Haydeeite: a spin-1/2 kagome ferromagnet

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The mineral haydeeite, α-MgCu2(OD)6Cl2, is a \( S = 1/2 \) kagome ferromagnet that displays long-range magnetic order below \( T_C = 4.2 \) K with a strongly reduced moment. Our inelastic neutron scattering data show clear spin-wave excitations that are well described by a Heisenberg Hamiltonian with ferromagnetic nearest-neighbor exchange \( J_1 = -1.64 \) meV and antiferromagnetic exchange \( J_d = +0.48 \) meV between neighbors across the hexagons of the kagome lattice. This places haydeeite very close to the quantum phase transition between ferromagnetic order and non-coplanar twelve-sublattice cuboc2 antiferromagnetic order. Diffuse dynamic short-range ferromagnetic correlations observed above \( T_C \) persist well into the ferromagnetically ordered phase with a behavior distinct from critical scattering.

Quantum \( S = 1/2 \) spins localized on the vertices of the corner-sharing triangular network of a two-dimensional kagome lattice are highly frustrated magnetic model systems that are predicted to form quantum spin liquids (QSL) with exotic ground states and excitations [1]. While initial work focused on nearest-neighbor Heisenberg kagome antiferromagnets [2–7], such as the mineral herbertsmithite [8], it has been realized that further neighbor interactions or the antisymmetric Dzyaloshinski-Moriya (DM) interaction, which is intrinsically allowed in the kagome lattice, may lead to even more fascinating ground states [9–12]. Even for the case of classical spins, the kagome lattice with interactions beyond nearest neighbors (NN) [see Fig. 1(a)] shows a very rich magnetic phase diagram with complex non-coplanar, sometime chiral, multi-k magnetic structures [13–15]. This is illustrated by the uniformly filled areas in Fig. 1(b) for the case of ferromagnetic NN interaction \( J_1 \). Very recently, it was shown that for quantum spins, QSL phases “invade” part of the classical phase diagram [16–18], as shown by the open circles in Fig. 1(b).

An experimental realization of such a system is the mineral kapellasite [19–23], where high-temperature fits to the magnetic susceptibility [22] put this system into the area of the phase diagram that corresponds to the non-coplanar twelve-sublattice magnetically ordered cuboc2 phase [see (blue) solid square in Fig. 1(b)]. However, kapellasite does not actually order magnetically, but forms a QSL with gapless spinon-like excitations and short-range correlations, which are reminiscent of the cuboc2 phase [21]. Following recent theoretical work [18], it can now be understood that kapellasite falls in the region of the phase diagram where quantum fluctuations favor a chiral gapless spin liquid state labelled CSL-A, which has similar short-range correlations to kapellasite.

In this Work, we explore experimentally other parts of the phase diagram shown in Fig. 1(b). By replacing the Zn\(^{2+}\) ion [green open circle in Fig. 1(a)] of kapellasite by Mg\(^{2+}\), we expect the \( J_d \) exchange integral to change the most. Indeed, such a substitution leads to the mineral haydeeite, where \( J_d \) is decreased such that the system orders ferromagnetically [20]. Our inelastic neutron scattering data allow us to characterize the ground state and determine the exchange integrals via spin-wave theory. We find that haydeeite is very close to a quantum phase

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transition between a ferromagnetic state and the cuboc2 antiferromagnetic state, and shows unusual dynamic diffuse scattering.

Haydeeite, α-MgCu2(OH)6Cl2, crystallizes in the trigonal P3m1 space group (164) with lattice parameters a = 6.2885(1) Å and c = 5.7271(1) Å. It has the same crystallographic structure as kapellasite [19, 20], with S = 1/2 Cu2+ spins forming a highly two-dimensional kagome lattice of undistorted corner-sharing triangles. The kagome lattice is sketched in Fig. 1(a) with the main exchange interactions J1, J2, and Jd. The diamagnetic Mg ions sit at the centers of the hexagons. Note that haydeeite should not be confused with its polymorph 'Mg-herbertsmithite', which has the same chemical formula but a different crystallographic structure and different magnetic properties [24].

A 1.75 g powder sample of fully deuterated haydeeite was synthesized using a high-yield variant of the standard synthesis method [20, 25]. Powder diffraction using x-rays and neutrons confirms the crystallographic structure [20] and, as expected, a higher degree of site order than in kapellasite. In haydeeite, there are no Cu ions on the Mg site and about 16% Mg ions on the Cu sites, resulting in a slightly diluted kagome lattice.

Measurements of the magnetic susceptibility $\chi(T)$ at a field of $H = 5$ T and the magnetization $M(H)$ at $T = 2$ K show that deuterated and hydrogenated haydeeite have the same magnetic properties. Ferromagnetic ordering sets in at $T_C = 4.2$ K, the saturated moment is 0.83 $\mu_B$ per mole of Cu, the Curie-Weiss temperature is essentially zero, and a drop in $\chi T$ at low temperatures suggests antiferromagnetic components.

Inelastic neutron scattering measurements on the fully deuterated α-MgCu2(OD)6Cl2 powder sample were performed on the time-of-flight (TOF) spectrometers IN5 and IN4 at the Institut Laue-Langevin, using incident energies $E_i$ of 3.55 and 16.6 meV. These measurements show both acoustic and optic spin-wave branches in the ferromagnetically ordered phase as well as weak magnetic Bragg peaks. The high sensitivity of the inelastic TOF technique allows us to conclude that these Bragg peaks, which could not be observed by standard (energy-integrating) neutron diffraction techniques, correspond to a $k = 0$ propagation vector. Combined with the magnetic susceptibility measurements, this confirms the ferromagnetic ordering.

However, the inelastic TOF technique is not well suited to actually determine the magnetic structure. We have compared the observed magnetic scattering to that calculated for the three irreducible representations (IREP) obtained using representation analysis [20]. The best description obtained using a single IREP corresponds to a collinear magnetic structure with the moments along the $b$ axis, see Fig. 2. A rough estimate of the magnetic moment gives a strongly reduced magnitude of 0.2 $\mu_B$ at $T = 1.5$ K, which suggests strong quantum fluctuations.

A slightly improved description of the data can be found combining two IREPs, in which case the magnetic moments are still collinear but tilted 20 degrees out of the kagome plane.

The observed inelastic neutron scattering intensity is proportional to the dynamic magnetic susceptibility $\chi''(Q, E)$, shown in Fig. 3 for α-MgCu2(OD)6Cl2 before correction for the magnetic form factor. Acoustic spin waves are clearly observed in the low-energy data of the ferromagnetically ordered phase shown in Fig. 3(a), and even better after subtraction of the paramagnetic high-$T$ data of Fig. 3(b), see Fig. 3(c). Optic spin waves are observed at higher energies, see Fig. 3(e).

The magnetic scattering can be modelled using standard linear spin-wave theory for an isotropic Heisenberg Hamiltonian with further-neighbor interactions. Since haydeeite has three magnetic ions per magnetic unit cell and a propagation vector $k = 0$, there are three spin-wave modes, whose energies and intensities are obtained by diagonalizing a real $3 \times 3$ matrix. Standard Monte Carlo techniques are then used to obtain the powder-averaged dynamic susceptibility $\chi''(Q, E)$. The best agreement is found for $J_1 = -1.62$, $J_2 = 0$, and $J_d = 0.48$ meV, where negative exchange integrals correspond to ferromagnetic interactions. The corresponding calculated $\chi''(Q, E)$ is shown in Figs. 3(d) and 3(f). The quality of the agreement is clearly seen in $Q$ cuts at constant energy, see Fig. 4. The calculated spectra are very sensitive to the value of $J_2$, and from our spin-wave analysis we infer that $|J_2|/|J_1| < 0.1$.

Diffuse magnetic scattering is clearly observed at temperatures above $T_C$, as shown in Fig. 3(b) at $T = 8$ K.

FIG. 2. (Color online) Wave-vector dependence of the magnetic scattering integrated over the elastic peak ($|E| < 0.02$ meV) from haydeeite, α-MgCu2(OD)6Cl2, at $T = 1.5$ K after subtraction of 8 K data. The (red) dots are experimental data, the solid (black) line going through the data points is the calculated diffraction pattern, and the (blue) line at the bottom is the difference.
FIG. 3. (Color online) Dynamic magnetic susceptibility $\chi''(Q, E)$ on a linear intensity scale as a function of wave vector $Q$ and energy $E$ of fully deuterated haydeeite. Low-energy data measured with $E_i = 3.55$ meV are shown in the panels: (a) ferromagnetic state at $T = 1.5$ K, (b) paramagnetic state at $T = 8$ K, and (c) magnetic part of the scattering after subtraction of the $T = 8$ K data. Panel (e) shows the magnetic scattering at higher energies ($E_i = 16.6$ meV) in the ferromagnetic state at $T = 2.2$ K after subtraction of the high-temperature data at $T = 60$ K. Spin-wave calculations at low and high energies are shown in panels (d) and (f), respectively.

In contrast to the kagome antiferromagnets kapellasite ($S = 1/2$) [21] and deuterium jarosite ($S = 5/2$) [27], this scattering is clearly dispersive, mimicking the spin-wave dispersion, and thus resembles so-called paramagnons. However, this diffuse scattering seems to exist with the spin waves below $T_C$, which can be inferred from the anomalously large $Q$-width of the scattering [see Fig. 3(a)]. Complementary measurements using the powder diffractometer WISH at ISIS show that the diffuse scattering corresponds to short-range ferromagnetic correlations with a correlation length of about 35 Å (see Fig. 5). Within the ferromagnetic state, the intensity of the short-range ferromagnetic correlations increases initially with increasing temperature, but levels off at $T = 3.5$ K, well before the ferromagnetic transition, above which the intensity becomes temperature independent. This intensity increase is observed in the temperature range where static susceptibility measurements shows an increase in $\chi T$ (see inset of Fig. 5). The behavior of the rather strong diffuse dynamic magnetic scattering in haydeeite is thus very different from what is expected for frozen-in magnetic disorder and also from critical scattering, for which the correlation length should diverge at $T_C$. The presence of strong short-range correlations close to a quantum phase transition where ferromagnetic order disappears is intriguing.

FIG. 4. (Color online) Cuts along $Q$ of of $\chi''(Q, E)$ at constant energies $E$ as specified in the ferromagnetically ordered phase of $\alpha$-MgCu$_3$(OD)$_6$Cl$_2$ (closed circles) and the powder-averaged spin-wave calculation for $J_1 = -1.64$ and $J_2 = 0.48$ meV (solid line). (a)–(b) Excitation energies $E = 1.0 \pm 0.015$ and $1.4 \pm 0.015$ meV measured with $E_i = 3.55$ meV at $T = 1.5$ K. (e)–(f) Excitation energies $E = 8 \pm 1$ and $9 \pm 1$ meV measured with $E_i = 16.6$ meV at $T = 2.2$ K.

FIG. 5. (Color online) Energy-integrated diffuse scattering from haydeeite for various temperatures after subtraction of the low-$T$ data. Inset: Magnetic susceptibility data $\chi_T$ vs. $T$ of $\alpha$-MgCu$_3$(OD)$_6$Cl$_2$ at $H = 5$ T showing ferromagnetic ordering at $T_C = 4.2$ K and a weak field cooling/zero-field cooling (FC-ZFC) splitting at lower temperatures.
We will now discuss the role of the Dzyaloshinskii-Moriya interaction in haydeeite. The DM interaction is of current strong interest in kagome ferromagnets, since an out-of-plane DM vector opens up gaps at finite energies in the spin-wave spectrum. This leads to a topological structure of the magnon bands and a finite Berry curvature in momentum space, resulting in the magnon Hall effect. The DM interaction is intrinsic to the kagome lattice, since the midpoint of the nearest-neighbor bond lacks inversion center, and the DM vector is perpendicular to the kagome plane. In haydeeite, the symmetry is lowered further since the CuO$_6$ octahedra of the crystal structure are slightly tilted with respect to the kagome planes, which implies that the DM interaction can have both in-plane, $D_{xy}$, and out-of-plane, $D_z$, components. We consider the ferromagnetic case, assume that the magnitude of the DM interaction is smaller than $|J_1|$, and take the experimentally determined exchange integrals (see above). For $D_{xy} = 0$, the magnetic structure is a collinear ferromagnet. A finite value of $D_{xy}$ leads to a $k = 0$ umbrella structure with the magnetization perpendicular to the kagome plane and where the opening angle of the umbrella increases with increasing $|D_{xy}|$. A finite value of $D_z$ creates gaps at finite energies of the spin-wave spectrum between the different branches, provided the spins have a component perpendicular to the kagome plane. However, our neutron data are not compatible with the IREP that describes an umbrella-type structure with magnetization perpendicular to the kagome planes. Such an umbrella structure should have zero intensity for the (001) and (002) magnetic Bragg peaks, whereas the data show strong intensity there (see Fig. 2). Also, no finite-energy gaps are observed in the spin-wave spectrum. In other words, there is no experimental evidence that the DM interaction plays a significant role in haydeeite.

We conclude that haydeeite appears to be a rare example of an isotropic $S = 1/2$ Heisenberg kagome ferromagnet. The ordered moment is strongly reduced to $\sim 0.2 \mu_B$ and coexists with diffuse dynamic short-range ferromagnetic correlations below $T_C$. We speculate that the reduction of the ordered moment is due to quantum fluctuations in the proximity to the quantum phase transition between the Heisenberg kagome ferromagnet and the Heisenberg cuboc2 antiferromagnet. A small increase in the third-neighbor across-hexagon antiferromagnetic exchange interaction $J_3$ would push haydeeite into the magnetically ordered cuboc2 phase, and a further increase of $J_4$ or a slightly ferromagnetic second-neighbor interaction $J_2$ would lead to a gapless chiral spin liquid state with spinon Fermi surfaces (CSL-A), which breaks reflection and time-reversal symmetries. Such a state has possibly been observed in kapellasite, where the diamagnetic Mg ion, which mediates the $J_4$ exchange, is replaced by diamagnetic Zn. Studies of these compounds under pressure or with some partial Zn-Mg substitution may allow to experimentally access a quantum spin-1/2 kagome systems at the border of a ferromagnetic instability.

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