Diffuse spin waves, zero modes and cluster excitation in the spin-3/2 kagomé antiferromagnet chromium jarosite, KCr$_3$(OD)$_6$(SO$_4$)$_2$

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The dynamics of the $S = 3/2$ kagomé antiferromagnet chromium jarosite, KCr$_3$(OD)$_6$(SO$_4$)$_2$, was studied using high-resolution neutron time-of-flight spectroscopy on a polycrystalline sample with a nearly stoichiometric magnetic lattice (2.8(2)% Cr vacancies). Neutron spectroscopy reveals diffuse spin wave excitations in the ordered phase with an incomplete gap and significant finite life-time broadening as well as a pronounced zero mode. Using linear spin wave theory, we estimate the exchange couplings, with the leading nearest neighbor value being $J_1 = 0.884$ meV. Above $T_N$ diffuse excitations from cooperative paramagnetism dominate. A model for two-dimensional magnetic cluster excitations is shown to capture the essential features of the data in the cooperative paramagnetic phase.

I. INTRODUCTION

Emergent phenomena occur within geometrically frustrated spin systems, where competing interactions suppress the normal ordering of the spins, and create a macroscopic ground state degeneracy with a flat energy landscape for excitations. This allows other exotic order and disorder phenomena to emerge, such as spin ice [1-3] and spin liquids [4,7]. Spin liquids are states where the spins fluctuate in a correlated liquid-like manner. In quantum spin liquids, the system eludes order at finite temperatures due to the frustrated interactions [7]. While experimental verification of a quantum spin liquid has proven contentious, also due to inherent problems with structural defects in synthesized samples [8], two-dimensional spin liquids are more prolific but studied comparatively less. Here, the frustration only partially suppresses the magnetic ordering, so that the system still orders at finite temperatures. These systems still show the hallmark liquid-like fluctuations at intermediate temperatures due to the frustrated interactions [7].

The kagomé antiferromagnet has taken a center stage in the study of geometrically frustrated spin liquids. This is due to the two-dimensional nature and the low connectivity of $z = 4$ nearest neighbors in the kagomé geometry as illustrated in Fig. 1(b), which combined with the frustration from the antiferromagnetic couplings creates a macroscopic ground state degeneracy. The presence of dispersionless zero-energy excitations in the ground state manifold prevents long-range order even at $T = 0$, both in the classical and quantum spin system [9]. These zero-energy modes (or zero modes) are a special property of the kagomé geometry, and originate from the fact that coherent local rotations of the spins in two sublattices around the third may occur at no energy cost [9]. In most physical realizations of the kagomé antiferromagnet, the presence of additional, non-dominant interactions will cause the systems to order magnetically at finite temperatures. These additional interactions will cause the zero-energy mode to be lifted up to finite energy transfers, which has the fortunate consequence that they can be observed more easily experimentally. In spite of this, the kagomé zero mode has only been observed so far in the three classical kagomé antiferromagnets.

One of the most studied classical kagomé antiferromagnetic materials is exactly the jarosite family of magnets with the general chemical composition AM$_3$(OH)$_6$(SO$_4$)$_2$, where A is a monovalent ion (Na$^+$, K$^+$, H$_3$O$^+$, Ag$^+$, NH$_4^+$) and M is a trivalent ion, which may be magnetic (Fe$^{3+}$, Cr$^{3+}$, V$^{3+}$). Jarosites crystallize in the $R3m$ space group with magnetic ions positioned in stacked kagomé planes, as shown in Fig. 1. The parent compound is the $S = 5/2$ iron mineral jarosite, KFe$_3$(SO$_4$)$_2$(OH)$_6$. Jarosite is a frustrated antiferromagnet, which orders at $T_N = 65$ K, and is well-described as a Heisenberg antiferromagnet with a Dzyaloshinskii-Moriya (DM) interaction, which causes a spin canting within the kagomé layers [10]. The magnetic properties of jarosite have been studied extensively [10-17], both in powders and single crystal specimens. Exchanging the magnetic ion to V$^{3+}$ lifts the frustration and causes ferromagnetic ordering [15,19]. While the magnetism and excitations of jarosite are now well-understood, markedly fewer studies have studied the magnetic behavior of the $S = 3/2$ Cr-analogue, KCr$_3$(OH)$_6$(SO$_4$)$_2$ (Cr-jarosite). Cr-jarosite is also a frustrated antiferromagnet [20,22], but the lower spin value may lead to enhanced quantum effects related to the frustration. This compound shall be the focus of this paper.

Studies of jarosites, and in particular Cr-jarosite, have suffered significantly from the difficulty in synthesizing...
pure and stoichiometric compounds. This is a general and significant problem for many types of frustrated compounds, since the lack of strong magnetic order allows for structural disorder and defects to play a large role in the material properties [8]. However, this was improved for jarosites by introduction of the redox-hydrothermal synthesis in the early 2000’s [10, 11, 18] for B = Fe and V. For jarosites, the two main defects are a vacancy on the magnetic B site, and mixed occupancy on the A site, which may or may not be correlated[20, 23]. An M site vacancy will locally destroy the kagomé lattice by lifting the magnetic frustration leading to local antiferromagnetic interactions and an A site vacancy [24]. It is an experimental fact that while jarosites with A = K+, NH4+, Na+, Ag+ will order magnetically, jarosites with A = H3O+ instead show spin glass behavior. Thus, the A site cation(s) also affect the magnetic properties, but currently a detailed understanding lacks [25–27]. Although the redox-hydrothermal synthesis has improved the stoichiometry, our recent study of Cr-jarosite prepared using this approach revealed significant (2-27%) substitution of K by D3O+ and D2O species [20]. While the static magnetic behavior of Cr-jarosite has previously been contested (see e.g. [28,31]), all recent results point to the same overall conclusions: Cr-jarosite orders antiferromagnetically at T_N ≈ 4 K, and assumes a 120° noncollinear ground state with a small ferromagnetic canting in each layer due to a small DM interaction, see Fig. 1(b) [20,22]. The kagomé layers are coupled ferromagnetically, causing the spins to cant the same way in each layer which adds up to a small positive magnetization. However, the excitations in Cr-jarosite have only previously been investigated in a single study before the advent of the redox-hydrothermal synthesis on a sample with 26% Cr vacancies and an undisclosed amount of K vacancies [22]. Such a high Cr vacancy content significantly affects the magnetism of the sample, as 33% Cr vacancies completely lift the magnetic frustration, making the study not representative of stoichiometric Cr-jarosite.

In this paper we will remedy this lack of excitation studies in Cr-jarosite by use of neutron spectroscopy on a well-defined sample with a stoichiometric magnetic lattice. The vacancy levels were quantified using 2H MAS NMR, which is highly sensitive to local environments within crystal lattice, and therefore poised as a tool for defect quantification. In the ordered state below T_N, the excitation spectrum can be described by dampened spin waves which is modeled using linear spin-wave theory to extract estimates of the exchange interactions. In the cooperative paramagnetic state between T_N and the Curie-Weiss temperature the excitations are of a short-ranged nature. By modeling both the energy- and Q-dependence of the excitations we link the behavior to that of a classical spin liquid.

II. EXPERIMENTAL DETAILS

6.9 g of deuterated Cr-jarosite, KCr3(OD)6(SO4)2, was prepared by the redox-hydrothermal method [10]. The purity of the sample as well as each batch prior to mixing was assessed by powder X-ray diffraction (PXRD) and 2H MAS NMR. The synthesis and characterization followed our recently reported procedure [20] with further details are given in appendix A.

2H MAS NMR single-pulse and rotor-synchronized Hahn-echo (90°–τ–180°–τ–acquisition) spectra were performed on an Agilent INOVA spectrometer at 14.1 T equipped with a 1.6 mm triple-resonance MAS probe using several spinning speeds in the range 30-35 kHz for unambiguous identification of the isotropic regions, see [20]. The echo delay (τ) was one rotor period. The 2H MAS NMR spectra were referenced relative to TMS using D2O (δiso = 4.6 ppm) as secondary reference. The 2H MAS NMR data were processed in the MestReNova software (ver. 12.0.1). Spectral deconvolution and fitting of the chemical shift anisotropy (CSA) parameters (Δ and ηq) and quadrupole coupling (CQ and ηQ), were performed in the ssNake software [33] (ver. 1.2), see [20]. The CSA parameters are reported in the Haebelen convention [34], where the Euler angle β relates the principal axis of the CSA and quadrupole tensor [35].

Susceptibility data was measured between 5 K and
370 K using a Quantum Design MPMS-5 SQUID. Low-temperature measurements of the magnetization was made using a Quantum Dynacool Physical Property Measurement System (PPMS).

Neutron spectroscopy was performed at the ISIS neutron facility (UK). Initially, the excitations were studied using the time-of-flight spectrometer MARI using a He-4 cryostat [37], which revealed a need for better low-energy resolution. Thus, we proceeded to the time-of-flight spectrometer LET (ISIS) [37], where the powder was loaded into a hollow cylindrical aluminum canister in a helium atmosphere, and placed in an orange-type cryostat. Repetition rate multiplication energies of 2.20 meV, 3.70 meV, 7.60 meV, and 22.20 meV provided simultaneous access to different parts of reciprocal space. LET has estimated energy resolutions of \( \delta E/E_i \approx 1\% \) [37]. For investigations of Bragg reflections, \( E_i = 2.20 \) meV was used for better Q-resolution, while \( E_i = 3.70 \) meV data is used for all other investigations as the best compromise between resolution and \((Q, \omega)\) coverage of the excitations. Data was taken at 9 different temperatures between 1.8 K and 100 K. The initial data reduction was performed with Mantid [38], and data analysis was performed using Horace [39]. Data modeling of spin waves was performed using a linear spin-wave theory based on the Holstein-Primakoff framework as implemented in the SpinW package [40].

### III. CHARACTERIZATION

PXRD and SEM-EDS was used to determine the purity and chemical composition of the combined sample. The PXRD diffractograms (see appendix B) showed only reflections from chromium jarosite, and are in excellent agreement with our recent study [20]. Thus, no crystalline impurities were identified by PXRD. It is noted that the (107) reflection shows a complex line shape indicative of partial hydronium substitution on the K site, as discussed in detail in Ref. [20].

The concentration of defects were quantified by \(^2\)H MAS NMR spectroscopy for the combined sample following the same procedure as earlier reported [20]. The Cr and K defects have previously been shown to be correlated, and can be summarized in the general chemical formula as [20]:

\[
[K_{1-x-y}(D_nO)_{y+x}]Cr_{3-x}(SO_4)_{2}(OD)_{6-4x}(OD_2)_{4x},
\]

where \( D_nO \) refers to the total concentration of deuterium species on the A site, which is the sum of \( D_2O \) and \( D_3O^- \). This highlights that Cr vacancies also cause K vacancies, but K vacancies can also occur on their own. The concentration of the defects may be determined by deconvolution of the \(^2\)H MAS NMR spectrum (see appendix D). The Cr-vacancies are then determined from the integrated intensities of the appropriate \(^2\)H NMR resonances [23]:

\[
4x = \frac{1}{2} I(CrOD_2) \frac{1}{I(CrOD) + \frac{1}{2} I(CrOD_2)}. \tag{2}
\]

The average number, \( n \), of deuterons on the A-site may similarly be estimated by [23]

\[
n = \frac{I(D_nO)}{I(Cr_2−OD) + \frac{1}{2} I(Cr−OD_2)}, \tag{3}
\]

where values of \( n = 3, 2, \) or 0 corresponds to the A-site being fully occupied by \( D_3O^- \), \( D_2O \), or \( K^+ \) respectively.

![Fig. 2. \(^2\)H MAS NMR spectrum (Hahn Echo) of polycrystalline Cr-jarosite recorded at 14.1 T with 33 kHz spinning speed. The left insert illustrates the isotropic region for the Cr-\(OD_2\) (D) and Cr-\(OD_2\) (K) resonances. The right insert shows the isotropic region for the Cr-\(OD_2\) and water (\(D_nO\)) resonances.](image)

The \(^2\)H MAS NMR spectrum (Fig. 2) contains the spinning side band manifold for 4 resonances located at \( \delta_{iso} = 872(10), 828(5), 229(5), \) and 7(2) ppm, which are assigned to Cr-\(OD_2\) (D), Cr-\(OD_2\) (K), Cr-\(OD_2\) and D\(_n\)O, respectively, using earlier reported data [20, 41]. The Cr-\(OD_2\) resonances stem from stoichiometric Cr-jarosite with either \( D_nO \) or \( K^+ \) on the A-site. The Cr-\(OD_2\) resonance stem a Cr next to a Cr vacancy (defect), whereas the \( D_nO \) resonances contain the overlapping resonances from \( D_nO \) on the A-site and surface adsorbed \( D_2O \). Moreover, a negligible amount (\(< 1\%)\) of a sharp D\(_n\)O resonance at 11(1) ppm from an unknown impurity were observed. Thus, the \(^2\)H MAS NMR spectra also confirm partial substitution of hydronium in the sample.

Based on these values, eq. 2 yields \( x = 0.0850(6) \), corresponding to 2.8(2)\% Cr vacancies (97.2(2) \% occupancy on the magnetic lattice). Eq. 3 yields \( n \approx 0.41(9) \) and thereby a K occupancy of 80-86 \%, where the upper and lower boundary corresponds to substitution by only \( D_2O^- \) or \( D_3O^- \) on the A-site, respectively. Thus, the analysis of the combined sample by PXRD, SEM/EDS, and \(^2\)H MAS NMR confirms the formation of Cr-jarosite. Based on the quantified level of defects, the magnetic kagomé lattice of Cr ions is almost perfectly intact.
The K-defects are at a manageable, quantified level and match our earlier study [20].

The susceptibility was measured from 5 K – 370 K in applied fields of 3 T, see Fig. 3(a). Fitting the data with the Curie-Weiss law and assuming \( g = 1.97 \) as determined from electron spin resonance (ESR) [22], yields a Curie-Weiss temperature of \( \theta_{CW} \approx -58 \) K, in close agreement to previously obtained values [20, 21]. Assuming that the nearest-neighbor interactions within the kagomé plane dominates, a mean-field estimate for the magnetic interaction can be obtained as

\[
J_{MF} = \frac{3k_B|\theta_{CW}|}{zS(S+1)} \approx 1.0 \text{ meV}, \tag{4}
\]

where \( z = 4 \) is the number of nearest-neighbors.

The magnetization of the sample for low temperatures in 0.02 T is shown in Fig. 3(b), which shows an antiferromagnetic phase transition with weak ferromagnetic canting in the region 3–4 K. At 1.7 K, the magnetization is measured as 0.024 \( \mu_B/\text{Cr}^3^+ \) in the powder sample, corresponding to 0.05 \( \mu_B/\text{Cr}^3^+ \) in a single crystal with magnetic field along the \( c \) axis, matching previous results [20, 21]. Assuming a saturated magnetization of 3.87 \( \mu_B \) for \( \text{Cr}^3^+ \) in an octahedral ligand field, this corresponds to a spin canting angle of approximately \( \alpha = \sin^{-1}(M/M_s) \approx 0.7^\circ \).

The magnetic and structural Bragg reflections in Cr-jarosite were investigated to ascertain the magnetic ordering. This low-resolution, elastic scattering data was obtained by taking constant-energy cuts around the elastic line using the LET data with \( E_i = 2.20 \) meV. The results for temperatures between 1.8 K to 8 K can be seen in Fig. 4(a). The magnetic (012) reflection appears between 3 K and 4 K, consistent with both the susceptibility measurements in Fig. 3 and the results of \( T_N = 3.8 \) K from our careful neutron investigation [20] for samples with a similar vacancy profile. Figure 4(b) shows the intensity difference between 1.8 K and 4 K, and highlights the purely magnetic Bragg reflections. All reflections can be indexed by using a magnetic unit cell identical to the structural. This is consistent with a ground state with the 120°, \( q = 0 \) spin arrangement with a small ferromagnetic canting out of the kagomé plane.

### IV. EXCITATIONS

The temperature development of the excitation spectra can be seen in figure 5. In the magnetically ordered phase at \( T = 1.8 \) K \( \approx T_N/2 \) (upper left corner), distinct spin wave excitations can be seen. The data reveal a continuum of high intensity scattering centered at \( Q \approx 1.1 \) Å\(^{-1}\) and \( h\omega = 0.7 \) meV with indications of a gap. The spin wave branches continue up to roughly 5 meV as seen with the data with higher \( E_i \) (see appendix E). Additionally, a gapped, broad, and approximately flat mode exists at \( h\omega = 0.4 – 0.9 \) meV extending up to \( Q \approx 3.5 \) Å\(^{-1}\). As shall be shown later, this flat mode is a realization of a kagomé zero mode lifted to finite energies due to the DM interaction.

Beginning from the low-temperature data, the inten-
sity moves towards lower energies as the temperature increases from 1.8 K through \( T_N \), and the spectra starts to lose the distinct spin waves. Above \( T_N \), the excitations remain as a distinct feature with intensity above \( Q \approx 1.1 \text{ Å}^{-1} \) and no gap to the elastic line visible in the \( E_i = 3.70 \text{ meV} \) data. This feature remains visible up to \( \sim 15 - 35 \text{ K} \). Some broader, increased intensity is also present at \( 55 - 100 \text{ K} \), which can be recognized as paramagnetic scattering that is practically constant within the energy scale of the system and decreases in a way consistent with the magnetic form factor for larger \( Q \). The distinct excitations in the range \( \sim 4 - 15 \text{ K} \) are magnetic in nature, as they are continuously connected to the spin wave excitations at low temperatures, disappear at higher temperatures, and originate from the position of the strong magnetic Bragg reflections. Given their diffuse nature, they indicate short-ranged magnetic correlations within the cooperative paramagnetic phase.

The existence of a gap in the excitations illustrated in Fig. 6, where (a) shows a cut through the strong continuum centered at \( Q \approx 1.1 \text{ Å}^{-1} \), while (b) shows a cut through the lifted kagomé zero mode at higher \( Q \). For the spin wave continuum above the (101) reflection, the gap appears incomplete even at 1.8 K, although it may open fully at lower temperatures. The gap is still vaguely present in the 3.0 K data, while the gap is completely closed at 4.0 K. The gap from the elastic line to the kagomé zero mode around \( Q \approx 2 \text{ Å}^{-1} \) is, however, a complete gap with a value of \( \sim 0.4 \text{ meV} \) at 1.8 K. As the temperature increases, this gap also closes.

### A. Spin waves

Figure 7(a) shows the spin waves well within the ordered phase at \( T = 1.8 \text{ K} \). We will analyze the excitations in the ordered state with linear spin wave theory to obtain estimates for the exchange couplings. The spin wave excitations in Fig. 7(a) lack any clear van Hove singularities, and appear to be significantly broadened. This may either stem from finite lifetimes of the spin waves, which would cause a broadening in energy, or from co-existing, persistent short-ranged correlations, which would cause a broadening in \( Q \). Due to technical limitations in calculating powder averages using SpinW, we will treat the broadening of the spin waves as stemming from finite lifetimes.

We assume the magnetic ground state to be the 120°, \( q = 0 \) spin structure with equal canting in each layer. We assume the magnetic system to be described by the Hamiltonian,

\[
\mathcal{H} = \sum_{nn} \left[ J_1 \vec{S}_i \cdot \vec{S}_j + D_{ij} \cdot \vec{S}_i \times \vec{S}_j \right] + \sum_{nnn} J_2 \vec{S}_k \cdot \vec{S}_l,
\]

where \( J_1 \) and \( J_2 \) are the in-plane nearest- and next-nearest neighbor exchange couplings,
FIG. 6. Constant-Q cuts through the excitations integrated over energy for various temperatures. (a) Cut through the intense excitation at $Q \approx 1.07$ Å$^{-1}$ with $E_i = 2.20$ meV. (b) Cut through the flat mode at $Q \approx 2.1$ Å$^{-1}$ with $E_i = 3.70$ meV.

that are both fixed to be antiferromagnetic. $\vec{D}_{ij} = [\sqrt{3}D_y(i,j), D_y(i,j), D_z(i,j)]$ is the symmetry-allowed DM interaction, where we also assume both $D_y, D_z < 0$. While the exact role of each exchange parameter can be found analytically in Yildirim and Harris [42], their overall contribution is the following: $J_1$ controls the bandwidth of the high-intensity, higher-energy spin wave, $D_y$ and $D_z$ control the center of the flat mode and causes a canting of the spins, and $J_2$ causes dispersions of the flat mode, such that $D_y, D_z,$ and $J_2$ together control the bandwidth of this mode.

The spin wave dispersions were calculated using the SpinW package, and then powder-averaged to compare with experimental data. In order to account for the experimental resolution along $Q$, the powder-averaged spectra were convoluted with a Gaussian with full-width half-maximum (FWHM) of $\Delta Q = 0.1$ Å$^{-1}$ as estimated from the width of the Bragg reflections. In order to account for the overall smearing stemming from the finite lifetimes of the excitations, an additional variable parameter is introduced by convolution of the spectra with a Lorentzian with FWHM $\Delta E$. We used a constrained particle swarm algorithm to perform $\chi^2$ fitting of constant-$Q$ cuts through data. To capture most features of the spin waves while also keeping run times manageable, we simultaneously fitted 5 cuts through $Q$ at $Q = 0.55, 0.8, 1.07, 1.5, 1.85$ Å$^{-1}$, with width $dQ = 0.1$ Å$^{-1}$, as illustrated in Fig. 7. We fitted the data using 6 free parameters: $J_1$, $J_2$, $D_y$, $\Delta E$, as well as a common intensity scale and constant background. We assumed that the DM interaction had the same $D_z/D_y = 0.255$ ratio as the values obtained by Okubo et al. [22] based on antiferromagnetic resonances, but we allowed the strength to vary. The next-nearest neighbor $J_2$ was included in the fit since it significantly improved the reduced $\chi^2$ of the fit. The spin canting was optimized for each choice of the exchange parameters to minimize the ground state energy.

The resulting best fit can be seen in Fig. 7. Fig. 7(a) shows the experimental spectrum, Fig. 7(b) shows the resulting SpinW spectrum, and Fig. 7(c) shows the
four 1D cuts that the fit was made to. The best fit has the parameters $J_1 = 0.884$ meV, $J_2 = 0.015$ meV, $D_y = -0.024$ meV, $D_z = -0.006$ meV, and a Lorentzian broadening of $\Delta E = 0.730$ meV for a combined reduced $\chi^2$ of 17.1. The fit captures the dominant features of the spin waves quite well, as is especially evident in Fig. 7(c) of the actual fit. A key feature of the fit is the Lorentzian broadening in energy, $\Delta E = 0.730$ meV. This is 20 times larger than the instrumental resolution of the elastic line, $\delta E = 0.035$ meV, and will be discussed in the detail in section VB. When the ground state is optimized, SpinW achieves a $120^\circ$ spin structure as expected with a spin canting angle of $1.01^\circ$ out of the kagomé plane. This matches well with the canting angle estimated from our magnetization measurements of $0.7^\circ$. Furthermore, the sum of all exchange interactions from SpinW matches well with the mean-field $J_{MF} \approx 1.0$ meV estimate from the susceptibility data.

B. Diffuse excitations above $T_N$

For $T > T_N$ the diffuse excitations in the range 0-3 meV persist, and above $\sim 35$ K ($> 9 T_N$) the signal resembles simple, paramagnetic background. We will attempt to model the excitations above $T_N$ by describing the excitations along the energy and Q axis respectively.

1. Energy dependence

The temperature evolution of constant-Q cuts around the magnetic Bragg reflection at 1.1 Å$^{-1}$ is shown in Fig. 8. The data can be modeled assuming a quasielastic behavior with broadening in energy due to finite life-times and a damped harmonic oscillator (DHO) to account for the inelastic response at low temperatures [13][14]. Thus, we fit the data with the following model:

$$S(\omega, T) = S_E(\omega, T) + S_{QE}(\omega, T) + S_{DHO}(\omega, T),$$

where $S_E(\omega, T)$ is a Gaussian to account for the elastic line. $S_{QE}(\omega, T)$ is the quasielastic response as modeled by an exponential spin relaxation in the form of a Lorentzian

$$S_{QE}(\omega, T) = \frac{1}{1 - e^{-\hbar \omega / k_B T}} \frac{\chi_0 \omega \Gamma}{\omega^2 + \Gamma^2},$$

where the first term represents the detailed balance factor describing the thermal population of excited states, $\Gamma$ is the energy line width, and $\chi_0$ is the static susceptibility. The inelastic response $S_{DHO}(\omega, T)$ is fitted by a damped harmonic oscillator (DHO) including detailed balance factor and corresponding to the double Lorentzian

$$S_{DHO}(\omega, T) = \frac{1}{1 - e^{-\hbar \omega / k_B T}} \frac{A_{DHO} \omega \Gamma}{(\omega^2 - \omega_{DHO}^2)^2 + (\omega \Gamma)^2},$$

where $A_{DHO}$ is the oscillator strength and $\omega_{DHO}$ is the eigenfrequency. $S_{DHO}(\omega, T)$ is only included in the fit for 4 K and below, since the scattering above could easily be reproduced without the inelastic response.

The fit to data is shown in Fig. 8 and shows that the inelastic response at low temperatures is pronounced, but decreases steadily as the temperature increases. Simultaneously, the energy line width $\Gamma$, which is common to both $S_{QE}(\omega, T)$ and $S_{DHO}(\omega, T)$, increases as the temperature increases as expected. It should be noted that the line width at 1.8 K of $\Gamma = 0.6 \pm 0.2$ meV is consistent with the energy broadening obtained by the SpinW model of 0.73 meV (see table I).

2. Q-dependence

The temperature evolution of the Q-dependence of the excitations may reveal information about the short-ranged nature of the correlations. Fig. 8 shows...
the Q-dependence of the excitations for various temperatures obtained by integrating the spectroscopy data for excitations above the elastic line. The data shows a very broad and asymmetrical peak at \( Q \approx 1.1 \text{ Å}^{-1} \). The diffuse appearance and the broadness in \( Q \) of the excitations indicate short-ranged magnetic correlations. These excitations are strongest for lowest temperatures, but persist until around \( |\theta|/2 \), much above \( T_N \). Due to the dominating in-plane couplings between spins, we hypothesize that this arises from short-ranged correlations that are purely two-dimensional and occur between spins within the kagomé planes. In order to model this, we employ a heuristic model for obtaining powder-averages of 2D excitations with characteristic length scale \( \xi \).

In this model, we assume that the 2D excitations will occur around the 2D ordering vector \((hk) = (10)\) located at \( Q_0 = 1.005 \text{ Å}^{-1} \), but with constant intensity independent of the \( l \) component of \( Q \). This 2D scattering rod must then be powder-averaged in three-dimensional \((hkl)\) space. The geometrical derivation of this can be found in appendix \[^{10}\] and yields a effective expression for the powder-averaged Q-dependence of the intensity as \( I(Q) \propto 1/(Q\sqrt{Q^2 - Q_0^2}) \) for \( Q > Q_0 \) and zero for \( Q < Q_0 \). The divergence at \( Q = Q_0 \) is essentially of a square root type and thus integrable. Our result is identical to the treatment of Yang and Frindt \[^{15}\], which is an improvement of the classical Warren function \[^{16}\], valid for powder-averaged diffraction of a 2D system. To account for the short-ranged correlations of our magnetic system, we perform a convolution of the expression with a Lorentzian with a full-width-half-max given by \( \gamma = 1/\xi \), where \( \xi \) is the correlation length. Thus, the resulting convoluted line shapes is

\[
C_L(Q) = |f(Q)|^2 \times \int_{-\infty}^{\infty} \frac{1}{Q' \sqrt{Q'^2 - Q_0^2}} \frac{\gamma^2}{(\gamma/2)^2 + (Q' - Q)^2} \, dQ',
\]

where \( f(Q) \) is the magnetic form factor for Cr\(^{3+}\). The equation is fitted to the data including an overall scaling parameter and a variable background. In our data analysis, \( \gamma \) is sufficiently broad that convolution with an experimental resolution function is unnecessary.

The fitting of this model to the data can be seen in Fig. 9 which shows the Q-dependence of the data integrated from 0.11 – 2.5 meV, i.e. the excitations above the elastic line. Temperatures above 55 K \( \approx \theta_{\text{CW}} \) have not been fitted due to lack of distinct features. For the lower temperatures, the model works surprisingly well, as it reproduces both the peak position and asymmetric line shape; both in the cooperative paramagnetic regime and below \( T_N \). The temperature dependence of the effective 2D correlation length \( \xi \) is shown in Fig. 9(b). At the highest fitted temperature, \( \xi \approx 4 \text{ Å} \) which is close to the distance between nearest-neighboring Cr atoms in the kagomé plane of 3.65 Å. The correlation length increases for decreasing temperature, and reaches \( \xi \approx 17 \text{ Å} \) at 1.8 K, which corresponds to 4.6 times the separation distance of the Cr atoms.

V. DISCUSSION

A. Effects of the sample quality

In our sample, there are 2.8% magnetic Cr\(^{3+}\) vacancies and 14–20% K\(^+\) vacancies that may either be replaced by H\(_2\)O or H\(_3\)O\(^+\). It is well-established that H\(_3\)OFe\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) is a spin glass \[^{25,27}\], and furthermore, the magnetic behavior changes gradually between KFe\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) and H\(_3\)OFe\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) with increasing H\(_3\)O\(^+\) content \[^{26}\]. The precise magnetic behavior of H\(_3\)OCr\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) remains largely unexplored, although it has been established that it eludes long-range order and appears to differ significantly from analogues with other cations \[^{9,30,31}\]. Assuming that H\(_3\)OCr\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) follows the overall trends found in the iron-analogue, it seems fair to assume that the defects

FIG. 9. (a) Q-dependence of data integrated in the range 0.11 – 2.5 meV for various temperatures. Full lines are fit to eq. \(^9\) Each temperature has been offset for clarity. (b) Resulting correlation length.
are approximately randomly located throughout the lattice, and that this could lead to a distribution of exchange interactions.

### B. Spin waves and coupling constants

The resulting exchange parameters as obtained from powder-averaged linear spin wave theory are summarized in table I, where they are compared with values from the literature. Our exchange parameters improve on the previously published estimates of the exchange couplings, as our model is the first to include all the interactions simultaneously. The value of the nearest neighbor coupling parameter, $J_1$, is around 17% smaller than previously estimated by magnetization measurements \[21\], however our inelastic neutron spectroscopy is expected to be a much more precise estimator. The DM coupling we obtain via SpinW is almost 50% lower than determined by electron spin resonance (ESR) \[22\]. However, ESR, which provides man order of magnitude estimate, matches well with our results. The spin wave spectrum calculated with the same parameters but using the DM couplings suggested by \[22\] decrease the match with data significantly. Furthermore, the spin canting angle of 1.01° obtained by the SpinW model matches well with both our estimate from susceptibility of 0.7°, as well as the canting angles measured in the literature in the range 0.86–1.44° \[21,22\].

| $J_1$  | $J_2$  | $D_y$  | $D_z$  | $\Delta E$ | Canting |
|-------|-------|-------|-------|------------|---------|
| Lee et al. \[32\] | 1.21 | - | - | - | - |
| Okuta et al. \[21\] | 1.06 | - | - | - | 0.86° |
| Okubo et al. \[22\] | - | - | -0.0470 | -0.0120 | -0.0120 | 1.44° |
| Our data | 0.884 | 0.015 | -0.024 | -0.006 | 0.730 | 1.01° |

TABLE I. Exchange couplings, energy broadening and spin canting for Cr-jarosite estimated in the literature and from the SpinW simulation of our data based on the Hamiltonian in eq. \[3\]. All values are given in units of meV, unless otherwise stated.

The spin waves appear diffuse in both $Q$ and $\hbar \omega$. A number of possible, non-exclusive reasons for this exist: it could indicate a broadening due to finite life times of the excitations, caused by the frustration in the lattice or by the relatively low spin value ($S = 3/2$); or it could indicate a distribution of exchange interactions due to randomly located vacancies at the A-site. Our spinW model attempts to take this into account in an effective way by including the Lorentzian broadening, $\Delta E$.

The intense spin wave feature at $Q \approx 1.1 \text{ Å}^{-1}$ has an incomplete gap, but the flat mode has a full gap of $\sim 0.2$ meV. Both gaps close at the $T_N \approx 3.8$ K. Our measurement thus provides evidence of the flat kagomé zero mode lifted to finite energies by the DM interaction, so far only observed in iron jarosite, in the compound NaBa$_2$Mn$_3$F$_{11}$ \[43\], and indirectly via magnetic resonance in Li$_9$Fe$_3$(P$_2$O$_7$)$_3$(PO$_4$)$_2$ \[47\].

FIG. 10. Left column: raw LET data for selected temperatures. Right column: Results of the factorization of the $Q$ and $\omega$ models described in sections IV.B.2-IV.B.1 for the same temperatures on the same color scale.
C. Classical spin liquid phase

Having obtained working models of the energy- and $Q$-dependence of the excitations, it is natural to investigate whether the dynamical response can be factorized as

$$S(Q, \omega, T) = S(Q, T) \times S(\omega, T) \quad (10)$$

combining the two descriptions obtained in sections IV B 1 and IV B 2. The results of this analysis is displayed in Figs. 10, which compares the raw LET data to the model resulting from from sections IV B 2 and IV B 1.

Factorization of the excitations implies that the energy- and $Q$-response is fully decoupled in the system. As expected, the factorization model below $T_N$ (Figs. 10 top) does not capture the spin waves at higher energies, which is decidedly a phenomenon with coupled energy- and $Q$-response. In contrast, at temperatures of 15 K and higher (Figs. 10 bottom) the factorization model matches the data quite well, as the system has progressed into a phase dominated by a simple paramagnetic response. However, it is interesting to note that in the strongly cooperative paramagnetic regime between $T_N$ and $2T_N \approx 8$ K, the system remain dominated by strongly coupled excitations that are correlated in energy- and $Q$-response. This is in line with observations of other frustrated compounds, including the pyrochlore MgCrO$_2$O$_4$ [18]. Furthermore, the $Q$-response of the dynamics indicate that the 2D dynamics coexist with the 3D magnetic ordering of the system, which is corroborated by the fact that the spin waves in the ordered state, at $T \sim T_N/2$, appear strongly damped, as judged from the large Lorentzian broadening obtained by the modeling. This is akin with recent observations in a similar compound, the classical spin liquid $h$-YMnO$_3$, which is a triangular-lattice Heisenberg magnet with $S = 2$ [20]. These singly-crystal neutron studies showed that small 2D clusters fluctuate in the cooperative paramagnetic phase, and coexist with the spin waves below the 3D ordering transition in a non-interacting manner. As a consequence, the spin waves appear more diffuse in powdered samples than in a single-crystal specimen [20]. As the temperature is decreased significantly, the spin waves increasingly dominate the picture. Thus, for Cr-jarosite, the diffuse appearance of the spin waves could also stem from a coexistence and superposition of the 2D dynamics appearing in the cooperative paramagnetic phase above $T_N$. This could also explain the lack of a complete spin wave gap at $Q = 1.1 \text{ \AA}^{-1}$ at 1.8 K, if 2D scattering is superimposed on the spin waves. While we have not seen any features in the data on powders to indicate a strongly enhanced quantum nature from the lower spin value, the effect of the geometrical frustration has been clear. Further investigation of these highly interesting phenomena in classical spin liquids and well as more detailed spin wave investigations would require a single-crystal specimen of Cr-jarosite.

VI. CONCLUSION

We have measured the excitations in well-characterized powder samples of Cr-jarosite. Neutron spectroscopy at low temperatures revealed diffuse spin waves with zero mode excitations, which were modeled with linear spin wave theory to obtain estimates for the exchange couplings. Persistent, diffuse excitations above $T_N$ in the cooperative paramagnetic phase were also observed. The energy-response of these were modeled assuming an exponential spin relaxation as well as a damped harmonic oscillator model representing the inelastic response below $T_N$. The $Q$-response were modeled based on 2D cluster excitations. The energy- and $Q$-response was found to be strongly coupled in both the ordered and cooperative paramagnetic phase, until it decoupled in the fully paramagnetic phase close to $\theta_{CW}$. This is indicative of classical spin liquid behavior.

ACKNOWLEDGMENTS

We thank the ISIS neutron facility, Rutherford Appleton Laboratory (United Kingdom) for awarding us beam time. The experimental work was supported by the Danish Foundation for Independent Research through the DANScatt (Grant No. 7055-00010B) and Research Council for Natural Sciences (U.G.N., A.B.A.A. and S.L.L.;Grant No. DFF-FNU-7014-00198). We acknowledge Hogni Weihe for helpful insight into ESR, and Christian B. Jørgensen for assistance with NMR measurements. S.J. thanks the Oticon Foundation and the Knud Højgaard Foundation for financial support.

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Appendix A: Synthesis details

KC$_3$(OD)$_6$(SO$_4$)$_4$ was synthesized using the redox-hydrothermal method. 4.65 g of K$_2$SO$_4$ (99.0 %, Sigma Aldrich) was dissolved in 42 mL D$_2$O (98 %, Cambridge isotopes laboratories), 2 mL of concentrated sulfuric acid (18 M) was added and the solution transferred to a 80 mL teflon lined stainless steel hydrothermal reaction vessel, which contained 0.67 g Cr (99.5 %, Sigma Aldrich)
pellets were placed in a Binder oven. The reaction vessel was heated at 210 °C for 5 days for samples 1 to 4 whereas a reaction time of 7 days were used for samples 5 and 6. The product was isolated by filtration, washed with D$_2$O, and dried in an oven at 60 °C for 4-24 hours. The details of the synthesis is summarized in table II.

| Sample no. | K$_2$SO$_4$ (g) | Cr (g) | D$_2$O (mL) | H$_2$SO$_4$ (mL) | Yield (g) | Yield (%) |
|------------|-----------------|-------|------------|----------------|-----------|-----------|
| 1          | 4.6596          | 0.6835| 42         | 2              | 1.5052    | 77        |
| 2          | 4.6578          | 0.6960| 42         | 2              | 1.4238    | 72        |
| 3          | 4.6710          | 0.6775| 43         | 2              | 1.4403    | 75        |
| 4          | 4.6657          | 0.6760| 42         | 2              | 1.6017    | 83        |
| 5          | 4.6670          | 0.6715| 42         | 2              | 1.72      | 90        |
| 6          | 4.6818          | 0.6740| 42         | 2              | 1.6       | 84        |

TABLE II. Amount of reactants used in each synthesis, yield of each synthesis, and percentage of the theoretical yield.

**Appendix B: PXRD**

The PXRD diffractograms of all samples were recorded on a Rigaku Miniflex using a copper target (K$_\alpha$ = 1.5405 Å) and collected in range 5°−70° (2θ) with a step size of 0.02° and a scan rate of 10° pr min. Fig. 11 shows the PXRD diffractogram of the Cr-jarosite sample. This matches earlier reported diffractograms [20, 41].

**Appendix C: SEM**

Selected samples including the combined Cr-jarosite were characterized by Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) for quantitative analyses of the heavier elements (K, S, and Cr) and sample morphology. This was performed on a Hitachi S-4800 scanning electron microscope equipped with an EDS. The elemental composition was determined at five random positions on the sample grid. Approximately 1 mg sample was dispersed into 1 mL of ethanol by ultrasonification for 15 min. A drop of the suspension was placed on a silicon wafer and then dried at 50° C for 10 min. Subsequently, the surface of the sample was coated with an approximately 15 nm layer of gold. EDS was measured in five random areas of the sample using a 15 kV accelerated electron beam and 15 mm working distance. Only sample batches 2 and 3 were measured.

Figure 12 shows the sample at different magnification levels illustrating the particle morphology. The measurements reveal both irregularly shaped and aggregated particles of size 10-50 µm, in agreement with the stacking disorder reported in the earlier study [20]. No additional phases were observed by SEM. The EDS measurements of the Cr-jarosite samples showed an average K:Cr:S ratio of 0.99(1):3.29(27):2.00(7) normalized to a S occupancy of 2. This is agreement with the stoichiometric 1:3:2 ratio taking the experimental uncertainties into consideration. The Cr content, which is slightly above the expected, which is ascribed to the presence of smaller pieces of unreacted chromium metal. Several larger chromium metal pieces were present in the isolated product and removed manually. However, such small amounts of unreacted Cr within the sample will not affect the NMR and neutron scattering studies.

![FIG. 11. PXRD spectrum of combined sample.](image1)

![FIG. 12. SEM images of a Cr-jarosite sample at magnifications 25 µm to 2.5 µm illustrating the particle morphology.](image2)
Appendix D: 2H MAS NMR simulation

Figure 13 illustrates the experimental and simulated $^2$H MAS NMR spectrum of the combined Cr-jarosite sample using the parameters obtained from fitting of the experimental data in table III.

![Experimental and simulated 2H MAS NMR spectrum](image)

**FIG. 13.** Experimental and simulated $^2$H MAS NMR spectrum (Hahn Echo) of combined sample recorded with 33 kHz spinning speed using the parameters in Table III.

Appendix E: Neutron spectroscopy plots for higher energies

The neutron spectroscopy data was performed with multirepping energies of $E_i = 2.20, 3.70, 7.60,$ and $22.20$ meV. For the lowest temperature of 1.8 K, the data with $E_i = 7.60$ meV in Fig. 14 more clearly shows the extend of the spin waves excitations, measurable up to approximately 4 meV.

![Excitations at 1.8 K in Cr-jarosite measured using $E_i = 7.60$ meV](image)

**FIG. 14.** Excitations at 1.8 K in Cr-jarosite measured using $E_i = 7.60$ meV.

Appendix F: Derivation of Q-dependent model

We hypothesize that the excitations above $T_N$ originate from two-dimensional dynamics of correlated spin clusters within the kagomé planes. Thus, we assume that the 2D excitations will be centered at the 2D ordering vector $(hk) = (10)$, located at $Q_0 = 1.005$ Å$^{-1}$. Due to the lack of 3D correlations, this scattering will occur as scattering rods around $Q = (10l)$. To obtain the observed pattern, the rods must then be powder-averaged in three-dimensional $(hkl)$ space. This is sketched geometrically in Fig. 15. Here the shaded area represents the overlap between the sphere of $(hkl)$ points of constant length, $Q$, and the cylindrical rod at $(10l)$, which has its smallest $Q$-value at $(100)$, with the length $Q = Q_0$. The shape of the scattering intensity is thus related to the overlap volume, which must be calculated.

The $(hk)$ rod has width $dw$, and the $Q$-sphere has width $dq \ll Q$ as illustrated in figure 15. Assuming that the intersection is not curved appreciably over the area, then the overlap area is $A = h dw$, where $h$ is the effective height. $h$ is also the hypotenuse in the triangle as indicated, and can be written as $h = dq / \sin \phi$, which thus makes the area $A = dw dq / \sin \phi$. By realizing that

![Reciprocal lattice representation of scattering by 2D reflections](image)

**FIG. 15.** Reciprocal lattice representation of scattering by 2D reflections.

the $\phi$ is equivalent in the triangles sketched in the left and right panels in figure 15, then it can be related to the scattering vectors via $\cos \phi = Q_0 / Q$.

The scattering intensity can be found as the ratio between the overlap volume, $V_o = A \ dw$ and the volume of the spherical shell, $V_s = 4 \pi Q^2 dq$:

$$V(Q) = \frac{V_o}{V_s} = \frac{dq \ dw^2 / \sin \phi}{4 \pi dq Q^2} \propto \frac{1}{Q \sqrt{Q^2 - Q_0^2}}, \quad (F1)$$

where the constants can be accounted for in an overall scaling factor. Now, this expression is only valid for $Q > Q_0$, and takes a value of zero for $Q < Q_0$. The expression diverges at $Q = Q_0$ in a square root manner, making the integral $\int V dQ$ take a finite value. This expression was also found in Ref. 15, which also finds a modification to eq. (F1) close to the divergence that is unnecessary for
TABLE III. $^2$H MAS NMR parameters for the combined sample recorded at 33 kHz spinning speed. The CSA parameters (Δ and ηω), quadrupole coupling ($C_Q$ and $η_Q$), signal intensities (Int.), Cr-site and K-site vacancies were found by fitting of the recorded $^2$H MAS NMR spectrum. The CSA parameters are given in the Haeberlen convention, where β is an Euler angle between principal axis of the CSA and quadrupole tensor. The vacancies are given per mol. The errors were estimated from the upper and lower boundaries of the fitted parameters.

| Site          | $δ_{iso}$ [ppm] | Δ [ppm] | ηω     | $C_Q$ [MHz] | $η_Q$ | β [deg] | Intensity [%] |
|---------------|----------------|--------|---------|------------|-------|---------|----------------|
| Cr$_2$-OD (D) | 872(10)        | -1020(100) | 1.00(10) | 0.216(40) | 0.10(10) | 45(10)  | 15(1)         |
| Cr$_2$-OD (K) | 828(5)         | -935(50)  | 1.00(10) | 0.214(10) | 0.09(10) | 55(5)   | 69(1)         |
| Cr$_2$-OD     | 229(5)         | 830(50)  | 0.00(10) | 0.101(5)  | 0.064(10) | 74(10)  | 10(1)         |
| Cr$_2$-OD (sharp) | 11(1)     | 0(10)   | 0.00(10) | 0.100(5)  | 0.00(10) | 0(5)   | 1>            |
| Cr$_2$-OD (sharp) | 7(2)        | 0(10)   | 0.00(10) | 0.050(5)  | 0.00(10) | 0(5)   | 6(1)          |
| D$_n$O (sharp) | 7(2)          | 0(10)   | 0.00(10) | 0.050(5)  | 0.00(10) | 0(5)   | 6(1)          |
| D$_n$O (sharp) | 7(2)          | 0(10)   | 0.00(10) | 0.050(5)  | 0.00(10) | 0(5)   | 6(1)          |
| δ:            | 0.085(5)       |         |         |            |        |         |                |
| Cr [%]:       | 2.8(3)         |         |         |            |        |         |                |
| K [%]:        | 0.41(10)       |         |         |            |        |         |                |

Here the magnetic form factor $f(Q)$ for Cr$_3^+$ has been added using tabulated values from ref. 49. The intensity has zero value for small values of $Q$, but starts to increase when the Lorentzian just touches $Q_0$. As $Q$ approaches $Q_0$ the value increases rapidly. At values clearly larger than $Q_0$, the value slowly decays. Thus, the asymmetric peak shape is caused by the asymmetry of the overlap function $V(Q)$. As an additional result of the convolution, the peak position is displaced to a value of $Q$ slightly larger than $Q_0$. 

A way to account for the short-range correlations in the magnetic system is to assume a finite-size broadening of the value of $Q_0$. We obtain this by a convolution of $V(Q)$ with a Lorentzian to model smearing by short-ranged correlations with correlation length $\xi = 1/\gamma$, where $\gamma$ is the full-width-half-max of the Lorentzian. Thus, the resulting convoluted line shapes is

$$C_L(Q) = \int_{-\infty}^{\infty} \frac{1}{Q^* \sqrt{Q'^2 - Q_0^2}} \frac{\gamma^2}{(\gamma/2)^2 + (Q' - Q)^2} dQ'.$$

Here the magnetic form factor $f(Q)$ for Cr$_3^+$ has been added using tabulated values from ref. 49. The intensity has zero value for small values of $Q$, but starts to increase when the Lorentzian just touches $Q_0$. As $Q$ approaches $Q_0$ the value increases rapidly. At values clearly larger than $Q_0$, the value slowly decays. Thus, the asymmetric peak shape is caused by the asymmetry of the overlap function $V(Q)$. As an additional result of the convolution, the peak position is displaced to a value of $Q$ slightly larger than $Q_0$. 

our purpose. These results are, in turn, a correction of the classical results for 2D line shapes by Warren [46].