Fractionalized excitations in the spin–liquid state of a kagome–lattice antiferromagnet

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The experimental realization of quantum spin liquids is a long-sought goal in physics, as they represent new states of matter. Quantum spin liquids cannot be described by the broken symmetries associated with conventional ground states. In fact, the interacting magnetic moments in these systems do not order, but are highly entangled with one another over long ranges. Spin liquids have a prominent role in theories describing high-transition-temperature superconductors and the topological properties of these states may have applications in quantum information. A key feature of spin liquids is that they support exotic spin excitations carrying fractional quantum numbers. However, detailed measurements of these fractionalized excitations have been lacking. Here we report neutron scattering measurements on single-crystal samples of the 1/2 kagome-lattice antiferromagnet ZnCu$_3$(OD)$_6$Cl$_2$ (also called herbertsmithite), which provide striking evidence for this characteristic feature of spin liquids. At low temperatures, we find that the spin excitations form a continuum, in contrast to the conventional spin waves expected in ordered antiferromagnets. The observation of such a continuum is noteworthy because, so far, this signature of fractional spin excitations has been observed only in one-dimensional systems. The results also serve as a hallmark of the quantum spin-liquid state in herbertsmithite.

In a spin liquid, the atomic magnetic moments are strongly correlated but do not order or freeze even in the limit as the temperature, $T$, goes to zero. Although many types of quantum spin-liquid states exist in theory, a feature that is expected to be common to all is the presence of deconfined spinons as an elementary excitation from the ground state. Spinons are spin-half ($S = 1/2$) quantum excitations into which conventional spin-wave excitations with $S = 1$ fractionalize. In one dimension, this phenomenon is well established for the $S = 1/2$ Heisenberg antiferromagnetic chain, where spinons may be thought of as magnetic domain boundaries that disrupt Neél order and are free to propagate away from each other. In the one-dimensional compound KCuF$_3$, a continuum of spinon excitations has been well characterized using neutron scattering. In two dimensions, the nature of the spinon excitations is less clear. First, the existence of two-dimensional magnets with a quantum spin-liquid ground state is still a matter of great debate. Second, the various spin-liquid states which are proposed in theory give rise to a variety of spinon excitation spectra, which may be either gapped or gapless.

The $S = 1/2$ kagome-lattice Heisenberg antiferromagnet has long been recognized as a promising system in which to search for quantum spin-liquid states, because the kagome network of corner-sharing triangles frustrates long-range magnetic order. We have devised synthetic methods to produce herbertsmithite (ZnCu$_3$(OH)$_6$Cl$_2$) in which the $S = 1/2$ Cu$^{2+}$ moments are arranged in a structurally perfect kagome lattice and nonmagnetic Zn$^{2+}$ ions separate the lattice planes. A depiction of the crystal structure is shown in Supplementary Fig. 1. Whereas herbertsmithite typically contains a small percentage of excess Cu$^{2+}$ ions (~5% of the total) substituting for Zn$^{2+}$ ions in the interlayer sites, the kagome planes contain only Cu$^{2+}$ ions. Measurements on powder samples indicate strong antiferromagnetic superexchange ($J \approx 17$ meV, where $J$ is the exchange coupling that appears in the nearest-neighbour Heisenberg Hamiltonian) and the absence of long-range magnetic order or spin freezing down to temperatures of $T = 0.05$ K. The bulk magnetic properties reveal a small Dzyaloshinskii–Moriya interaction and an easy-axis exchange anisotropy, both of order $J/10$. Despite these small imperfections, the nearest-neighbour Heisenberg model on a kagome lattice is still an excellent approximation of the spin Hamiltonian for herbertsmithite. This is especially important, because recent calculations on record lattice sizes indicate that the ground state of this model is in fact a quantum spin liquid. Thus, experiments to probe the spin correlations in herbertsmithite are all the more urgent.

To this end, we recently succeeded in developing a technique for the growth of large, high-quality single crystals of herbertsmithite, and small pieces have been used in studies involving local probes. In this Letter, we report inelastic neutron scattering measurements on a large, deuterated, single-crystal sample of herbertsmithite. The neutron scattering cross-section is directly proportional to the dynamic structure factor $S_{\text{tot}}(Q, \omega)$ (where $Q$ and $\omega$ stand for the momentum and energy transferred to the sample, respectively), which includes both the nuclear and magnetic signals. The magnetic part, $S_{\text{mag}}(Q, \omega)$, is the Fourier transform (in time and space) of the spin–spin correlation function and can be obtained by subtracting the nuclear scattering as described in the Supplementary Information. After calibration with respect to a vanadium standard, the measured structure factors are expressed in absolute units.

Contour plots of $S_{\text{tot}}(Q, \omega)$ are shown in Fig. 1a–c for $T = 1.6$ K and three different energy transfers $h\omega$ ($h$ denotes Planck’s constant divided by $2\pi$). Figure 1a shows data for $h\omega = 6$ meV. Surprisingly, the scattered intensity is exceedingly diffuse, spanning a large fraction of the hexagonal Brillouin zone. A similar pattern of diffuse scattering is observed for $h\omega = 2$ meV (Fig. 1b). The diffuse nature of the scattering at a temperature that is two orders of magnitude below the exchange energy scale, $J$, is in strong contrast to observations in nonfrustrated quantum magnets. The $S = 1/2$ square-lattice antiferromagnet La$_2$CuO$_4$ develops substantial antiferromagnetic correlations for $T < J/2$ (ref. 21), temperatures at which the low-energy scattering is strongly peaked near the $(\pi, \pi)$ point in reciprocal space. In herbertsmithite, the scattered intensity is not strongly peaked at any specific point, and this remains true for all energies measured from $h\omega = 0.25$ to 11 meV. This behaviour is also markedly different from that observed in the larger, $S = 5/2$ kagome antiferromagnet KFe$_2$(OH)$_6$(SO$_4$)$_2$, which becomes magnetically ordered at low temperatures and has magnetic peaks at $q = 0$ wavevectors above the ordering temperature.
Therefore, the ground-state wavefunction of herbertsmithite has a singlet on a kagome lattice is shown in Fig. 1e. To a first approximation the observed magnetic signal resembles this calculation. the time structure factor for a collection of uncorrelated nearest-neighbour singlets on a kagome lattice is plotted in Fig. 1d. This quantity serves as an approximation of the dynamic structure factor over the integration range 1 \( Q \) for uncorrelated nearest-neighbour singlets on a kagome lattice. The data presented in a–c are expressed in barn sr\(^{-1}\) ev\(^{-1}\) per formula unit, as shown by the left colour bars. The data presented in parts d and e are dimensionless, with the scale given by the right colour bar. The Brillouin zone boundaries are drawn in the figure for clarity; they correspond to the conventional unit cell with parameters \( a = 6.83 \) Å, \( \beta = 90^\circ \) and \( \gamma = 120^\circ \).

The observed \( Q \) dependence of the scattered intensity provides important information on the ground-state spin correlations. The scattering in reciprocal space has the shape of broadened hexagonal rings centred at (0, 0, 0)- and (2, 0, 0)-type positions. All of the scans that we have performed with \( h\omega = 1.5 \) to 11 meV show similar patterns for the scattered magnetic intensity. The energy-integrated dynamic structure factor over the integration range \( 1 \leq h\omega \leq 9 \) meV is plotted in Fig. 1d. This quantity serves as an approximation of the equal-time structure factor. For comparison, a calculation of the equal-time structure factor for a collection of uncorrelated nearest-neighbour singlets on a kagome lattice is shown in Fig. 1e. To a first approximation, the observed magnetic signal resembles this calculation. Therefore, the ground-state wavefunction of herbertsmithite has a large component resembling randomly arranged nearest-neighbour singlets, similar to a short-range resonating valence-bond state\(^{2,16,23}\). However, it is also clear that the data have a narrower width in reciprocal space than does the model calculation. Thus, the spin–spin correlations in herbertsmithite extend beyond nearest neighbours, as further discussed below. The intensity in Fig. 1e corresponds to 1/8 of the total moment sum rule\(^4\). For the data, the integrated intensity up to \( h\omega = 11 \) meV corresponds to 20(3)% of the total moment (where the uncertainty represents 1 s.d.). This indicates that the excitations extend up to much higher energies (a few multiples of \( J \)), and future inelastic measurements up to these energies would be of great interest.

At the lowest measured energy transfers, we observe additional features in the pattern of magnetic scattering. Figure 1c depicts the intensity contour plot for \( h\omega = 0.75 \) meV, showing additional broad peaks centred at (1, 0, 0) and equivalent positions (seen as the yellowish spots near the centres of the low-\( Q \) Brillouin zones). The (1, 0, 0) position does not correspond to a nuclear Bragg position for this crystal structure. Additional scans taken with \( h\omega \) between 0.25 and 1 meV confirm that this feature is generic to the low-energy transfers. This peak is probably influenced by the weakly coupled Cu\(^{2+}\) ions at the interlayer Zn\(^{2+}\) sites, which are believed to affect the low-energy scattering\(^{25}\).

The scattering pattern’s overall insensitivity to energy transfer is another remarkable feature of the data. Conventional spin-wave excitations take the form of sharp surfaces of dispersion in \( Q–\omega \) space. Such spin-wave excitations were indeed observed in the \( S = 5/2 \) kagome antiferromagnet KFe\(_3\)(OH)\(_6\)(SO\(_4\))\(_2\) (ref. 26). In herbertsmithite, no surfaces of dispersion are observable in the low-temperature data. The dependence of \( S_{\text{mag}}(Q, \omega) \) on \( h\omega \) and \( Q \) is plotted in Fig. 2 for two high-symmetry directions in reciprocal space: the (\( H, 0, 0 \)) direction (Fig. 2a) and the (\( H, H, 0 \)) direction (Fig. 2b). These directions are indicated by thick black lines in Fig. 2d. These plots show that the spin excitations form a broad, continuous band (or a continuum), extending up to the highest measured energy, 11 meV. This is direct evidence that the excitations are fractionalized, forming a continuum in this two-dimensional antiferromagnet.

In Fig. 2c and its inset, the energy dependences of \( S_{\text{mag}}(Q, \omega) \) and \( S_{\text{mag}}(Q, \omega) \) are plotted for high symmetry \( Q \) positions as indicated in the reciprocal space map in Fig. 2d. The scattered signal is rather flat for \( 2 \leq h\omega \leq 10 \) meV but increases significantly with decreasing energy transfer below \( h\omega = 1.5 \) meV. There is no indication of a spin gap down to \( h\omega = 0.25 \) meV at the measured reciprocal space positions.

The magnetic intensity can be plotted as one-dimensional ‘line scans’ along specific directions in reciprocal space. In Fig. 3a, \( S_{\text{mag}}(Q, \omega) \) is shown along the \((-2, 1 + K, 0)\) direction, indicated by the thick red line on the reciprocal space map in Fig. 3d. Three energy transfers, \( h\omega = 2, 6 \) and 10 meV, are plotted, and there is no substantial change in the peak width as a function of energy transfer. The width of these line scans, determined by fits, can be found in Supplementary Fig. 3. In Fig. 3b, \( S_{\text{mag}}(Q, \omega) \) is integrated over \( 1 \leq h\omega \leq 11 \) meV and compared with the calculated equal-time \( S_{\text{mag}}(Q, \omega) \) for uncorrelated nearest-neighbour singlets. The solid line corresponds to the result of the uncorrelated nearest-neighbour singlet model multiplied by \( |F(Q)|^2 \), where \( F(Q) \) is...
Figure 2 | Inelastic neutron scattering measured along symmetry directions and at high-symmetry locations. a, b, Intensity contour plots of the dynamic structure factor as a function of \( h\omega \) and \( Q \) for the \((H, 0, 0)\) direction (a) and the \((H, H, 0)\) direction (b). These directions are indicated by the thick black lines on the reciprocal space map shown in d. Along the \((H, H, 0)\) direction, a broad excitation continuum is observed over the entire range measured. The colour bar shows the magnitude of \( S_{\text{tot}}(Q, \omega) \). Energy dependence of \( S_{\text{tot}}(Q, \omega) \) is integrated over 1 to 11 meV. The solid lines in b are the calculated equal-time structure factors for uncorrelated nearest-neighbour singlets multiplied by \( |F(Q)|^2 \). d. The trajectories in reciprocal space referred to in a–c. Error bars, 1 s.d.

Figure 3 | The measured dynamic structure factor along specific directions in reciprocal space with comparison to the nearest-neighbour singlet model. a, \( S_{\text{mag}}(Q, \omega) \) along the \((-2, 1 + K, 0)\) direction, indicated by the thick red line on the reciprocal space map in d. Three energy transfers, \( h\omega = 2, 6 \) and 10 meV, are shown. b, \( S_{\text{mag}}(Q, \omega) \) along the \((-2, 1 + K, 0)\) direction integrated over 1 \( \leq h\omega \leq 7 \) meV. The solid lines in b and c are the calculated equal-time structure factors for uncorrelated nearest-neighbour singlets multiplied by \( |F(Q)|^2 \). d. The trajectories in reciprocal space referred to in a–c. Error bars, 1 s.d.
Further evidence of the continuum nature of the scattering is shown in Fig. 4a, where $S_{\text{mea}}(Q, \omega)$ is plotted along the K–Γ–K direction in the (1,0,0) Brillouin zone. For $2 \lesssim h\omega \lesssim 7$ meV, the scattered intensity is nearly constant along this direction. The data also show another point of contrast to the nearest-neighbour singlet calculation, which predicts slightly larger intensities near the K points, which is not seen in the measurements. Instead, at low energy transfers, $h\omega < 2$ meV, the intensity has a broad maximum at the Γ point, as shown in Fig. 4b for $h\omega = 0.75$ meV. Interestingly, available theoretical calculations for $S_{\text{mea}}(Q, \omega)$ based on spinon excitations are reasonably consistent with the measured intensity pattern, except for discrepancies near the K points.

A central question for classification of the ground state of herbertsmithite is whether a spin gap exists. One surprising aspect of our data is that the spin excitations seem to be gapless over a wide range of Q positions, at least down to $h\omega = 0.25$ meV. This observation is difficult to reconcile with the ground-state properties of valence-bond crystals or gapped spin liquids (such as a short-range resonating valence-bond state). Even most theories for gapless spin liquids predict only a small set of reciprocal lattice points for which the excitations are truly gapless. One possible caveat to our finding is that the small percentage of weakly interacting impurities in the interlayer sites may hide the intrinsic spin gap of the kagome spins. However, it is likely that the impurities affect only the excitations below 1 meV, where the upturn in intensity is seen with decreasing energy transfer. Thus, the hexagonal ring pattern of the structure factor for $1.5 \lesssim h\omega \lesssim 11$ meV is undoubtedly intrinsic to the kagome layers. And, consequently, this sets a conservative upper bound for the intrinsic spin gap of $\sim 10$, if a gap exists. Again, this applies to every Q position at which the low-energy magnetic signal is seen. It may also be necessary for the theoretical calculations based on the Heisenberg model on the kagome lattice to be modified to match more closely the spin Hamiltonian of herbertsmithite.

The observed spinon continuum is the strongest evidence yet that the ground state of the $S = 1/2$ kagome antiferromagnet herbertsmithite is a quantum spin liquid. The measured spin correlations are short ranged; however, no spin gap is observed. An intriguing aspect of quantum spin liquids is that whereas the spin correlations may be short ranged, the quantum coherence is long ranged. These neutron results serve as a strong foundation for detailed tests of theoretical proposals for spin liquid states on the kagome lattice.

**METHODS SUMMARY**

Single-crystal samples of ZnCu$_3$(OD)$_2$Cl$_2$ were grown hydrothermally in tube furnaces under a temperature gradient. Fifteen of the largest crystals were co-aligned on an aluminium sample holder, yielding a total mass of 1.2 g. The overall mosaic (the full-width at half-maximum of the angular distribution of crystallites that comprise the sample) was determined by neutron diffraction to be $\sim 2^\circ$. An identical aluminium sample holder was prepared for the purpose of background subtraction. Inelastic neutron scattering experiments were performed using the multi-axis crystal spectrometer at the NIST Center for Neutron Research. The incident neutron energy was selected using a doubly focused pyrolytic graphite monochromator. The final analysed neutron energy was fixed to be either $E' = 5.1$ or 3.0 meV, for energy resolutions of 0.21 meV (half-width at half-maximum) and 0.08 meV, respectively. The sample was mounted in the (H, K, 0) scattering plane, and a pumped helium cryostat with a base temperature of $T = 1.6$ K was used to control the temperature of the sample.

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