Short-range order in the topological spin glass $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ using xyz polarized neutron diffraction

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We use polarized xyz neutron diffraction to examine the nature of the freezing transition to an unconventional topological spin-glass state in the $S=5/2$ *kagomé* antiferromagnet $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$. Measurements of the total magnetic scattering cross-section, $S(Q)$, were taken in the momentum-transfer range $0.5 \leq Q \leq 2.5 \text{ \AA}^{-1}$ between the temperatures 1.5 and 250 K. The observation of two-dimensional correlations at 250 K, i.e., in excess of 14 times the freezing temperature, is in agreement with predictions of an anisotropy-induced spin-glass freezing transition in an ordered *kagomé* antiferromagnet.

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I. INTRODUCTION

Fully frustrated magnetic lattices, notably of the *kagomé* and *pyrochlore* geometries, have been the subject of intense interest in recent years after predictions that at low temperatures, they could condense into unconventional ground states.¹ This has indeed been found to be the case in experimental realizations of these lattices. In fact, the variety of exotic low-temperature physics exhibited in these lattices is astounding, e.g., topological spin glass, spin fluid, spin ice, colossal magnetoresistance, heavy fermion, and superconductivity. One particular area of interest involves the possibility of disorder-free spin-glass states, of the types observed in the *kagomé* antiferromagnet $(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, the pyrochlores $\text{Y}_2\text{Mo}_2\text{O}_7$, $\text{Tb}_2\text{Mo}_2\text{O}_7$, and $\text{Y}_2\text{Mn}_2\text{O}_7$ and the pyrochlore slab $\text{SrCr}_x\text{Ga}_{1-x}\text{O}_{19}$.^{2–12} These spin-glass states are believed to be a consequence of the vertex sharing geometries, and they have been termed *topological* spin glasses in order to distinguish them from conventional site-disordered systems.^{13,14}

In this article we report xyz polarized neutron-scattering measurements of a powder sample of the two-dimensional (2D) *kagomé* antiferromagnet $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ between 1.5 and 250 K. Unpolarized neutron-diffraction measurements of this material are hindered by the large background from strong nuclear Bragg reflections and incoherent scattering from protons present in partially deuterated samples. These limit accurate determination of the form of the diffuse scattering from the short-ranged correlations in the paramagnetic- and spin-glass-like phases, and as a consequence, only approximate characterization of spin-spin correlations and their temperature dependence is possible. Polarization analysis provides a simple means of separating the coherent and incoherent magnetic contributions from other scattering present since scattering with a change in the polarization direction of a neutron (spinflip) can only be magnetic. The improved signal-to-noise ratio that this leads to, when compared to unpolarized experiments, has enabled observation of magnetic correlations in

$(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ at higher temperatures and with greater accuracy than in previous experiments.³ Their temperature dependence suggests that the spin-glass freezing transition is a consequence of two energy scales, as has been proposed for an anisotropy-induced glass transition in Refs. 13 and 14. Investigation was also carried out of additional features predicted by theoretical calculations.^{15,16}

The *kagomé* antiferromagnet is particular as the sharing of only one vertex between triangular plaquettes (Fig. 1) is insufficient to define a unique ground state. Rather, this special topology gives rise to a highly degenerate ground-state manifold and a finite ground-state entropy. In the absence of any additional influences, the nearest-neighbor Heisenberg *kagomé* antiferromagnet is not expected to order, even at $T=0$.^{15,17–19} Further-neighbor interactions, quantum or thermal fluctuations, select symmetric states that have the highest density of low-energy excitations from this infinite manifold, by an effect that Villain termed *order by disorder*.²⁰ Two particular symmetric states, termed the $q=0$ and $\sqrt{3} \times \sqrt{3}$ configurations, are favored and these are depicted in Fig. 2.^{18,21–24} The $q=0$ and $\sqrt{3} \times \sqrt{3}$ states correspond, re-

FIG. 1. The two-dimensional *kagomé* lattice realized by vertex sharing coordination octahedra of the Fe^{3+} in the jarosite crystal structure.

FIG. 2. The formation of (a) open and (b) closed spin folds in the $q=0$ and $\sqrt{3} \times \sqrt{3}$ spin configurations, respectively.

spectively, to configurations with uniform (*ferromagnetic*) and staggered (*antiferromagnetic*) chiralities, where the chirality κ is defined as the pairwise vector product clockwise around a triangle:

$$\kappa = \frac{2}{(3\sqrt{3})} [\mathbf{S}_1 \times \mathbf{S}_2 + \mathbf{S}_2 \times \mathbf{S}_3 + \mathbf{S}_3 \times \mathbf{S}_1], \quad (1)$$

In addition to this degeneracy, the special exchange topology of this lattice provides a medium for the formation of collective zero-energy spin rearrangements that allow the system to explore the ground-state manifold. These take the form of line defects that involve the continuous rotation of moments on two sublattices about the direction defined by the third. They may either traverse the entire lattice (“open” spin folds) or form localized loops (“closed” spin folds) depending on the initial spin configuration.^{13,14,25} Examples of these topological defects in the $q=0$ and the $\sqrt{3} \times \sqrt{3}$ spin configurations are given in Fig. 2. It has been argued that interactions between such defects can give rise to spin-glasslike responses even in the absence of significant disorder.^{13,14} However, in the proposed model, an easy plane-spin anisotropy is required in order to induce a critical transition at a finite temperature. The presence of such a finite-temperature freezing transition would mark a sharp contrast with conventional two-dimensional site-disordered spin glasses, as these display a critical transition only at $T=0$.²⁶

The spin-glass state of the $S=5/2$ *kagomé* antiferromagnet $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ has attracted interest recently due to its unconventional nature.^{2–4,27,28} Rather than resulting from a competition between random superexchange paths, as is the situation in site-disordered spin glasses, this glassy magnetic phase exists in a system with only a small amount of disorder (the coverage of the magnetic lattice is $\sim 97\%$) and it is possible that it is based on the interactions between topological defects. Remarkably, reduction in the coverage of the magnetic Fe lattice is found to first cause an

increase in the freezing temperature T_g and, if sufficient, to destabilize this glass-like state sufficiently for the formation of long-range Néel order with the $q=0$ spin configuration.^{4,27,29}

Both the thermodynamic and dynamic properties of this glassy phase are in clear contrast to those of site-disordered systems: the magnetic contribution to the specific heat has a quadratic dependence on temperature, rather than the linear dependence typically observed in site-disordered spin-glass systems,^{30,31} and the out-of-equilibrium dynamics of this glassy phase have a far weaker temperature dependence than seen in conventional systems.⁵ The studies of how these slow “aging” dynamics are affected by temperature cycling have also shown that the hierarchical image of metastable states that evolve as a function of temperature, that is extensively used for conventional site-disordered systems,²⁶ is not appropriate to this *kagomé* spin glass.⁵

II. SAMPLE PREPARATION

A powder sample of $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ was prepared by hydrothermal reaction of anhydrous $\text{Fe}_2(\text{SO}_4)_3$ in D_2O . Anhydrous $\text{Fe}_2(\text{SO}_4)_3$ was synthesized by refluxing 100 g of $\text{FeSO}_4 \cdot 7(\text{H}_2\text{O})$ in 1 liter of $\text{c.H}_2\text{SO}_4$ under continuous nitrogen gas flow.³² Unreacted $\text{FeSO}_4 \cdot 7(\text{H}_2\text{O})$ was removed by washing the resulting pink precipitate with $\text{c.H}_2\text{SO}_4$ with vacuum filtration. The iron sulfate was then well dried under vacuum before being washed with acetone. To prevent absorption of water, the resulting product was stored in a dry atmosphere. The yield was approximately 120 g of $\text{Fe}_2(\text{SO}_4)_3$. Examination by powder x-ray diffraction indicated that the anhydrous sulfate while being of low crystallinity was phase pure. $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ was synthesized from a solution of 40 g of $\text{Fe}_2(\text{SO}_4)_3$ in 300 ml D_2O .³ The solution was preheated in a PTFE lined stainless steel bomb at 70°C for 4 hours to solubilize the iron sulfate, before being heated at 155°C for 4 hours to precipitate the jarosite. After cooling, the ochre product was washed with D_2O and dried in a vacuum furnace at 120°C . From the starting purity of the chemicals, we estimate a residual hydrogen/deuteride (H/D) ratio for our samples of ~ 0.05 . This level of deuteration was later confirmed during the polarized neutron-diffraction experiments using the degree of incoherent scattering from the sample.

III. NEUTRON DIFFRACTION

Approximately 11 g of $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ was contained in a 15 mm aluminum can and measurements taken at a number of temperatures between 1.5 and 250 K using a standard Institut Laue-Langevin (ILL) “orange” cryostat. The polarized neutron experiments were performed on the multipurpose neutron-scattering spectrometer D7 at the high-flux reactor of the ILL. D7 operates on the cold source and data were collected using incident neutrons with wavelengths of $4.8 \text{ \AA}$ (3.5 meV). Some additional measurements were taken at $3.1 \text{ \AA}$ (8.5 meV). Polarization of the incident neutrons and polarization analysis using the xyz difference technique^{33,34} are achieved by supermirrors. In this configu-

FIG. 3. Sum of magnetic and nuclear components to the scattering from $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ at $T = 1.5$ K.

ration, 32 scattering angles are recorded simultaneously. Spin-flip (SF) and nonspin-flip (NSF) intensities are measured for the polarization of the incident beam in the x , y , and z directions. In xyz polarization analysis, the x - y plane is the scattering plane and is defined by the incident beam and the positions of the detectors. Six different data sets are recorded with the incident beam polarized successively in x , y , and z directions. The recorded intensities are labeled $I_{SF}^{(xyz)}$ and $I_{NSF}^{(xyz)}$. The measurements were taken as a function of scattering angle without time-of-flight analysis, and so $S(Q, \omega)$ (where $Q = 2\pi/d$) is integrated over all energy transfers ω . The absolute normalization by use of a vanadium standard allows the pure magnetic intensity, I_{magn} , in units of $\text{barn}(\text{sr})^{-1} (\text{fmu})^{-1}$, to be obtained from either:

$$\frac{1}{2} I_{\text{magn}} = I_{SF}^{(x)} + I_{SF}^{(y)} - 2I_{SF}^{(z)} \quad (2)$$

or

$$\frac{1}{2} I_{\text{magn}} = 2I_{NSF}^{(z)} - I_{NSF}^{(x)} - I_{NSF}^{(y)} \quad (3)$$

The two different combinations correspond to independent measurements and the final intensity is taken as their average.

IV. RESULTS

Figure 3 shows the total diffraction pattern, obtained from the summation of all SF and NSF data collected with incident neutrons of $\lambda = 4.8$ Å at 1.5 K. In the vicinity of strong nuclear Bragg peaks the corrections due to imperfect spin-flipping ratios are important despite their high values (≥ 50), because of the relative weakness of the magnetic scattering. This accounts for the slightly larger error bars at $Q \approx 2.0$ Å $^{-1}$.

The differential magnetic cross section, $d\sigma/d\Omega$, is displayed at 2, 20, 50, 70, 100, 140, and 250 K in Fig. 4. In a truly paramagnetic regime the Fe^{3+} moments would have no significant spatial correlations and the Q dependence of the scattering would be given by the paramagnetic form factor. Instead of this, at 250 K there is a broad maximum in $S(Q)$ centered at $Q \approx 1.2$ Å $^{-1}$. The large width of this reflection and its maximum at finite Q indicates that this reflection is

FIG. 4. The temperature and Q dependence of the magnetic scattering. The data for each temperature are separated by an increment of one to the differential magnetic cross section.

due to short-ranged antiferromagnetic correlations. The broad peak is seen to sharpen and increase in intensity upon cooling.

As data were collected without energy analysis, the total magnetic cross section for all energy transfers is given by the integral of the total scattering intensity over all Q . To investigate the cross section of the diffuse magnetic scattering, this integration was carried out over the Q -range $0.15 \leq Q \leq 2.5$ Å $^{-1}$. The temperature dependence of the integrated area is displayed in Fig. 5 and shows a gradual increase from 250 K upon cooling, rising more rapidly at lower temperatures, and finally saturating near T_g at ~ 20 K. At 1.5 K the value of the total magnetic cross section is $\sigma_{\text{tot}} = 2.57$ $\text{barn}(\text{fmu})^{-1}$ in zero external magnetic field.

The elastic differential magnetic cross section of a primitive paramagnet, ignoring Debye-Waller terms, is given by³⁵

$$d\sigma/d\Omega = \frac{2}{3} (\gamma r_0)^2 \left\{ \frac{1}{2} g f(Q) \right\}^2 S(S+1) \text{ barns}(\text{sr})^{-1}. \quad (4)$$

Where $\gamma = 1.9132$, r_0 is the classical radius of the electron and has a value of 2.818×10^{-15} m, g is the Landé splitting factor, S is the spin of the magnetic ions, and $f(Q)$ is the magnetic form factor. Upon substitution of the values for the constants and assuming $g = 2$ this reduces to

$$d\sigma/d\Omega = \frac{2}{3} \times 0.29 \times \{f(Q)\}^2 \times S(S+1) \text{ barns}(\text{sr})^{-1}. \quad (5)$$

FIG. 5. (a) Total magnetic cross section ($\circ$) integrated over the Q -range $0.5 \text{ \AA}^{-1} \leq Q \leq 2.5 \text{ \AA}^{-1}$ and the correlation length ($\bullet$) range from Eq. (7) as a function of temperature. The line is drawn as a guide to the eye.

While in the fluctuating paramagnetic phase, each moment has contributions from all the m_s states, below the ordering transition, the spins are static. Consequentially, only the lowest m_s state is occupied and the expectation value of the S^2 is reduced from $\hbar^2 S(S+1)$ to $\hbar^2 S^2$. Therefore, in the spin-glass phase, Eq. (5) becomes

$$d\sigma/d\Omega = \frac{2}{3} \times 0.29 \times \{f(Q)\}^2 \times S^2 \text{ barns(sr)}^{-1}. \quad (6)$$

For an ion with $S=5/2$, the total cross section for static random spins is thus 1.21 barn. There are 3 Fe^{3+} ions per formula unit, which, upon taking an average value of the magnetic form factor as $\langle f(Q)^2 \rangle = 0.76$ over this Q range, predicts the total cross section per formula unit to be $\sigma_{tot} = 2.76$ barn. Therefore, within the energy-transfer range of D7, $-0.13 \leq \hbar\omega \leq 10$ meV for neutrons of wavelength 4.8 Å, over the Q range of our measurements, 93% of the cross section expected for the static random spins of a spin glass is observed at $T=1.5$ K.

A model for the diffuse scattering $S(Q)$ is described in Sec. IV A. From the analysis in Sec. IV A, we extract the static two-dimensional spin-spin correlation length from $S(Q)$ as a function of temperature.

A. Two-dimensional short-range order

The most striking feature of the reflection with a maximum at $Q \approx 1.2 \text{ \AA}^{-1}$ is its asymmetry, as shown in Fig. 4. The sharp edge on the low- Q side of the peak, and slow fall off with increasing Q , is characteristic of a two-dimensional system with short-range correlations within a plane, but without correlations between them. The static structure factor, $P(Q)$, of such quasi-two-dimensional short-range order is described analytically by a Warren function.³⁶ This function was originally developed to describe diffuse scattering of x rays from amorphous graphite, a material in which there is short-range structural order within a set of planes, but no structural correlations between these planes. It can be adapted to describe magnetic scattering by the addition of a

FIG. 6. Diffuse component to the scattering from $\text{RbFe}_3(\text{SO}_4)_2(\text{OD})_6$ at $T=1.5$ K and fit to a Warren peak [Eq. (7)] centered at $Q=1.06 \text{ \AA}^{-1}$ with a correlation length of $\approx 20 \text{ \AA}$.⁴

magnetic form factor $f(Q)$.³⁷ The static structure factor, $P(Q)$ close to the peak maximum is then expressed by:

$$P(Q) = Km \frac{F_{hk}^2 \left[1 - 2 \left(\frac{\lambda Q}{4\pi} \right)^2 + 2 \left(\frac{\lambda Q}{4\pi} \right)^4 \right]}{\left(\frac{\lambda Q}{4\pi} \right)^{3/2}} \times \left(\frac{\xi}{\lambda \sqrt{\pi}} \right)^{1/2} F(a) [f(Q)]^2, \quad (7)$$

where

$$a = \frac{\xi \sqrt{\pi}}{2\pi} (Q - Q_0) \quad (8)$$

and

$$F(a) = \int_0^{10} \exp[-(x^2 - a)^2] dx. \quad (9)$$

Here ξ is the spin-spin correlation length, K is a scaling constant, m is the multiplicity of the reflection, F_{hk} is the two-dimensional structure factor for the spin array, and Q_0 is the center of the peak. Strictly speaking, the upper limit of the definite integral of Eq. (9) should be infinity, but the value of the integral does not converge for this boundary condition so it is usually evaluated to a limit that is both convergent³⁷ and sufficiently large not to introduce significant errors. An upper limit of ten serves this purpose well, and reproduces the values tabulated in Ref. 36.

It has been previously noted that those Fe jarosites that display long-range order at low temperatures, also possess extensive amounts of short-range correlations that give rise to similar Warren-type scattering. As an example of the use of this function, the diffuse scattering from the closely related material $\text{RbFe}_3(\text{SO}_4)_2(\text{OD})_6$ collected at 1.5 K,⁴ and a fit to Eq. (7) are displayed in Fig. 6. When the form of the Warren function is compared with the diffuse scattering from

FIG. 7. Magnetic component to the scattering from $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ at $T=1.5$ K and fit to a Warren peak [Eq. (7)] centered at $Q=1.2$ $\text{\AA}^{-1}$ with a correlation length of ≈ 10 $\text{\AA}$.

$(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$, additional scattering at high Q that is not taken into account by Eq. (7) is evident.

The failure of the Warren line shape to describe the scattering at higher Q indicates that there is either a failure in its applicability in the description of the static spin correlations in this magnetic system, or that there is an additional scattering component from fluctuating spins. As the static short-ranged correlations of the isostructural $\text{RbFe}_3(\text{SO}_4)_2(\text{OD})_6$ and $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ are expected to be very similar, we deduce that this additional component is likely to be dynamic in origin, and is the result of strong fluctuations in $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ that exist even far below the freezing temperature. Scattering from these fluctuating moments will contribute to these measurements as collections were made without energy analysis. Despite this additional scattering, Eq. (7) can still be used to estimate the spin-spin correlation length as this quantity is principally dependent on the half width of the diffuse peak. For this reason the region used for the fits to Eq. (7) was limited to the range 0.5 $\text{\AA}^{-1} \leq Q \leq 1.5$ $\text{\AA}^{-1}$.

An example of such a fit to the data collected from $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ at 1.5 K is given in Fig. 7 and the temperature dependence of the two-dimensional spin-spin correlation length from fits of Eq. (7) to the peak at $Q \approx 1.2$ $\text{\AA}^{-1}$ is shown in Fig. 5.

Additional insight into the physical nature of the short-ranged correlations can be gained by Fourier transforming the data to give the radial correlation function $g(r)$:^{38–41}

$$g(r) = \int_{Q_{\min}}^{Q_{\max}} I(Q) J(Q)^{-2} Q \sin(Qr) dQ, \quad (10)$$

where $I(Q)$ is the magnetic scattering intensity at Q . Figure 8 shows the Fourier transform of the data collected from $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ at temperatures between 2 and 250 K taking the same limits for Q as the fits to the Warren equation. The arrows indicate the first to third-neighbor Fe-Fe bond distances in the *kagomé* plane, as taken from previous work.⁴ The main contribution to the error of this

FIG. 8. Real-space radial correlation function for $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ at $T=2, 20, 70$, and 250 K. Arrows indicate the three nearest-neighbor distances for the Fe^{3+} sublattice.

transform is likely to arise from the truncation effects from the limited Q range of the datasets.

For scattering from an isotropic system of static spins, strong minima and maxima are present in the radial correlation function at nearest- and further-neighbor distances. Anisotropic correlations, as are present in a 2D antiferromagnet, would not give rise to extrema at these characteristic distances.⁴¹ Despite this, qualitative information on the spin-spin correlations can still be derived simply from these Fourier Transforms. From Fig. 8, we see that there are strong antiferromagnetic nearest-neighbor correlations and ferromagnetic correlations at a distance that approximates to the second-neighbor distance. Comparison of the radial correlation functions obtained from the data collected at different temperatures indicates that there is no marked change in the nature of these correlations upon cooling, other than an increase in their degree. That is to say, their spatial dependence is found to be largely insensitive to the temperature within the error of these experiments, as is confirmed by fits to Eq. (7).

Again, a comparison with $\text{RbFe}_3(\text{SO}_4)_2(\text{OD})_6$ is useful if the assumption is made that its short-ranged order is based on domains of triangles with the same $q=0$ structure as is responsible for the magnetic Bragg reflections, the ordered magnetic structure of $\text{RbFe}_3(\text{SO}_4)_2(\text{OD})_6$ is presented in Fig. 9. The radial correlation for $\text{RbFe}_3(\text{SO}_4)_2(\text{OD})_6$ at 1.5 K obtained from the data published in Ref. 4 is presented in Fig. 10. The general forms of the correlation functions for these two materials are very similar: they have strong nearest-neighbor antiferromagnetic correlations, and weaker ferromagnetic second-neighbor correlations. Given the similarity of the radial correlation functions of these two materials, it is tempting to suggest that the short-ranged correlations in $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ are also based around the $q=0$ ordering pattern. However, as noted in Sec. IV C, the special symmetry of the *kagomé* lattice limits the determination of the detailed nature of the short-ranged correlations from powder-diffraction data.

FIG. 9. The $q=0$ magnetic ordering of $\text{RbFe}_3(\text{SO}_4)_2(\text{OD})_6$. The three *kagomé* layers of the hexagonal cell are labeled *ABC*. The moments in the second half of the magnetic unit cell are reversed.

B. Variation of short-range correlation length and total magnetic cross section with temperature

The integrated magnetic cross section of the diffuse peak, and the two-dimensional spin-spin-correlation length determined from fits to Eq. (7), follow a very similar temperature dependence: both show a gradual increase upon cooling below 150 K with a maximum in the slope at ~ 50 K. A saturation value of $2.57 \text{ barn (fmu)}^{-1}$ is observed in the magnetic cross section below ~ 12 K. Unfortunately, the large statistical error in the correlation length determined from the fits to the data prevents us from determining whether it rises to a maximum, or if the spin-spin correlations continue to evolve in spatial extent once the degree of short-range ordering has saturated. However, the improved statistics afforded by polarization analysis and the extended Q range of the data have allowed a more accurate analysis of the diffuse scattering function, and the observation of significant short-range spin-spin correlations at 250 K, far higher than observed previously in unpolarized experiments.³ We note that the spa-

FIG. 10. Real-space radial correlation function for $\text{RbFe}_3(\text{SO}_4)_2(\text{OD})_6$ at $T=2$ K. Arrows indicate the three nearest neighbor distances for the Fe^{3+} sublattice.

tial extent of the correlations at low temperature is found to be significantly less than formerly deduced from unpolarized experiments: at 1.5 K, the spin-spin correlation length corresponds to $\xi = 10 \pm 1 \text{ \AA}$.

C. Comparison with Monte Carlo and Spin-Wave Results

The form of $S(Q)$ has been predicted by theorists for elastic scattering from a *kagomé* antiferromagnet with nearest-neighbor exchange, using both Monte Carlo methods and spin-wave analysis around the $q=0$ and $\sqrt{3} \times \sqrt{3}$ spin structures.^{15,16,42} When adjusted so that their scale in Q is appropriate to the cell parameter of $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ ($a=7.237 \text{ \AA}$), the main feature of these predictions is a broad reflection centered at $Q \approx 1.1 \text{ \AA}^{-1}$, in good agreement with our data. Unfortunately, little more can be deduced about the form of these short-ranged correlations from the experimentally observed $S(Q)$, because to a first approximation, the symmetry of the *kagomé* lattice prevents the powder average from being characteristic of the local chirality of the ordering.

Monte Carlo simulations also revealed additional diffuse features in $S(Q)$ at higher values of Q , for example at $Q = 1.16, 2.40$, and $3.15 \text{ \AA}^{-1}$. Unfortunately, the presence of strong nuclear Bragg peaks for $Q \geq 1.9 \text{ \AA}^{-1}$, and the lower neutron flux of the D7 diffractometer at $3.1 \text{ \AA}$, prevented the unambiguous determination of the presence or absence of any such features within the statistical accuracy of the data.

V. DISCUSSION

$(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ presents a very interesting example of a 2D spin glass. One of the contrasts that it displays with conventional site-disordered 2D spin glasses,⁴³ is a critical glass transition at finite temperature.⁵ While the details of this transition are still unclear, our data are in agreement with the hypothesis that this transition to a topological spin-glass state is brought about by a *combination* of two different energy scales.^{13,14,5} The first is set by the nearest-neighbor exchange integral J and the second is presumed to be that of an easy-plane anisotropy. In an unfrustrated antiferromagnet with nearest-neighbor correlations, long-range ordering, would occur at a temperature approximating to θ_{CW} . In the case of the *kagomé* antiferromagnet this transition is suppressed by the high frustration of the system, and only short-range correlations form. These are evidenced by the diffuse function observed in the neutron scattering and a curvature of the inverse susceptibility away from the Curie-Weiss law, such as that found in $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ below 300 K ($> 14T_g$).⁴ It is only at far lower temperatures that the presence of a second energy scale causes the topological spin-glass phase transition to take place, still at finite temperature. According to the model presented in Refs. 13 and 14, this freezing occurs when the spin dimensionality is reduced from being completely Heisenberg. An upper limit of the freezing temperature may therefore be taken by assuming the *spin stiffness* is that of the *xy* system. This then leads to a transition at $T_g \sim \theta_{CW}/48$, in good agreement with a Weiss temperature of $\theta_{CW} \sim -600 \text{ K}$ and the observation of a criti-

cal spin glass temperature at $T_g \approx 17$ K.

Analysis of the diffuse scattering by the short-ranged correlations is complicated by the symmetry of the *kagomé* lattice: short-range ordering with the $q=0$ and $\sqrt{3} \times \sqrt{3}$ spin structures, or indeed any structure based on local 120° correlations, display similar elastic powder neutron diffraction averages and it is consequentially not possible to determine the detailed nature of the spin-spin correlations from powder diffraction without more specialized calculations that include the inelastic responses of the system. However, some information can be deduced from comparison with the jarosites that do possess a transition to a long-range ordered state. In all cases studied to date, that is for the jarosites $A\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ with $A=\text{Na}, \text{K}, \text{Rb}, \text{Ag}$, and NH_4 ,^{4,44–46} the long-range order is found to be based on the $q=0$ spin configuration. In addition to the magnetic Bragg peaks that are the result of long-range order, diffuse scattering due to short-range correlations is seen above and below T_c .^{4,44} It is natural to assume that such short-range correlations are also based on domains of the $q=0$ configuration, i.e., domains of triangles with uniform chirality. Given the structural similarities between these jarosites and $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$, we might expect that in this material, the short-range order observed at high temperatures has a bias towards similar local orderings, and is not simply made up of 120° motifs with purely disordered chiralities. Our experiments show that the degree of these correlations increases only gradually upon cooling with no appreciable divergence at T_g . While our data show that their spatial extension also increases smoothly from 250 K, statistical errors prevent the determination of whether they too have a maximum value.

The apparent conflict between the observation of essentially static spins in this work and in recent neutron spin-echo experiments,²⁸ and the finding from μSR that $\sim 50\%$ is of the moments are dynamic at low temperature,⁴⁷ arises

because of the different timescales of these techniques. While muon depolarization is influenced by spin fluctuations with a lifetime of $10^{-7} - 10^{-8}$ s, neutrons probe faster dynamics: in the case of neutron spin echo these are of the order of 10^{-9} s and in the experiments we report here 10^{-12} s.

VI. CONCLUSION

In conclusion, using polarized neutron diffraction we have examined the diffuse scattering from the topological spin glass $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$. The temperature dependence of $S(Q)$ from the short-ranged antiferromagnet correlations indicates a gradual freezing of spins below $T > 250$ K that is in agreement with the involvement of two energy scales in the spin freezing process, i.e., the exchange integral J and the easy-plane anisotropy energy. In the spin-glass phase, $\sim 93\%$ of the magnetic cross section expected for a collection of frozen static moments is observed, which indicates that the spins are largely static within the energy resolution of these data. At the lowest temperatures studied, the topological spin-glass phase is found to have antiferromagnetic correlations that extend to ~ 10 Å.

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