Evidence for a $Z_2$ topological ordered quantum spin liquid in a kagome-lattice antiferromagnet

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A quantum spin liquid with a $Z_2$ topological order has long been thought to be important for the application of quantum computing and may be related to high-temperature superconductivity [1,2]. While a two-dimensional kagome antiferromagnet may host such a state [4,5], strong experimental evidence is still lacking. Here we show that $\text{Cu}_2\text{Zn(OH)}_6\text{FBr}$ exhibits gapped spin continuum at low temperature and is not magnetically ordered down to 20 mili Kelvin. The spin triplet gap value is about twice of the spinon gap value reported previously [10]. Our results provide firm ground for the existence of spin-1/2 spinon excitations in $\text{Cu}_2\text{Zn(OH)}_6\text{FBr}$, whose ground state is thus a gapped quantum spin liquid with $Z_2$ topological order.

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A quantum spin liquid (QSL) is an unconventional symmetric state of matter that is characterized by highly entangled quantum states and fractional quantum numbers [11,12]. However, these properties are not subjected to direct experimental probes which usually are coupled to local order parameters, therefore experimental identification of QSL is difficult. It is typically believed that the lack of magnetic ordering at low temperature is a hint of a QSL state, but this is certainly not a necessary condition [13–16]. In fact, even the presence of magnetic order may not prevent the QSL physics [17,18]. Among various classes of QSLs, the one with $Z_2$ topological order is relatively easier to be identified since one may be satisfied as far as no symmetry breaking and gapped spin excitation continuum are observed [12]. Theoretically, the $Z_2$ topological ordered QSL is originated from the idea that the low-energy physics of the spin system can be understood as fractionalized elementary excitations subject to effective $Z_2$ gauge theory [2].

Herbersmithite, $\text{ZnCu}_3\text{(OH)}_6\text{Cl}_2$, is one of the most promising candidates for a $Z_2$ topologically ordered QSL [19]. Its crystal structure consists of layered kagome $\text{Cu}^{2+}$ ions with spin 1/2 [20]. Earlier measurements suggested that it is a gapless system [21,22], but it is found that the low-temperature and low-energy results are significantly affected by a few amount of residual Cu on Zn sites as spin impurities [23]. Later, both nuclear magnetic resonance (NMR) and inelastic neutron scattering (INS) measurements suggest the existence of a spin gap [24,25], but the gap values are not consistent and some of the analysis contain certain degree of arbitrariness, casting doubts on the factuality of the spin gap and its value.

The recent discovery of a new kagome material $\text{Cu}_3\text{Zn(OH)}_6\text{FBr}$ bestows us promising opportunity of finding kagome QSL with $Z_2$ topological order [10]. It is obtained by replacing Cu with Zn in the parent compound $\text{Cu}_4\text{(OH)}_6\text{FBr}$ [26,27], as shown by the crystal structure in the inset of Fig. 1a. NMR measurements suggest a spin gap of about 0.65 meV, and the magnetic field dependence of the gap is consistent with fractionalized $S = 1/2$ spinon excitations [10]. It is thus crucial to see whether the $S = 1$ spin excitations are also gapped to nail down the nature of the ground state of $\text{Cu}_3\text{Zn(OH)}_6\text{FBr}$. Indeed, in this work, we observe a spin triple gap by INS with gap size consistent with the simple fact that $S = 1$ excitation is the two-spinon convolution of the $S = 1/2$ spinon excitation.

Polycrystalline $\text{Cu}_3\text{Zn(OH)}_6\text{FBr}$ were synthesized at 200 °C by the hydrothermal method with a mixture of $\text{Cu}_2\text{(OH)}_2\text{CO}_3$, $\text{NH}_3\text{F}$, $\text{ZnF}_2$ and $\text{CuBr}_2$ sealed in a reaction vessel with water. The deuterated samples were grown in the same way with basic copper carbonate, $\text{NH}_3\text{F}$ and water replaced by $\text{CuO}$, $\text{ZnF}_2$ and $\text{D}_2\text{O}$, respectively. The magnetic susceptibility is measured by a Magnetic Property Measurement System (MPMS, Quantum Design). Neutron diffraction pattern was measured on the HB-2A diffractometer at HFIR, USA, with wave-
FIG. 1: Neutron diffraction and μSR results of Cu$_3$Zn(OD)$_6$FBr and Cu$_3$Zn(OH)$_6$FBr, respectively. a. Neutron powder diffraction intensities of Cu$_3$Zn(OD)$_6$FBr (red dots) at 4 K and calculated intensities (black line). Short vertical green lines represent Bragg peak positions. The blue line shows the difference between measured and calculated intensities. The star symbols indicate unknown chemical impurity phase that is most likely created during the synthesis process for the deuterated sample since they are not present in the regular Cu$_3$Zn(OH)$_6$FBr sample [10]. See supplementary materials for detailed refinement results. The insets plot its nuclear structure. b. Time evolution of asymmetry of Cu$_3$Zn(OH)$_6$FBr in μSR measurements. ZF and LF represent zero field and longitudinal field, respectively. A constant background signal from muons that stop in the silver sample holder has been subtracted from the μSR asymmetry spectrum. The solid lines of ZF data are fitted by the damped Kubo-Toyabe function [28]. The solid lines of LF data are fitted by exponential function. c. Temperature dependence of the muon spin exponential relaxation rate $\lambda$. The dashed line is fitted from bulk susceptibility measured above 2 K.

length of 2.4103 Å. The INS experiment was carried out on the TOFTOF spectrometer at FRM-II, Germany with the incoming beam wavelength $\lambda$ of 5 Å. The muon spin relaxation (μSR) measurements were performed on the M15 beam line of TRIUMF, Canada with a top-loading-type dilution refrigerator.

Figure 1a shows neutron powder diffraction data of Cu$_3$Zn(OD)$_6$FBr at 4 K, which gives a hexagonal nuclear structure with $P6_3/mmc$ space group that is the same as that at room temperature [10]. This means that this material maintains the perfect kagome motif at low temperature, which provide necessary frustration and spin symmetry for the presence of the $Z_2$ topological order.

In the previous work [10], we have shown that Cu$_3$Zn(OH)$_6$FBr is not magnetically ordered down to 50 mK as illustrated by the specific heat measurements. Here we further push this low temperature limit to 20 mK by μSR measurements, which is four orders lower than the antiferromagnetic Curie-Weiss temperature of 200 K [10]. As shown in Fig. 1b, the zero-field asymmetry shows no evidence for magnetic order, such as loss of initial asymmetry or oscillations due to precession in an internal field. No pronounced qualitative differences among the asymmetry spectra are observed for temperature between 20 mK and 5 K. To suppress the nuclear contribution to the muon asymmetry function, longitudinal fields of 250 and 500 Gauss were applied. This yields almost constant asymmetry with no field dependence, which suggests the absence of persistent spin dynamics [29]. Figure 1c shows the temperature dependence of the muon spin relaxation rate $\lambda$, which is consistent with the result of bulk susceptibility.

Figure 2a-2c show raw data of INS measurements on Cu$_3$Zn(OD)$_6$FBr below 1 meV. Very strong excitations are observed at small $|Q|$ and low energy. With increasing temperature, the intensities become smaller, suggesting its magnetic origin. Figure 2d gives the $Q$ cuts at 0.5 meV, which shows that the spectra weight shifts to smaller $|Q|$ with increasing temperature. These behaviors are consistent with the observation of a weak ferromagnetism in our deuterated samples that is not present in normal samples (see supplementary materials), demonstrating that the strong excitations at small $|Q|$ are not related to intrinsic quantum spin liquid physics in the kagome planes of Cu$_3$Zn(OD)$_6$FBr.

Figure 2e-2g give INS results at higher energies, where continuum of spin excitations can be observed. The excitations show a broad peak around $|Q| \sim 1.25 \text{Å}^{-1}$ as shown in Fig. 2h, whose intensity decreases with increasing temperature. Considering that our sample is polycrystalline and there is no L-dependence for spin excitations, our results are consistent with those in hetbersmithite, where in-plane spin excitations become strongest around (1,0,0) [22]. At high temperature, another broad peak appears at small $|Q|$, which is associ-
associated with the low |Q| excitations discussed in the preceding paragraph. The presence of low |Q| excitations strongly affects the analysis of intrinsic low-energy spin excitations from kagome planes, but we can still have a proper analysis for those with |Q| larger than 1.6 Å⁻¹, which is the focus of our narrative below.

Figure 3a shows the energy cuts for |Q| = 1.8 Å⁻¹ at several temperatures. The imaginary part of dynamic susceptibility χ''tot(Q, ω) can thus be calculated based on the principle of detailed balance by considering the negative-energy-transfer part in Fig. 3a at 0.5 K are just background [21]. Figure 3b shows the energy dependence of χ''tot(Q, ω) at several temperatures. While no spin gap can be directly observed, the temperature dependence of χ''tot(Q, ω) at low energies is significantly different from that at high energies, as shown in Fig. 3c. The low-energy part may be dominated by the contribution from residual interkagome Cu²⁺ due to imperfect Zn²⁺ substitution, or impurities as called in herbertsmithite [22]. These low energy contribution need to be subtracted in a systematically manner as discussed below, such that the spin gap of spin excitations from the intrinsic kagome planes can be revealed.

Assuming that different sites of interkagome Cu²⁺ are weakly correlated, they will contribute to the INS signal as quasielastic scattering with the lorentzian lineshape, which may be written as [30] (see supplementary materials)

$$\chi^\prime\prime_{\text{imp}}(Q, \omega) = \frac{2(\gamma r_0)^2}{\pi \mu_B^2} |f(Q)|^2 \chi_{\text{st}}(T) \frac{\hbar \omega W}{(h\omega)^2 + W^2}, \quad (1)$$

where γ is the gyromagnetic ratio, r₀ is the classical electron radius, W is the width of the lorentzian function, and |f(Q)| is the magnetic form factor of Cu²⁺. χ_{st}(T) is the static susceptibility measured by the MPMS. Therefore, the only fitting parameter is W.

Accordingly, we fit the χ'' at |Q| = 1.8 Å⁻¹ and E = 0.175 meV as shown by the solid line in Fig. 3c. It is worth noting that W here (∼ 0.41 meV) is about twice of kBT_{LT}, where θ_{LT} (∼ 2 K) is the Curie temperature of the low-temperature magnetic susceptibility (Fig. 1c). The dashed lines in Fig. 3c are the calculated χ''_{imp}(Q, ω) using this W according to Eq. 1. While χ''_{imp}(Q, ω) at low energies are consistent with the calculated values, significant deviation is found above 1 meV. It also fails to describe the high-temperature data at 0.375 meV. The energy dependence of χ''_{tot}(Q, ω) at 2 K is shown in Fig. 3d, where the calculated χ''_{imp}(Q, ω) can well describe the low-energy part.

The above analysis confirms that the high-energy spin excitations actually contains the intrinsic magnetic response of the kagome spin liquid, and one needs to subtract the low-energy contribution from interkagome Cu²⁺, to reveal the genuine spin liquid signal. Figure
Figure 4a shows the energy dependence of $S_K(Q, \omega)$ at several temperatures with the subtraction of the quasielastic scattering modeled by Eq. [1] Here, $S_K(Q, \omega)$ is the dynamic spin structure factor, which is calculated as $(\chi''_{\text{tot}}(Q, \omega) - \chi''_{\text{imp}}(Q, \omega))/(1 - e^{-h\omega/k_B T})$. The opening of a spin gap can be easily seen at 2 K. The spin gap value $\Delta$ can be obtained through the fitting of $S_K(Q, \omega)$ as proportional to $(1 + \tanh(\frac{\Delta}{2}))/\Delta$, where both $\Delta$ and $\Gamma$ are fitting parameters.

Figure 4b gives the temperature dependence of $\Delta$. At low temperature, $\Delta$ linearly decreases with increasing temperature, which gives $\Delta(0)$ at zero K as 1.13 $\pm$ 0.02 meV. Interestingly, the temperature where the gap becomes zero is almost the same as $\Delta(0)/k_B$ if we follow the straight line in Fig. 4b. However, deviation from such linear temperature dependence of $\Delta$ happens above 4 K and $\Delta$ becomes zero above 30 K. It is certain that the gap function used here is not valid at such high temperature, but it seems to be consistent with the observation by NMR that the Knight shift starts to decrease below about 30 K [10].

Figure 4c shows $S_K(Q, \omega)$ at different $Q$ at 2 K, which suggests that the above analysis is reasonable for $Q > 1.6 \text{ Å}^{-1}$. We plot the colormap of $S_K(Q, \omega)$ at 2 K in Fig. 4d, which clearly shows a nearly uniform spin gap presents for $1.6 \text{ Å}^{-1} < |Q| < 2.2 \text{ Å}^{-1}$. While we cannot derive the spin gap value at smaller $|Q|$, we note that the present $|Q|$ range covers about half of the second Brillouin zone.

The INS and $\mu$SR data in this paper, provide concrete evidence for gapped spin excitations in kagome quantum spin liquid material Cu$_3$Zn(OH)$_6$FBr. Moreover, the zero-temperature gap value in our work is about twice of $\Delta(0)/k_B$ [24]. While we cannot determine whether these inconsistencies between herbertsmithite and Cu$_3$(OH)$_6$FBr are intrinsic or just due to different methods in data analysis.

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