at the expense of magnetic volume fraction for the host.

Microscopic ferrimagnetism in the compound also explains the experimentally observed magnetic response functions. In agreement with previous studies, we find a large cusp in the linear susceptibility \( \chi \) at temperatures above 12 K (Fig. 3d). The susceptibility curve resembles the SANS intensity, indicative of a common origin. The position in temperature \( T_f \) of the peak shifts with the ac frequency \( f \), a dependence that is characterised by the quantity \( g = \Delta T_f/|T_f\Delta(\log f)| \). Here we find \( g = 0.17 \), which is too big to be consistent with spin glass \( (g \lesssim 0.01) \) or cluster glass \( (g \approx 0.05) \) relaxations. Instead larger spin structures are implied, tying in with values \( g \gtrsim 0.1 \) exhibited by frequency-dependent blocking transitions in superparamagnetic nanostructures. The observed frequency dependence directly reveals the characteristic temporal scales of the nano-fluctuations. As the temperature is lowered, they slow down from the...
This quantity is proportional to the magnetic neutron scattering and so originates from the ferrimagnetic fluctuation energies in the surface of crystalline ice. The phenomenology of modulated phases.

FIG. 3: Temperature dependent properties of ferrimagnetic nanophases. a. Correlation lengths of SANS scattering $\xi _{ab}$ and $\xi _c$. b. A typical neutron diffraction antiferromagnetic peak showing two components with different length-scales. The sharper Gaussian comes from the antiferromagnetic order, while the broad Gaussian relates to the SANS ($Q = 0$) scattering and so originates from the ferrimagnetic microstructures. c. Neutron diffraction intensity of long-range order and short-range correlations. The short-range order in diffraction has a comparable $T$-dependence to the SANS intensity. d. AC susceptibility data at several frequencies with superimposed SANS intensity (blue) for comparison. e. Spin-spin correlation function derived by a Monte-Carlo approach. This quantity is proportional to the magnetic neutron scattering intensity.

millisecond (16 K) to the second (12 K) timescale, effectively producing stable spatiotemporal objects. Large spin structures are also supported by nonlinear susceptibility measurements (see Supplementary information).

To shed some light on the origin of the nanophases in $\text{Ca}_3\text{Co}_2\text{O}_6$, we studied the simplified system of the strongly anisotropic stacked triangular lattice. Our Monte Carlo simulations confirm a finite-temperature order–by–disorder phase transition from the disordered high-temperature phase into the partially ordered PDA. This transition is signaled by an extensive peak at the anti-ferromagnetic points in the Brillouin zone (see Fig. 3e and the Supplementary Information). Theoretically it is known that the ferrimagnetic state (which has the same energy as the PDA state) unsuccessfully competes with the PDA state. Despite this, our Monte Carlo simulations evidence residual ferrimagnetic fluctuations in the structure factor around $Q = 0$ which are non-extensive in their magnitude. The fact that such fluctuations do occur for our model Hamiltonians suggests that additional interactions may further stabilise ferrimagnetic fluctuations in $\text{Ca}_3\text{Co}_2\text{O}_6$, leading to a plausible explanation for the observed nanophases. These additional interactions will likely entail a coupling of the magnetism to other degrees of freedom. Recent dielectric measurements indicate magnetoelectric coupling in $\text{Ca}_3\text{Co}_2\text{O}_6$, which might be envisaged to help stabilise nanophases via local distortions of oxygen octahedra, in a manner analogous to the structural nano-phase separation recently reported in the frustrated antiferromagnet $\alpha$-NaMnO$_2$ or to the accommodation-strain-mediated phase separation in the colossal magnetoresistant manganites.

Methods Summary Susceptibility measurements were performed on a CryoBIND ac susceptometer. Direct measurements of the ferrimagnetic nanophases using small-angle neutron scattering were made using the SANS-I and SANS-II instruments at the Swiss Spallation Neutron Source (SINQ) and the D22 instrument at the Institut Laue Langevin. Neutron diffraction measurements on our single crystals were performed on the TASP and Rita-II triple-axis instruments at SINQ.

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