Co-existing chiral and collinear phases in a distorted triangular antiferromagnet

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The entire magnetic phase diagram of the quasi two dimensional (2D) magnet on a distorted triangular lattice KFe(MO₄)₂ is outlined by means of magnetization, specific heat, and neutron diffraction measurements. It is found that the spin network breaks down into two almost independent magnetic subsystems. One subsystem is a collinear antiferromagnet that shows a simple spin-flop behavior in applied fields. The other is a helimagnet that instead goes through a series of exotic commensurate-incommensurate phase transformations. In the various phases one observes either true 3D order or quasi-2D order. The experimental findings are compared to theoretical predictions found in literature.

Helical magnetic structures in frustrated spin networks have been known for several decades, see, e.g. [1, 2, 3, 4]. The interest in this phenomenon was recently rekindled by a discovery of a new class of multiferroic compounds, where ferroelectricity is inherently connected to chiral incommensurate magnetic order (e.g. [1, 2]). This enables a coupling between the ferroelectric order parameter and a magnetic field, usually forbidden due to their respective symmetries. Perhaps the simplest, yet fundamentally the most important model that can provide the necessary chiral state is the two-dimensional triangular-lattice antiferromagnet (TLAF) that has a well-known “120°” spin structure.

A spectacular example of a multiferroic behavior due to the TLAF environment was recently found in the layered molybdenate RbFe(MO₄)₂ [7]. In that material triangular planes of almost classical Fe³⁺ S = 5/2 spins are well separated by non-magnetic MoO₄ layers. The Fe³⁺ subsystem is an almost perfect realization of the TLAF model [8, 9]. In RbFe(MO₄)₂ an external magnetic field disrupts the chiral magnetic structure and thereby removes the multiferroic effect. Even more interesting behavior can be expected in materials with a slightly distorted TLAF spin network. The distortion will unbalance the 120° structure and produce an incommensurate planar spin spiral. In an external magnetic field, theory predicts a multitude of exotic incommensurate and commensurate, chiral and centrosymmetric phases [2]. The chiral states could, at least in principle, possess multiferroic properties. The focus of this work is KFe(MO₄)₂, a material structurally similar to RbFe(MO₄)₂ but one that actually realizes the distorted TLAF model. Using a combination of experimental techniques, we find a remarkably complex magnetic phase diagram with co-existing collinear and helical structures, ordered in either three or two dimensions.

At high temperatures KFe(MO₄)₂ has a perfect triangular spin network due to the crystal symmetry of D₃d group with a = 5.66 Å and c = 7.12 Å. The distortion occurs as a result of a crystallographic phase transition at T = 311 K [10, 11]. The low-temperature phase is monoclinic, with a doubling of the period along the c axis. Each Fe-plane becomes a distorted triangular lattice with two unequal exchange constants J₁ and J₂ (Fig. 1). Moreover, the adjacent Fe-layers become crystallographically inequivalent, with exchange constants J₁' and J₂'. The actual lattice distortion is too small to be detected with the resolution of our experiments, and we shall henceforth adopt a hexagonal lattice notation. A previous ESR study [12] of KFe(MO₄)₂ came to a seemingly paradoxical conclusion: at low temperatures, in zero field, a helical spin structure coexists with a collinear state. It was hypothesized that the two type of magnetic order reside almost independently in the two inequivalent types of distorted triangular spin lattices, referred to as “S-layers” and “C-layers”, respectively.

To verify this bold assumption we performed magnetic neutron diffraction experiments using single-crystal samples from the same batch [12]. The crystals are transparent thin plates, of a natural triangular shape, typically 1-5 mm, with the planes of natural growth perpendicular to the 3-fold axis. The data were taken on the HB-1 and HB-1A 3-axis spectrometers at ORNL operating in 2-axis mode, using a Pyrolytic Graphite PG(002) monochromator to select λ = 2.46 Å for HB-1 and λ = 2.37 Å for HB-1A. At low temperatures, two sets of magnetic Bragg peaks emerge, with propagation vectors (1/3 − ζ, 1/3 − ζ, 0), ζ = 0.038, and (1/2, 0, 0), respec-
The observed ordering temperatures for the two sets of reflections are identical within experimental accuracy: $T_N = 2.4$ K. An analysis of 19 inequivalent Bragg reflections in the $(h, k, 0)$ plane at $T = 1.5$ K revealed that the $(1/3 - \zeta, 1/3 - \zeta, 0)$ peaks can be entirely accounted for by a planar helimagnetic state, with spins rotating in the $(a, b)$ plane. At the same time, the 14 inequivalent sets of $(1/2, 0, 0)$-type Bragg intensities measured in the $(h, k, 0)$ plane are consistent with a collinear AF spin arrangement, with spins in the $(a, b)$ plane and forming a small angle of $15^\circ$ with the $a$ axis. Thus the diffraction data confirm the original two-layer model depicted in Fig. 1a. As discussed in Ref. [12], the drastically different spin arrangement in C- and S-layers can be accounted for by a helimagnetic to a collinear state at $R > 2.2$. The complexity of the $H - T$ phase diagram of KFe(MoO$_4$)$_2$ was revealed in bulk magnetic and calorimetric measurements. Steady-state magnetization data were collected in fields up to 12 T using an Oxford Instruments vibrating sample magnetometer and specific heat data were collected on a Quantum Design PPMS at Warwick University. High-field magnetization data were taken in the fields up to 25 T using a pulsed magnet at the KYOKUGEN center. Typical experimental $C(T)$ and $dM/dH$ curves are shown in Fig. 2. In zero field we observe a sharp specific heat anomaly at $T_1 = 2.5$ K. In a magnetic field applied in the $(a, b)$ plane this anomaly shifts to lower temperatures and survives up to $H = 5$ T. For $H > 2$ T an additional peak is observed at $T_2 > T_1$. Beyond $H > 5$ T the $T_1$ anomaly is replaced by a new feature at $T_3$. The latter also moves to lower temperatures with increasing field. Yet another maximum in specific heat is observed at $T_4 < T_2$ in the high field regime. In the magnetization data, for a field applied along the $c$ axis, the only observed feature is saturation at $H_{sat\parallel} = 16.9$ T. However, for a field in the $(a, b)$ plane, the magnetization curves show four distinct anomalies. A jump of the field derivative of magnetization $dM/dH$ at $H_1 \approx 1.2$ T is followed by sharp maxima at $H_2 \approx 4.5$ T and $H_3 \approx 7.5$ T. Finally, a saturation is reached at $H_{sat\perp} = 14.5$ T. For different orientations of the field within the $(a, b)$ plane, and for samples with varying populations of the three crystallographic domain types, the measured magnetization curves are very similar. In particular, the angular variation of $H_2$ and $H_3$ is $10\%$ and $7\%$, respectively. Some samples show a smeared peak in
$dM/dH$ in the field range above 8 T in the temperature interval $2 \text{ K} < T < 2.5 \text{ K}$. This anomaly, presented by the magnetic field $H_4$ in Fig. 3, was not visible in the sample used for pulse measurements. The magnetic and thermodynamic anomalies described above, together with the $M(T)$ data from Ref. 12, allow us to reconstruct the entire $H - T$ phase diagram, as shown in Fig. 3. The low-field part of the phase boundary at $T_2$ is uncertain because of the absence of this anomaly at $H < 2 \text{ T}$.

The propagation vectors in the various phases were determined in neutron experiments on the D23 lifting counter diffractometer at ILL using a PG(002) monochromator and $\lambda = 2.38 \text{ Å}$ neutrons. The field was applied along the $b$ axis (in hexagonal notations). Sample environment was a dilution refrigerator. Typical measured field dependencies of Bragg intensities are shown in Fig. 3. At $T = 100 \text{ mK}$ the intensities of commensurate $(1/2,0,0)$-type peaks go through two consecutive jumps at $H_1 = 1.3 \text{ T}$ and $H'_1 = 2.1 \text{ T}$. These transitions seem to have no effect on the incommensurate reflections. At $T = 1.5 \text{ K}$ a single intensity jump is detected at $H_1 = 1 \text{ T}$. As previously discussed in Ref. 12, the transition is to be associate with a spin flop in the $C$-planes, all moments rotating to be perpendicular to the applied field. The additional transition seen at low temperature at $H'_1$ requires further investigation. At higher fields all the action occurs within the $S$-planes. The intensity of the incommensurate $(1/3 - \zeta, 1/3 - \zeta, 0)$-type reflections decreases and vanishes beyond $H_2 \sim 4 \text{ T}$. Within experimental resolution the value of the magnetic propagation vector is field-independent. Beyond $H_2$ the $(1/3 - \zeta, 1/3 - \zeta, 0)$-type peaks are replaced by commensurate reflections of type $(1/3, 1/3, 0)$. The latter first increases in intensity, peaks at around 6 T, and decreases at higher fields to vanish at $H_3 \sim 8 - 9 \text{ T}$. At still higher fields, no magnetic reflections were found on either the $(h, h, 0), (1/3 - \zeta, 1/3 - \zeta, l)$, or $(1/3, 1/3, l)$ reciprocal-space rods. At the temperature of neutron measurements ($T = 100 \text{ mK}$ and $T = 1.5 \text{ K}$) we found no signature of a high-field transition that could be associated with the $T_4$-anomaly described above.

A remarkable feature of the neutron data is the different dimensionality of magnetic ordering in the different phases. Scans across the $(1/2,0,0)$-type and $(1/3 - \zeta, 1/3 - \zeta, 0)$-type reflections are resolution-limited along the $h$, $k$, and $l$- directions. In contrast, the $(1/3,1/3,0)$-type peaks in the regime $H_2 < H < H_3$ are actually Bragg rods parallel to the $c$ axis, stretching across much of the Brillouin zone in the $l$-directions. The

![FIG. 3: (Color online) Cumulative magnetic phase diagram of KFe(MoO$_4$)$_2$ for a magnetic field applied in the $(a,b)$ plane.](image_url)

![FIG. 4: Main panels: field dependencies of magnetic Bragg intensities measured in KFe(MoO$_4$)$_2$ at $T = 100 \text{ mK}$. Insets: typical $l$-scans measured across the corresponding reflections.](image_url)
corresponding c-axis correlation length is only 6 lattice units. The measured correlation length within the \((a, b)\) plane is much larger, about 100 lattice units. The 2D character of the ordering persists in samples cooled in a 6 T applied field. The transition to the short ordered state at \(T_2\) naturally demonstrates a smeared \(C(T)\) anomaly in contrast to a sharp peak at the transition to the 3D ordered phase at \(T_1\).

Guidance to understanding the complex phases realized in the \(S\)-planes can be drawn from the theoretical work of Ref. [2]. At first, we can estimate the relevant exchange parameters from the saturation fields and susceptibility. Because the neutron reflections observed in high fields correspond to \(C\)-planes, we assume the saturation is associated with this kind of planes, though \(S\)-planes, naturally, also give a contribution to the magnetization. For the \(C\)-planes, the saturation fields are given by: 
\[ g\mu_B H_{\text{sat},1} = 8(J'_1 + J'_2)S \]
and 
\[ g\mu_B H_{\text{sat},1} = 8(J'_1 + J'_2)S + 2DS, \]
respectively, where \(D\) is the single-ion easy-plane anisotropy defined as in [3]. Using the observed values of \(H_{\text{sat},1}\) and \(H_{\text{sat}||}\) we get \(J'_1 + J'_2 = 0.96\) K and \(D' = 0.32\) K. Beyond the spin-flop at \(H_1\), the \(C\)-planes contribution to magnetic susceptibility should be constant: 
\[ \chi_C = g^2\mu_B^2/[8(J'_1 + J'_2)]. \]
Subtracting this value from \(dM/dH\) data for \(H_{\text{sat}} < H < H_{\text{sat}}\) we obtain the susceptibility of the \(S\)-planes: 
\[ \chi_S \simeq 0.12\, \mu_B/T \]
per Fe\(^{3+}\) ion. Using the latter value and the measured \(\zeta = 0.038\), by applying the equations in Ref. [2], we get \(J_1 = 0.37\) K; \(J_2 = 0.69\) K. As a self-consistency check, the experimental ratio \(R = 0.53\) warrants a helimagnetic ground state for the \(S\)-layers in zero field [2].

Now, the measured values \(\zeta\) and \(H_{\text{sat},1}\) can be applied to reconstruct the phase transitions in the \(S\)-planes. The critical fields \(H^\text{calc}_{1ac} = 5.7\) T, \(H^\text{calc}_{2ac} = 7.2\) T, calculated by use of \(\zeta\) and \(H_{\text{sat}}\) following the theory [2], are shown in dashed lines in Fig. 2a. As indicated by the arrow diagrams, and in perfect agreement with the diffraction experiments, at low fields one expects an incommensurate spiral structure confined to the \((a, b)\) plane. Beyond the phase transition at \(H^\text{calc}_{2ac}\) the spins should form a commensurate 3-sublattice configuration with the 2D propagation vector \((1/3, 1/3)\), as observed experimentally. At still higher fields, beyond \(H^\text{calc}_{3ac}\), the incommensurate state is expected to be restored. The spins will form a modulated fan-type structure, this time oscillating near the field direction in a small angular interval, still remaining within the \((a, b)\) plane. Note that neutron diffraction failed to detect any incommensurate peaks beyond \(H^\text{calc}_{3ac}\). This implies that either the system remains disordered, or that the ordering vector is outside our search range in reciprocal space and was simply overlooked. Besides, the flop of the spin plane perpendicular to the field direction is expected [2] at \(H = H_{sf} = 6.5\) T. Instead of this instability we observe a lost of the magnetic Bragg peaks from \(S\)-planes.

It is remarkable that even as the \(S\)-plane go through a series of phase transitions, the \(C\)-planes remain unaffected, and vice versa. This implies that magnetic interactions between each type are direct, rather than mediated by the intercalated layers of the other type. These long-range interactions are likely to be of dipolar origin.

In summary, we have demonstrated that KFe\(_2\)(MoO\(_4\))\(_2\) realizes not just one, but two co-existing and decoupled instances of the distorted TLAF model. While one has a commensurate ground state and rather simple behavior in applied fields, the other features a chiral incommensurate structure and a series of exotic high-field phases. Future work should consider the possibility of multiferroic behavior associated with the \(S\)-layers.

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