Spin chirality on a two-dimensional frustrated lattice

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The collective behaviour of interacting magnetic moments can be strongly influenced by the topology of the underlying lattice. In geometrically frustrated spin systems, interesting chiral correlations may develop that are related to the spin arrangement on triangular plaquettes. We report a study of the spin chirality on a two-dimensional geometrically frustrated lattice. Our new chemical synthesis methods allow us to produce large single-crystal samples of KFe₃(OH)₆(SO₄)₂, an ideal Kagomé lattice antiferromagnet. Combined thermodynamic and neutron scattering measurements reveal that the phase transition to the ordered ground-state is unusual. At low temperatures, application of a magnetic field induces a transition between states with different non-trivial spin-textures.

Geometrically frustrated magnets are unusual in that they may have disordered ground states in which an enormous number of spin configurations share the same energy1,2. The Kagomé lattice antiferromagnet, formed of corner-sharing triangles, is one of the most highly frustrated two-dimensional (2D) lattices. Although long regarded as a prime model for studying spin frustration1,3–6, the Kagomé lattice has escaped precise magnetic characterization because compounds that form this lattice are difficult to make pure and in large single-crystal form. We present a study of an ideal Kagomé lattice compound, the iron jarosite KFe₃(OH)₆(SO₄)₂. This material possesses robust chiral correlations related to the arrangement of spins around triangular plaquettes7,8. The presence of spin chirality in condensed-matter systems may play a role in important phenomena ranging from high-temperature (high-Tc) superconductivity9 to the anomalous Hall effect10,11. Currently, there are few experimental studies of spin chirality in frustrated magnets. Here, we study the non-trivial spin-textures related to chirality in a jarosite material in both the spin-ordered and spin-disordered states. Our measurements of magnetic susceptibility, specific heat and magnetic neutron scattering on pure single crystals show that the transition to the low-temperature ordered phase is unusual. In addition, we find that the spin texture of the ground state can be controlled by applying a magnetic field.

The magnetic Fe³⁺ ions of jarosite have spin-5/2 and lie at the corners of the triangles of the Kagomé lattice, shown in Fig. 1. To first approximation, the spin hamiltonian is given by:

\[ H = \sum_{<ij>} J \mathbf{S}_i \cdot \mathbf{S}_j \]

where \( J \) is the nearest-neighbour magnetic exchange interaction (\( J > 0 \)). Because the interaction is antiferromagnetic, the spin system is frustrated, and the corner-sharing arrangement leads to a higher degree of degeneracy for the ground state than for the triangular lattice. The iron jarosite is a particularly ideal Kagomé lattice compound for the following reasons. First, it consists of single layers of undistorted Kagomé planes, and these planes remain undistorted...
Figure 1 The Kagomé lattice with spins arranged in two different configurations. a, The ‘\( q = 0 \)’ structure, which is the ground-state configuration for iron jarosite. The spin arrangement has uniform, positive vector chirality, indicated by the + within each triangular plaquette. b, An alternative spin arrangement with staggered vector chirality, known as the \( \sqrt{3} \times \sqrt{3} \) structure.

down to the base temperatures of our measurements \((T = 5 \text{ K})\). Second, this jarosite can be synthesized with compositions that are stoichiometrically pure, as we describe below. This ensures that we are primarily studying the effects of geometric frustration rather than the effects of disorder. Third, large single crystals can be made, which allow investigations of the spin correlations of this Kagomé compound that would not be possible with powder samples alone.

Until recently, jarosites have been prepared typically by precipitation under hydrothermal conditions:

\[
3\text{Fe}^{3+} + 2\text{K}_2\text{SO}_4 + 6\text{H}_2\text{O} \rightarrow \text{KFe}_3(\text{OH})_6(\text{SO}_4)_2 + 3\text{K}^+ + 6\text{H}^+ \quad (1)
\]

Under these conditions, the monovalent K\(^+\) cation is susceptible to replacement by hydronium ions and the coverage of the Fe\(^{3+}\) lattice sites is incomplete. Also, only microcrystalline materials are obtained owing to the heightened acidity of the solution as well as the speed and intractability of the precipitation reaction\(^{7,12}\). The challenges confronting the synthesis of pure jarosites have been overcome with the development of redox-based hydrothermal methods\(^{13}\). Control over the precipitation of the jarosite is achieved by inserting two oxidation–reduction steps before reaction (1):

\[
\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \quad (2)
\]

\[
2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O} \quad (3)
\]

In this manner, the Fe\(^{3+}\) is slowly generated throughout the course of the hydrothermal process and the pH is moderated because three overall equivalents of protons are consumed in the production of an equivalent of jarosite. We have refined the synthesis process to optimize the size of the single crystals. Crystals as large as 10 mm in length and 48 mg in mass have been grown, making possible the inelastic neutron scattering measurements that we discuss below. Details of the single-crystal synthesis may be found in the Supplementary Information.

Even though the Kagomé lattice antiferromagnet should not order at any non-zero temperature, powder neutron diffraction measurements on KFe\(_3\)(OH\(_6\))\((\text{SO}_4)_2\), indicate that the spins order in a coplanar ‘\( q = 0 \)’ arrangement below the Néel temperature \(T_N = 65 \text{ K} \) (refs 7,8). In the \( q = 0 \) structure, the spins on each triangle are oriented at 120° to each other, and the 2D magnetic unit cell is identical to the 2D structure unit cell, as shown in Fig. 1a. The ordered spins can be decomposed into three sublattices, with the spins on each triangle labelled as \( S_1 \), \( S_2 \) and \( S_3 \). The vector chirality for each triangle may be defined as:

\[
K_q = [2/(3\sqrt{3})] \left( \hat{S}_1 \times \hat{S}_2 + \hat{S}_2 \times \hat{S}_3 + \hat{S}_3 \times \hat{S}_1 \right) \quad (4)
\]

For the coplanar arrangement, this vector is parallel to the c axis with amplitude +1 or −1 (ref. 7). The neutron powder results\(^{7,8}\) indicate that each triangle has positive chirality (+1) in the ordered state, such that the spins point directly towards or away from the centre of each triangle.

For this compound, as for all real magnetic materials, the interaction hamiltonian of the spins contains terms beyond isotropic Heisenberg exchange. These additional terms cause the system to order at a non-zero \( T_N \) and determine the ground-state spin arrangement. Currently, it is not clear whether the transition to long-range order is driven by weak interplanar coupling, spin anisotropy, anisotropic exchange or some combination of these. An ordered phase on a Kagomé lattice is characterized by two order parameters (the sublattice magnetization...
to (with neutron diffraction on a single crystal in zero field. This quantity is proportional
and above $T_0$.

To address the above issues, we have first measured the magnetization
$M$ versus temperature. The inset depicts the change in the spin configuration below
$H_{c1}$ and above $H_{c2}$. The critical field as a function of temperature is also
Fig. 3 Measurements of the field-induced transition to a state with non-
zero scalar chirality. a. Magnetization versus applied field for several temperatures
with $H \parallel c$. The $H_c$ values indicate the fields where $dM/dH$ is maximum. b. Values of $H_c$ versus temperature. The inset depicts the change in the spin configuration below
and above $H_c$. c. Integrated intensity of the (1,1,3/2) magnetic Bragg peak measured
with neutron diffraction on a single crystal in zero field. This quantity is proportional
to $(M^\parallel)^2$, the square of the staggered moment. The lines in b and c correspond to
power-law forms for $H_c$ and $M$ with the exponent $\beta = 0.25$ and $T_0 = 64.7$ K.

and the vector chirality), which have different symmetries. An intriguing
possibility is that these symmetries are broken at different temperatures.
This has been proposed as a result of numerical work on $XY$ or planar
triangular lattice systems$^{14,15}$. However, it has not been conclusively
observed by experiment$^{16,17}$. For Kagomé lattice systems, relatively little
is known about the nature of the phase transitions that occur.

MAGNETIZATION AND FIELD-INDUCED TRANSITION

To address the above issues, we have first measured the magnetization
of a single crystal sample (mass of 13.5 mg) of KFe$_3$(OH)$_6$(SO$_4$)$_2$ using a SQUID magnetometer. Measurements were taken with
the applied field oriented along the $c$-axis ($H \parallel c$), or within the
$a$-$b$ plane ($H \parallel ab$), as shown in Fig. 2a. At low fields ($H < 5$ T) with
the field along $c$, a sharp peak appears near 65 K, indicative of the transition to the 3D magnetically ordered state. This is consistent
with previous measurements on powder samples prepared under
similar synthesis conditions$^{18}$. When the field is aligned within the
$a$-$b$ plane, the sharp peak is absent and is replaced by a broad cusp.

In Fig. 2b, we plot the specific heat $C$ of powder samples of KFe$_3$(OH)$_6$(SO$_4$)$_2$. A peak in the specific heat is found at the magnetic
transition temperature of 65 K. The entropy associated with the 3D
magnetic transition (integrating $C/T$ over the temperature range
from 2 K to 100 K) represents ~50% of the $R \ln 6$ (where $R$ is the molar
gas constant) total entropy expected for the spin-5/2 system. This suggests that short-range correlations have already formed at
much higher temperatures.

At high temperatures ($T > 150$ K), the susceptibility is
isotropic and follows a Curie–Weiss law $\chi = C/(T - \Theta_{CW})$, consistent with previous results on powder samples$^{18}$. Fits to this
law between 150 K and 550 K yield the values $\Theta_{CW} = -800(30)$ K, and $C = 5.6(2)$ cm$^3$ K$^{-1}$ mol$^{-1}$ Fe). Because the data are taken for $T < |\Theta_{CW}|$, we extract the effective moment $\mu_{eff}$ and the nearest-
neighbour exchange coupling $J$ using the high-temperature series
analysis of Harris et al. for the Kagomé lattice$^2$. Our results indicate that $J = 45(2)$ K = 3.9(2) meV and $\mu_{eff} = 6.3(2) \mu_B$ (close to the spin-
only value of 5.92 $\mu_B$ for Fe$^{2+}$). We note that a small next-nearest
neighbour interaction ($J_2 > 0$) would serve to reduce the calculated
value of $J$ by an amount of order $J_2$.

The peak in $M/H$ for $H \parallel c$ at $T = 65$ K indicates the presence
of weak ferromagnetism along the $c$ direction. Recent theoretical
work$^{20}$ shows that antisymmetric exchange, by the Dzyaloshinsky–
Moriya (DM) interaction, may induce such a moment by canting
the spins slightly out of the plane. This interaction is present if there
is no inversion centre between magnetic ions and adds the term:

$$ \sum_{<i,j>} D \cdot (S_i \times S_j) $$

to the spin hamiltonian, where $D$ is the DM vector$^{20}$. This interaction
causes the spins on each triangle in the jarosite to form an ‘umbrella’
structure and gives each Kagomé plane a net ferromagnetic
moment. However, the interlayer coupling in iron jarosite causes the
ferromagnetic moments to couple antiferromagnetically between
layers in the absence of an applied field, as shown in the inset of
Fig. 3b. Our measurements on single crystals allow us to explore
this model of canted moments. The inset of Fig. 2a shows $M/H$ as a
function of temperature measured in high fields ($H \geq 7$ T). At these
high fields, the peak broadens and the downturn in the magnetization
shifts to lower temperatures. Such behaviour has been observed$^{21}$
in the square-lattice antiferromagnet La$_2$CuO$_4$ for which the DM
interaction does indeed result in weak ferromagnetism$^{22}$.

To investigate this spin canting further, we made magnetization
measurements as a function of magnetic field along the $c$ direction
as shown in Fig. 3a. The results show an abrupt change in the
magnetization at a critical field, $H_c$, which we define as the field
at which $dM/dH$ is a maximum. We interpret this abrupt increase
as a change from canted moments being oppositely directed
between planes to canted moments aligned in the same direction.
This is most likely to be caused by a 180° rotation of all spins on
the layers that were previously oppositely canted, as shown in
the inset of Fig. 3b. The critical field as a function of temperature is also
shown in Fig. 3b. For comparison, we plot the integrated intensity
of the (1,1,3/2) magnetic Bragg peak measured with neutron
diffraction in Fig. 3c. We find that $H_c$ scales quite closely with the
staggered moment $M^\parallel$ (which is proportional to the square-root
of the Bragg intensity). The mean-field result for La$_2$CuO$_4$ gives
There are few materials with non-zero scalar chirality in the ordered maximum field of our magnetometer. Hence, it is difficult to extract in the magnetization near the scalar chirality, defined on each triangular plaquette as $C(x) = 2\sum_{i} S_i \cdot (S_x \times S_y)$, where $S_x$ and $S_y$ are the 2D staggered moment per Fe atom, respectively, at $T = 0$. Our results indicate $|J| = 0.007(6)\,\text{meV}$ where the large error bar comes from the uncertainty in extrapolating $H_c$ and the canted moment. However, for temperatures above $T_{cN}$, the correlations between layers are destroyed, and the 2D spin fluctuations yield 'rods' of scattering in reciprocal space along the $L$ direction. We have verified that all of the signal in Fig. 4a disappears on cooling below $T_{cN}$, as expected for the transfer of the intensity of the 2D critical scattering into 3D Bragg points lying out of the scattering plane. Therefore, the scans in Fig. 4a pass through the 2D rods of scattering and directly measure the dynamic structure factor of the spin fluctuations.

A reciprocal space map of the intensity of the spin fluctuations is shown in Fig. 4a. Outlined in red are the boundaries of the structural Brillouin zones. The strongest scattering occurs at the position of an incident neutron, and the spin correlations of the single Kagomé planes in iron jarosite are equal and opposite. However, for $H > H_c$, the spins flip (as depicted in Fig. 3b), and the net scalar chirality becomes non-zero. There are few materials with non-zero scalar chirality in the ordered state, especially on a two-dimensional lattice. In iron jarosite, we have discovered a phase transition in which a net scalar chirality can be 'switched on' by a magnetic field.

**NEUTRON SCATTERING AND SPIN FLUCTUATIONS**

To probe the microscopic behaviour of the magnetism in the temperature regime above $T_{cN}$, we made inelastic neutron scattering measurements of the spin fluctuations at $T = 70\,\text{K}$ within the $L = 0$ plane of reciprocal space. For the temperature range $T_{cN} < T < 120\,\text{K}$, the susceptibilities for $H || c$ and $H || ab$ deviate from each other, indicative of the growing influence of spin anisotropy. For the three-dimensionally ordered spin structure below $T_{cN}$, the stacking arrangement of the planes doubles the magnetic unit cell with respect to the structural unit cell, such that the magnetic Bragg peaks occur at half-odd-integer values of $L$. However, for temperatures above $T_{cN}$, the correlations between layers are destroyed, and the 2D spin fluctuations yield 'rods' of scattering in reciprocal space along the $L$ direction. We have verified that all of the signal in Fig. 4a disappears on cooling below $T_{cN}$, as expected for the transfer of the intensity of the 2D critical scattering into 3D Bragg points lying out of the scattering plane. Therefore, the scans in Fig. 4a pass through the 2D rods of scattering and directly measure the dynamic structure factor of the spin fluctuations of the single Kagomé planes in iron jarosite. The instantaneous spin correlation length, measured separately in an energy-integrating configuration, is $\xi = 20(2)\,\text{Å}$ at this temperature.
where $a$, $b$ refer to $x$, $y$, $z$ vector components, $f(Q)$ is the magnetic form factor, and $S(Q, \omega)$ is the space and time Fourier transform of the spin–spin correlation function. The intensity variation reveals a wealth of information about the short-range ordered state in the critical regime just above $T_N$.

First, the fact that the intensities are centred within the structural Brillouin zones indicates that the fluctuations have the $q = 0$ arrangement. The absence of scattering at the $(2,0,0)$ position is consistent with this spin arrangement. Second, the nearly equivalent intensities at the $(1,0,0)$ and $(1,1,0)$ positions reveal that the spin direction on each sublattice is not fixed. Rather, the two orthogonal spin directions within the Kagomé plane are equally likely. Hence, the spin fluctuations have $XY$ symmetry at this temperature (the spin–rotational symmetry within the Kagomé plane is not broken).

In contrast, at low temperatures in the 3D ordered state, a preferred spin direction is chosen, and the intensities at $(1,0,L)$ and $(1,L,0)$ differ considerably.

The observation of short-range $q = 0$ correlations in the 2D fluctuations implies a particular arrangement of the vector chirality. In each region of correlated spins, the vector chirality must be uniform (all positive or all negative for each plaquette). Using equation (6), we calculated the neutron scattering intensity arising from $q = 0$ correlations between coplanar spins assuming only positive chirality. Our model calculations are based on 7-unit-cell clusters of spins, and we have averaged over all spin directions within the Kagomé plane.

The results are shown in Fig. 4b, and the agreement with the data is excellent. Also shown in Fig. 4b is a calculation for the intensity if correlations between coplanar spins assuming only positive chirality.

Magnetic behaviour related to two types of spin chirality: vector and scalar. The DM interaction is a significant perturbation to the Heisenberg hamiltonian and strongly influences the low-temperature physics. For $T > T_N$, the vector spin chirality is ordered even in the absence of broken spin-rotational symmetry. In the ordered state below $T_N$, we have discovered a field-induced transition to a state with non-zero scalar chirality. Thus, materials based on jarosites may be promising candidates for studies of the coupling between non-trivial spin textures and the transport of electrons in frustrated systems. For example, carrier-doped compounds would probably show an anomalous Hall effect of topological origin, and this might have useful applications in spin-based electronics.

**METHODS**

The neutron scattering data were taken at the NIST Center for Neutron Research. The integrated intensity of the $(1,1,3/2)$ magnetic Bragg peak (Fig. 3c) was measured using the BT7 spectrometer. The incident neutron energy was fixed at 13.46 meV and the horizontal collimation sequence was open–open–sample–$40^\circ$–open. The $(002)$ reflection of a pyrolytic graphite crystal was used as an analyser. For the two-axis (energy-integrating) measurement of the instantaneous spin correlation length at $T = 70$ K we used the BT9 spectrometer with the sample aligned in the (H00) scattering zone. The incident neutron energy was 10 meV, with a collimation sequence of $40^\circ$–$24^\circ$–sample–$20^\circ$. In both measurements, a pyrolytic graphite filter was placed in the incident beam to remove higher-order neutrons. The incident neutron scattering data shown in Fig. 4 were taken using the SPINS NG5 triple-axis spectrometer. The final neutron energy was fixed at 3 meV and the horizontal collimation sequence was guide–$80^\circ$–sample–$40^\circ$–radial–open. A liquid-nitrogen-cooled beryllium filter was placed in the scattered beam to remove higher-order neutrons.

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16. Mason, T. E., Guaid, B. D. & Collins, M. F. Neutron scattering measurements of critical exponents in XY physics. For $q = 0$ order (as opposed to $\sqrt{3} \times \sqrt{3}$ order which is predicted to be the preferred ground state for the pure Heisenberg model) is caused by interactions within a single Kagomé layer and is not controlled by the interplanar interaction. Second, our neutron measurements reveal critical spin fluctuations above $T_N$ that have $XY$ symmetry; hence, the magnetic ordering is not driven by 2D Ising physics.

First, we find that the instantaneous spin correlations above $T_N$ are two-dimensional in nature, and the $q = 0$ arrangement is preferred. Therefore, the selection of $q = 0$ order (as opposed to $\sqrt{3} \times \sqrt{3}$ order which is predicted to be the preferred ground state for the pure Heisenberg model) is caused by interactions within a single Kagomé layer and is not controlled by the interplanar interaction. Second, our neutron measurements reveal critical spin fluctuations above $T_N$ that have $XY$ symmetry; hence, the magnetic ordering is not driven by 2D Ising physics. Most interestingly, we find that the spin–rotational symmetry and the vector chirality are not broken simultaneously at $T_N$.

The presence of vector chiral order above $T_N$ may be naturally explained in light of the DM interaction. One possibility is that the DM interaction is the dominant source of spin anisotropy in iron jarosites. In this case, the vector chiral order appears concomitantly with the growing spin correlations and does not represent a spontaneously broken symmetry. Another possibility is that the $XY$ anisotropy has an origin (such as symmetric exchange anisotropy) distinct from the DM interaction. Once the spin correlations become coplanar within the Kagomé plane, the vector chirality of a triangular plaquette becomes a discrete symmetry (the chirality vector is either up or down with respect to the $c$ axis). Hence, long-range chiral order is not precluded by the Mermin–Wagner theorem.

However, chiral order is easily disrupted on a Kagomé lattice by the proliferation of domain walls (thermally induced defects) which can form with little cost in energy. Then the presence of a small DM interaction (in particular, the non-zero out-of-plane component $D_{ij}$) selects a particular chirality for each triangle, and thereby inhibits domain wall formation. It remains possible that the vector chirality represents a spontaneously broken symmetry; however, clarification of this point requires further neutron scattering measurements at higher temperatures.

Our measurements of this ideal Kagomé material reveal new...

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Competing financial interests

The authors declare that they have no competing financial interests.