Magnetic transition and spin dynamics in the triangular Heisenberg antiferromagnet \(\alpha\)-KCrO\(_2\)

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We present the results of muon-spin relaxation measurements on the triangular lattice Heisenberg antiferromagnet \(\alpha\)-KCrO\(_2\). We observe sharp changes in behaviour at an ordering temperature of \(T_c = 23\) K, with an additional broad feature in the muon-spin relaxation rate evident at \(T = 13\) K, both of which correspond to features in the magnetic contribution to the heat capacity. This behaviour is distinct from both the Li- and Na-containing members of the series. These data may be qualitatively described with the established theoretical predictions for the underlying spin system.

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The geometrical frustration of antiferromagnetic (AFM) interactions continues to be important as a route to creating exotic quantum mechanical ground states including various flavours of quantum spin liquid\(^{12-14}\). Frustration most obviously occurs for antiferromagnetically coupled spins on a triangular lattice but, until recently, there have been relatively few examples of materials well described by a model of Heisenberg spins on such a lattice. In this context the series \(\alpha\)CrO\(_2\) (where \(A = \text{Li, Na, K}\)) is of interest as its members comprise well-decoupled, highly ideal, triangular planes containing isotropic spins. While the members of the series with \(A = \text{Li}^{2-4}\) and Na\(^{3,4,12}\) have been well studied, the material KCrO\(_2\), which has the best-separated triangular layers and might be expected to best approximate the model, has previously proved difficult to stabilise chemically and has been the subject of less experimental work\(^{12,13}\). However, it was recently demonstrated\(^{13}\) that KCrO\(_2\) may be reliably synthesized in two different polymorphs, the \(\alpha\)- and \(\beta\)-phases, allowing the opportunity for renewed study. Muon-spin relaxation (\(\mu^+\)SR) has proven particularly useful in probing both the NaCrO\(_2\)\(^{11}\) and LiCrO\(_2\)\(^{8,9}\) materials, suggesting unusual spin relaxation spectra in both systems below their respective short- or long-range ordering temperatures, with an exotic fluctuating regime reported well below the short-range ordering temperature \(T_c\) in NaCrO\(_2\), which has better separated layers than LiCrO\(_2\). Here we present the results of muon-spin relaxation measurements on \(\alpha\)-phase KCrO\(_2\) (\(\alpha\)-KCrO\(_2\)). We find that the fluctuation spectrum in this compound, while showing features that are superficially similar to both the Na- and Li-containing materials, appears to be distinct and unusual. Moreover, although we find that \(\alpha\)-KCrO\(_2\) may be described qualitatively within the framework of two different theoretical approaches, it does not seem to admit a quantitative description consistent with either of them.

The structure of the \(\alpha\)CrO\(_2\) series comprises well-separated triangular planes of \(S = 3/2\) Cr\(^{3+}\) ions stacking in an \(ABCABC\) sequence with \(R\)\(^3\)m symmetry. The separation of the triangular sheets (1/3 of the lattice constant \(c\)) is found to vary from 4.81 Å for \(A = \text{Li}\) to 5.96 Å for \(A = \text{K}\), leading us to expect that the potassium-containing material will possess the most magnetically isolated two-dimensional layers. Electron spin resonance measurements on LiCrO\(_2\) and NaCrO\(_2\)\(^{12}\) indicate very small single-ion anisotropy, suggesting a strong Heisenberg character for the spins. The structural and magnetic parameters of the members of the series are summarized in Table II. Below \(T_N = 62\) K, LiCrO\(_2\) undergoes a transition to a phase of long-range magnetic order (LRO), adopting a 120° magnetic structure\(^14\) with a suggestion of AFM coupling between layers\(^2\). Short-range magnetic order (SRO) has been proposed to occur in NaCrO\(_2\) below \(T_c = 41\) K. No magnetic Bragg peaks (indicative of LRO) were observed in \(\alpha\)-KCrO\(_2\) down to 5 K, but SRO was originally suggested to occur at \(T_c = 26\) K on the strength of a diffuse neutron scattering peak\(^{14}\). The transition is also confirmed by the more recent heat capacity measurement where a peak is observed at 23 K and by magnetic susceptibility\(^{15}\) (where the extracted Fisher heat capacity\(^{14}\) shows a relatively sharp peak at 24 K). Previous \(\mu^+\)SR measurements on the Li\(^2\) and Na-containing\(^{11}\) materials revealed quite different behaviour in the muon-spin relaxation rate close to the respective ordering temperatures. In LiCrO\(_2\) there is a sharp peak in the relaxation rate at 0.97\(T_N\). This contrasts with the behaviour of the more two-dimensional NaCrO\(_2\) where the relaxation rate shows a far broader peak, with a maximum at 0.75\(T_c\). This unusual behaviour was justified by considering the nature of the fluctuations in triangular lattice antiferromagnets. It was suggested that NaCrO\(_2\) has an exotic, extended fluctuating regime, with a slow freeze-out of fluctuations below 41 K rather than a conventional ordering transition. It was speculated that this may relate to \(Z_2\) topological defects that have been predicted to occur in the spectrum of the triangular lattice. In contrast, the state of affairs in the more three...
resolution limit of the ISIS muon pulse, which prevents the observation of features with rate $\gtrsim 10$ MHz. The loss of asymmetry demonstrates the presence of large, slowly fluctuating moments (see below) which depolarize those muon spin components perpendicular to the local magnetic field (expected to be 2/3 of the total in a powder sample\(^{16}\)). Although it is not possible to tell whether this results from a state of static LRO or SRO on the basis of these measurements, the absence of magnetic Bragg peaks and the fact that the layer separation is greater than for NaCrO$_2$ where SRO is thought to occur, leads us to tentatively assign $T_c$ as a short-range ordering temperature.

TABLE I: Structural and magnetic parameters for compounds in the ACrO$_2$ series ($A = \text{Li, Na, K}$). The cell parameters $a$ and $c$ are from Ref. $^3$ and the exchange strengths $J$ are from Ref. $^3$. $\theta_{\text{CW}}$ is the Curie-Weiss constant derived from the magnetic susceptibility fit.

|         | LiCrO$_2$ | NaCrO$_2$ | KCrO$_2$ |
|---------|-----------|-----------|----------|
| $a$ (Å) | 2.898     | 2.975     | 3.042    |
| $c$ (Å) | 14.423    | 15.968    | 17.888   |
| $J$ (K) $^a$ | 78        | 40        | 24       |
| $\theta_{\text{CW}}$ (K) | $-620^{+12}_{-700}$ | $-290^{+12}_{-160}$ | $-220^{+12}_{-210}$ |
| $T_c$ (K) | 634$^{+18}_{-15}$ | 414$^{+11}_{-10}$ | 263, 233 |

$^a$Ref. $^3$ uses the Hamiltonian $-2J \sum_{ij} S_i \cdot S_j$ and we use the Hamiltonian $-J \sum_{ij} S_i \cdot S_j$, therefore the values of $J$ reported in Ref. $^3$ are doubled in the table for consistency.

dimensional LiCrO$_2$ leads to something closer to the expected behavior of a relaxation rate peaked at $T_N$.

In a $\mu^+\text{SR}$ experiment\(^{15}\) spin polarized muons are implanted into the sample. The quantity of interest is the angular asymmetry of the decay positrons, $A(t)$, which is proportional to the spin polarization of the muon ensemble. Zero-field muon-spin relaxation (ZF $\mu^+\text{SR}$) measurements were made on a polycrystalline sample of $\alpha$-KCrO$_2$ using the EMU spectrometer at the ISIS facility, UK. A sample of $\alpha$-phase KCrO$_2$ was prepared as previously described\(^{14}\). It was packed, under glove-box conditions, inside a Ti-foil packet (foil thickness 25 $\mu$m) and sealed in an air-tight Ti sample holder, which was mounted inside a $^4$He cryostat. The measurements described here were made in the temperature range 1.5 $\leq T \leq$ 200 K. After the measurements were completed the sample was heated above 500 K in an attempt to detect a transition to the $\beta$ phase, which we were unable to stabilize.

Example ZF $\mu^+\text{SR}$ spectra are shown in Fig. 1. Below 23 K we observe a loss of asymmetry in the signal with a transition region $20 \lesssim T \lesssim 23$ K. This is due to the time

![FIG. 1: (Color online.) Example $A(t)$ spectra of polycrystalline $\alpha$-KCrO$_2$ at (a) 9.15 K and (b) 25.7 K. Solid lines (red) represent the fit to Eq. (1).](image)

In order to compare to previous muon measurements on similar triangular materials\(^{8,11,17}\), the muon spectra were fitted to a model of stretched exponential decay with a background contribution:

$$A(t) = A_{\text{rel}}e^{-(\lambda t)^\beta} + A_{\text{bg}},$$  \hspace{1cm} (1)

where $A_{\text{rel}}$ represents the amplitude of the relaxing component, $\lambda$ is the relaxation rate and $A_{\text{bg}}$ accounts for the constant background contribution from muons stopping in the sample holder or cryostat tails. The values of $\lambda$, $\beta$ and $A_{\text{rel}}$ obtained from the fit are plotted against

![FIG. 2: Evolution of the parameters from Eq. (1) with temperature. Sharp features are observed at 22.6(5) K along with a broad maximum in $\lambda$ centred on 13 K. $T_c$ is identified from heat capacity peak and $T_v$ is defined in the discussion (see main text).](image)
temperature in Fig. 2. All three parameters show distinct changes at 22.6(5) K, in agreement with heat capacity measurements\(^\text{14}\) where a sharp peak was observed at \(T_c = 23\) K. In addition to the sharp peak in \(\lambda\), whose rapid decrease levels off below 20 K, the relaxation rate also shows a broad maximum near 13 K, similar to that observed in \(\text{NaCrO}_2\)^{15}.

The relaxation rate \(\lambda\) in Eq. (1) is expected to vary with the width of the local magnetic field distribution \(\Delta\) and correlation time \(\tau\) according to \(\lambda \propto \Delta^2 \tau\), and therefore the peak in \(\lambda\) is suggestive of a transition to a regime of large, slowly fluctuating moments as the temperature approaches \(T_c\).

The muon-spin relaxation rates for all three compounds in the \(\text{ACrO}_2\) family are plotted in Fig. 3 with normalized \(x\)-axis. For \(\alpha\text{-KCrO}_2\), the maximum in \(\lambda\) occurs at 22.6(5) K and we take \(T_c = 23\) K from the heat capacity peak. The relaxation rate for \(\alpha\text{-KCrO}_2\) is noticeably smaller than the Li- and Na- compounds, pointing to significantly smaller moments or to shorter fluctuation times. For \(\text{LiCrO}_2\), the sharp peak (corresponding to 3D LRO) occurs a few Kelvin below \(T_c\). \(\text{NaCrO}_2\) shows no features close to \(T_c\), but instead we see a broad peak below the critical temperature with the maximum centred on 0.75\(T_c\). Our measurements on \(\alpha\text{-KCrO}_2\), superficially seem to show a combination of both features: not only a sharp peak corresponding to an ordering transition very close to \(T_c = 23\) K, but also a very broad shoulder with a maximum centred on 0.57\(T_c\).

![Graph showing relaxation rates for LiCrO2, NaCrO2, and KCrO2](https://example.com/graph.png)

**FIG. 3:** (Color online.) Comparison of relaxation rates for materials in the series \(\text{ACrO}_2\) with \(A = \text{Li}, \text{Na}\) and \(K\). The solid lines are a guide to the eye. The peak of \(\alpha\text{-KCrO}_2\) appears to be located at a value slightly less than 1, this is due to the experimental uncertainty (we take \(T_c = 23\) K from the heat capacity peak for \(\alpha\text{-KCrO}_2\)). Inset: Dependence of \(\lambda/T^3\) on inverse temperature \(1/T\) for \(\alpha\text{-KCrO}_2\). The solid line represents the fit to Eq. (2) for \(T > T_c\), and the slope in this semi-log plot corresponds to \(T_0/\ln 10\).

It is illuminating to compare the heat capacity results for \(\alpha\text{-KCrO}_2\)^{15} with our muon measurements. The phonon component of \(C_p\) was obtained by fitting the high-\(T\) data to a Debye model with \(\theta_D = 552\) K. The lattice contribution was then subtracted from the total \(C_p\), so only the magnetic heat capacity \(C_{\text{mag}}\) is plotted in Fig. 4. The low-\(T\) region of \(C_{\text{mag}}\) (5 \(\leq T \leq 20\) K) exhibits a \(T^2\) temperature dependence (solid line in Fig. 4), which implies linearly dispersing 2D excitations. This form is also observed for triangular materials showing SRO such as \(\text{NiGa}_2\text{Se}_4\). In contrast, \(C_{\text{mag}}\) for \(\text{LiCrO}_2\) (which shows LRO) was found to have a \(T^3\) dependence below \(T_c\), consistent with a recent spin-wave theory calculation.\(^{16}\) It is also interesting to note that below \(3\) K \(C_{\text{mag}}\) suggests \(T^2\) behaviour but with a different scaling prefactor. In Fig. 4 (inset) the evolution of \(C_{\text{mag}}/T^2\) is shown. In addition to the sharp peak at \(T_c\), a broad shoulder is present below \(T_c\) with a maximum around 13 K, similar to that observed in the muon relaxation rate. No such shoulder is reported for \(\text{NaCrO}_2\).

![Graph showing magnetic specific heat](https://example.com/magnetic_specific_heat.png)

**FIG. 4:** The magnetic specific heat (\(C_{\text{mag}}\)) of \(\alpha\text{-KCrO}_2\). The solid line is a \(T^2\) fit to the data between 5 K and 20 K. The inset shows \(C_{\text{mag}}/T^2\) as a function of temperature.

The results of our \(\mu^+\text{SR}\) measurements may be compared against different theoretical descriptions of the triangular lattice AFM Heisenberg model. Above \(T_c\), the spin-wave theory developed by Chubukov, Sachdev, and Senthil (CSS)\(^{20}\) predicts that, for \(T < \frac{2\pi \rho_s}{\Delta_s}\), the muon relaxation rate follows\(^{17}\)

\[
\lambda = G_{\text{CSS}} \left( \frac{N_0 A_0}{\hbar} \right)^2 \frac{\hbar}{\rho_s} \left( \frac{T}{T_0} \right)^3 \exp\left( T_0/T \right), \tag{2}
\]

where \(N_0 A_0\) is a renormalized hyperfine coupling constant, \(\rho_s\) is the spin stiffness constant, \(G_{\text{CSS}}\) is a numerical constant and \(T_0 = 4\pi \rho_s\).

By fitting the data above \(T_c\) to Eq. (2), we are able to obtain \(T_0\) and \(\rho_s\). The fit to the data (Fig. 4 inset) yields \(T_0 = 130(2)\) K and \(\rho_s = 10.3(2)\) K, which is consistent with the limit \(T < 2\pi \rho_s\) for the validity of the model. With the value of \(\rho_s\), the effective exchange coupling \(J\)
can then be calculated based on the approximation\textsuperscript{20,21},
\[
\rho_s / JS^2 = 1 - 0.399 / 2S \sqrt[3]{3},
\]
where \(S\) is the spin quantum number (3/2 for \(\alpha\)-KCrO\(_2\)). The spin-wave exchange strength is found to be \(J_{SW} = 9.2\) K. Although the high-\(T\) dependence of the relaxation rate is well described by this model, the exchange constant \(J\) is much smaller than that obtained from the Curie-Weiss susceptibility fit, where \(J_0\) is found to be 29.3 K\textsuperscript{13} using \(|\theta_{SW}| = zJS(S + 1)/3\) with \(z = 6\), or the value from high temperature series expansion fit obtained in Ref\textsuperscript{2} where \(J = 24\) K. We therefore find a significant discrepancy between the quantitative values, which is unlike the case of NiGa\(_2\)S\(_4\)\textsuperscript{22} where good agreement was obtained for this model. However it is worth noting that the qualitative agreement with Eq. (2) might suggest that the CSS model captures some of the underlying physical behaviour.

Below \(T_c\), the experimental results are compared to another theoretical description of the triangular lattice system which has been invoked to describe previous \(\mu^+\)SR results\textsuperscript{14,17}, known as the spin-gel picture\textsuperscript{22,23} . Here it is suggested that vortex excitations and spin freezing provide two length scales which determine the behaviour: the vortex correlation length \(\xi_v\) and spin-wave correlation length \(\xi_{SW}\). The vortex correlation length diverges below a topological critical temperature \(T_v\), where \(Z_2\) vortex excitations undergo a binding transition. However, the spin-wave correlation length remains finite below this temperature, causing the overall effective spin correlation length to remain finite also\textsuperscript{23}. This \(T_v\) is predicted to lie slightly below the peak temperature in the heat capacity, \(T_{peak}\textsuperscript{22}\). Specifically, quantum Monte Carlo simulations\textsuperscript{24} have shown that with this model we should expect \(T_{peak} = 0.137\) \(\theta_{CW}\) and \(T_v = 0.123\) \(\theta_{CW}\) for classical Heisenberg triangular AFM lattices, where \(\theta_{CW}\) is the Curie-Weiss constant extracted from fits of the magnetic susceptibility. This picture may be applied to \(\alpha\)-KCrO\(_2\) if we identify \(T_{peak}\) with \(T_c = 23\) K and \(T_v\) with \(T = 20\) K, below which the heat capacity \(C_{mag}\) follows a \(T^2\) trend due to the dominance of spin-wave excitations and also where the rapid change in muon relaxation rate levels off. Using the relation between \(T_{peak}\), \(T_v\) and \(\theta_{CW}\), two values of \(\theta_{CW}\) are obtained \(\theta_{CW} = 23/0.137 = 168\) K and \(\theta_{CW} = 20/0.123 = 163\) K. (In Ref\textsuperscript{22} \(T_v\) is identified with the rounded shoulder in \(\lambda\) for NaCrO\(_2\). If we adopt the same procedure a value of \(\theta_{CW} = 13/0.123 = 106\) K is derived, which is inconsistent with the value from \(T_{peak}\)\textsuperscript{.})

The calculated \(\theta_{CW}\) values are in reasonable agreement with the \(\theta_{CW} = 160\) K measured in Ref\textsuperscript{3} but about 25\% smaller than the more recent \(\theta_{CW} = 220\) K measurement in Ref\textsuperscript{13}. We note that the latter value of \(\theta_{CW} = 220\) K corresponds to the material we measured, where the \(\alpha\)-phase was successfully isolated. Given this, and the ambiguity in identifying the features in the data corresponding to \(T_v\) it is unclear whether this model is applicable in this case.

In conclusion we have made \(\mu^+\)SR measurements on \(\alpha\)-phase KCrO\(_2\). The material undergoes a transition, most probably to a region of short-range magnetic order below \(T_c = 23\) K and shows evidence for further dynamics below this temperature with a peak seen in the muon-spin relaxation rate and a broad shoulder in the magnetic heat capacity at 13 K. Despite the superficial resemblance to the muon relaxation seen in the Li- and Na- containing members of the series, the features here appear to be unique. Although the behaviour is qualitatively consistent with two established models of the 2D triangular Heisenberg antiferromagnet, namely the CSS spin-wave theory and the spin-gel picture, a fully consistent quantitative description is not obtained with either model.

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