Gapped spin-1/2 spinon excitations in a new kagome quantum spin liquid compound Cu$_3$Zn(OH)$_6$FBr

Zili Feng, Zheng Li, Xin Meng, Wei Yi, Yuan Wei, Jun Zhang, Yan-Cheng Wang, Wei Jiang, Zheng Liu, Shiyan Li, Feng Liu, Jianlin Luo, Shiliang Li, Guo-qing Zheng, Zi Yang Meng, Jin-Wei Mei, Youguo Shi

1 Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
2 School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100190, China
3 State Key Laboratory of Surface Physics, Department of Physics, and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, China
4 Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA
5 Institute for Advanced Study, Tsinghua University, Beijing 100084, China
6 Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, China
7 Collaborative Innovation Center of Quantum Matter, Beijing 100190, China
8 Department of Physics, Okayama University, Okayama 700-8530, Japan
9 Institute for Quantum Science and Engineering, and Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China
10 Beijing Computational Science Research Center, Beijing 100193, China

(Dated: June 26, 2017)

We report a new kagome quantum spin liquid candidate Cu$_3$Zn(OH)$_6$FBr, which does not experience any phase transition down to 50 mK, more than three orders lower than the antiferromagnetic Curie-Weiss temperature ($\sim 200$ K). A clear gap opening at low temperature is observed in the uniform spin susceptibility obtained from $^{19}$F nuclear magnetic resonance measurements. We observe the characteristic magnetic field dependence of the gap as expected for fractionalized spin-1/2 spinon excitations. Our experimental results provide firm evidence for spin fractionalization in a topologically ordered spin system, resembling charge fractionalization in the fractional quantum Hall state.

When subject to strong geometric frustrations, quantum spin systems may achieve paramagnetic ground states dubbed quantum spin liquid (QSL) [1]. It is characterized by the pattern of long-range quantum entanglement that has no classical counterpart [2,3]. QSL is an unambiguous Mott insulator whose charge gap is not associated with any symmetry breaking [1]. It is related to the mechanism of high-temperature superconductivity [1] and the implementation of topological quantum computation [5]. The underlying principle of QSL, i.e. topological orders due to quantum entanglement [1,4], is beyond the Landau symmetry-breaking paradigm [2] and has been realized in fractional quantum Hall systems [6], resulting in fractionalized $e/3$ charged anyon [7,8]. Similarly, fractionalized spin-1/2 spinon excitations are allowed in QSL [9,12].

Kagome Heisenberg antiferromagnets are promising systems for the pursuit of QSL [13,14]. For example, herbertsmithite ZnCu$_3$(OH)$_6$Cl$_2$ is a famous kagome system, which displays a number of well-established QSL behaviors [16,29]. Inelastic neutron scattering measurements have detected continuum of spin excitations [24] while nuclear magnetic resonance (NMR) measurements suggest a finite gap at low temperature [29]. However, multiple NMR lines of nuclear spins with $I > 1/2$ can not be easily resolved, particularly in the presence of residual interkagome Cu$^{2+}$ spin moments even in high-quality single crystals [20,23,28,29]. Furthermore, although it is commonly accepted that the quantum number of spinons is spin-1/2, no direct evidence has been observed [29]. Therefore, it is crucial to find new QSL systems to unambiguously demonstrate the spin-1/2 quantum number of spinons.

Recently, barlowite Cu$_4$(OH)$_6$FBr has attracted much attention as a new kagome system with minimum disorder [30,31]. As opposed to herbertsmithite with ABC-stacked kagome planes, barlowite crystallizes in high-symmetry hexagonal rods owing to direct AA kagome stacking. It has also been found that the in-plane Dzyaloshinskii-Moriya interaction in barlowite is an order of magnitude smaller than that in herbertsmithite [35]. Consequently, the QSL physics has been suggested to be present at relative high temperature. Unfortunately, the material goes through an antiferromagnetic transition at $\sim 15$ K [32,35]. It has thus been proposed that substituting the interkagome Cu$^{2+}$ sites with non-magnetic ions may suppress the magnetic transition and ultimately lead to a QSL ground state [13,32,34,50].

In this Letter, we report a new kagome QSL candidate Cu$_3$Zn(OH)$_6$FBr. It does not experience any phase transition down to 50 mK, more than three orders lower than the antiferromagnetic Curie-Weiss temperature ($\sim 200$ K). $^{19}$F NMR measurements reveal a gapped QSL ground state in Cu$_3$Zn(OH)$_6$FBr. The field dependence of the gap implies a zero-field gap $\sim 200$ K. A clear gap opening at low temperature is observed in the uniform spin susceptibility obtained from $^{19}$F nuclear magnetic resonance measurements. We observe the characteristic magnetic field dependence of the gap as expected for fractionalized spin-1/2 spinon excitations. Our experimental results provide firm evidence for spin fractionalization in a topologically ordered spin system, resembling charge fractionalization in the fractional quantum Hall state.
We have successfully synthesized Cu$_3$Zn(OH)$_6$FBr polycrystalline samples by replacing the interkagome Cu$^{2+}$ sites in Cu$_4$(OH)$_6$FBr with non-magnetic Zn$^{2+}$. Our thermodynamical (e.g. magnetic susceptibility and specific heat) measurements were carried out on the Physical Properties Measurement Systems (PPMS). The NMR spectra of $^{19}$F with the nuclear gyromagnetic ratio $\gamma = 40.055$ MHz/T were obtained by integrating the spin echo as a function of the RF frequency at constant external magnetic fields of 0.914 T, 3 T, 5.026 T and 7.864 T, respectively.

Figure 1 (a) and 1 (b) depict the crystal structure of Cu$_3$Zn(OH)$_6$FBr. Micrometer-size crystals are easily observed by the scanning electron microscope (SEM) (Fig. 1 (c)). The refinement of the powder X-ray diffraction pattern (Fig. 1 (d)) shows that the material crystallizes in P6$_3$/mmc space group with Cu$^{2+}$ ions forming a direct stack of undistorted kagome planes separated by non-magnetic Zn$^{2+}$ ions (Fig. 1 (a) and (b)) as expected from theoretical calculations [34]. Cu$_3$Zn(OH)$_6$FBr is a charge-transfer insulator and the charge gap between Cu-3$d^9$ and O-2$p$ orbitals is around 1.8 eV according to first principles calculations [34, 37]. Powder X-ray diffraction measurements were carried out using Cu $K_\alpha$ radiation at room temperature. The diffraction data is analyzed by the Rietveld method using the program RIETAN-FP [38]. All positions are refined as fully occupied with the initial atomic positions taken from Cu$_4$(OH)$_6$FBr [31]. The refined results are summarized in Table I.

No phase transition is observed in our thermodynamical measurements (Fig. 2), establishing strong evidence for a QSL ground state in Cu$_3$Zn(OH)$_6$FBr. Tempera-

| Site | $w$ | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|------|-----|-----|-----|-----|-------------|
| Cu   | 6g  | 0.5 | 0   | 0   | 1.48(6)     |
| Zn   | 2d  | 1/3 | 2/3 | 3/4 | 1.93(8)     |
| Br   | 2c  | 2/3 | 1/3 | 3/4 | 1.99(5)     |
| F    | 4b  | 0.0 | 0.0 | 3/4 | 0.34(2)     |
| O    | 12k | 0.1887 | 0.8113(5) | 0.9021(7) | 2.22(2) |
| H    | 12k | 0.1225 | 0.8775 | 0.871 | 1.0        |
The temperature dependence of magnetic susceptibility under different magnetic fields does not display any magnetic transition down to 2 K as shown in Fig. 2 (a). No splitting is detected between the field-cooled (FC) and zero-field-cooled (ZFC) results down to 2 K, indicating the absence of spin glass transition. At high temperature, magnetic susceptibility can be well fitted by the Curie-Weiss law with the Curie temperature and Curie constant as -200 K and 1.57 K-emu/mol, respectively. This indicates a strong antiferromagnetic superexchange interaction \( J \sim 17 \text{ meV} \) among \( \text{Cu}^{2+} \) moments in the kagome planes. The \( g \)-factor is estimated to be about \( g = 2.4 \), consistent with the \( g \)-factor measurements in the Barlowite [35]. In Fig. 2 (b), no visible hysteresis loop is observed in the magnetic field dependence of magnetization at different temperatures. Figure 2 (c) is the specific heat measurement at zero field down to 50 mK. The inset shows the magnetic field effect on the specific heat at low temperatures, which exhibits upturn behavior at high-field due to nuclear Schottky anomaly.

There are residual interkagome \( \text{Cu}^{2+} \) (RIC) moments due to incomplete \( \text{Zn}^{2+} \) substitution in \( \text{Cu}_3\text{Zn(OH)}_6\text{F}_2\). Few \( \text{Zn}^{2+} \) exists in kagome planes according to the line shape of NMR spectra (see below in Fig. 3). The energy dispersive X-ray spectroscopy measurements at different locations indicate that the composition is stoichiometric with the atomic ratio between \( \text{Cu} \) and \( \text{Zn} \) as \( 1 : 0.36 \). The inductively coupled plasma atomic emission spectroscopy analysis suggests the atomic ratio between \( \text{Cu} \) and \( \text{Zn} \) as \( 1 : 0.30 \). From the chemical component analysis, we roughly estimate the concentration of the RIC moments to be \( \sim 10\% \), comparable to those in herbertsmithite [39].

At low temperatures, RIC moments obscure the intrinsic kagome plane QSL behaviors in the bulk magnetic susceptibility and heat capacity, similar to previous results of herbertsmithite [22, 39–43]. DC susceptibility at low temperatures in 0.1 T magnetic field is fitted by Curie-Weiss behavior with Curie constant and Curie temperature as \( 0.18 \text{ K} \) and \( 3 \text{ K} \), respectively, indicating weak antiferromagnetically interacting RIC moments. Under high magnetic fields, the RIC moments freeze and the AC susceptibility drops at low temperatures (see Fig. 2 (a)). We also measure T-dependent AC susceptibilities for various frequencies and magnetic fields at low temperatures, see Fig. S 7 in the supplementary materials (SM) [44]. The AC susceptibility is independent of frequencies, implying that RIC moments do not develop spin glass freezing down to 2 K. The RIC moments also contribute a shoulder in the specific heat measurements at low temperatures (see Fig. 2 (c)). The shoulder is suppressed in magnetic fields, as shown in the inset of Fig. 2 (c), along which the RIC moments are polarized, similar to herbertsmithite [44].

To directly unveil QSL physics in kagome plane, we implement NMR measurements to probe uniform spin susceptibility of kagome \( \text{Cu}^{2+} \) spin moment dependence of the specific heat at zero field down to 50 mK. The inset shows the magnetic field effect on the specific heat at low temperatures.

---

**FIG. 2.** (a) Temperature dependence of magnetic susceptibility under different magnetic fields measured by both DC and AC methods. In AC measurements, the oscillation filed amplitude is 17 Oe and the oscillation frequency is 633 Hz. The inset shows the temperature dependence of the inverse susceptibility \( 1/\chi \) at 1 T. (b) Magnetic field dependence of magnetization at different temperatures. (c) Temperature dependence of the specific heat at zero field down to 50 mK. The inset shows the magnetic field effect on the specific heat at low temperatures.
FIG. 3. (a) $^{19}$F NMR spectra under 3 T at different temperatures. The vertical dash line $f_0 = 120.199$ MHz, corresponding to the chemical shift, is a guide to the eyes. (b) Temperature dependence of the Knight shift $^{19}K$ determined from the peak positions of the spectra. The dotted horizontal line shows the position of $K_{\text{chem}}$ obtained from $^{19}K-\chi$ plot at high temperatures as shown in the inset. (c) Magnetic field dependence of the spin gap. The black short-dash line is fitted by $\Delta(B) = \Delta(0) - g\mu_B S B$ with spin quantum number $S = 1/2$. For comparison, we also plot $\Delta(B)$ for $S = 1$ shown by the blue dash line constrained by the value at 0.914 T, which hardly describes the data. Inset shows the Arrhenius plot of $^{19}K - K_{\text{chem}}$ with the vertical axis in logarithmic scale, which demonstrates visually that the gap decreases with increasing magnetic field. The solid curve is the fitting function $A \exp(-\Delta/T)$ for $^{19}K - K_{\text{chem}}$.

ments in Cu$_3$Zn(OH)$_6$FBr. A unique advantage of Cu$_3$Zn(OH)$_6$FBr for the NMR measurements is that it contains $^{19}$F. It is known that $^{2}$D, $^{17}$O and $^{35}$Cl NMR measurements in herbertsmithite are rather difficult due to multiple resonance peaks resulted from nuclear spins $I = 1$, $I = 5/2$ and $I = 3/2$, respectively [20, 23, 28, 29]. In contrast, only one resonance peak needs to be resolved for $^{19}$F with $I = 1/2$ nuclear spin, as shown in Fig. 3(a). The sharp high-temperature peaks suggest that few Zn$^{2+}$ exists in kagome planes. Moreover, no extra peak due to RIC moments is observed even at low temperatures. The line shape asymmetry may arise from the magnetic anisotropy, e.g. $g_\parallel/g_\perp = 2.42/2.21$ in Barlowite [33]. We have also carried out the measurements with different pulse interval ($\tau$) in NMR echo to exclude the possibility of impurity moment contributions in the NMR spectrum [14].

In a gapped QSL, the spin susceptibility should become zero at low temperature. The Knight shift is related to the uniform susceptibility $\chi$ as $^{19}K = A_{hf}\chi + K_{\text{chem}}$, where $A_{hf}$ is the hyperfine coupling constant between the $^{19}$F nuclear spin and the electron spins and $K_{\text{chem}}$ is the $T$-independent chemical shift. $K_{\text{chem}} = 0.015\%$ is obtained from $^{19}K-\chi$ plot at high temperatures as shown in the inset of Fig. 3(b), where $\chi$ is DC susceptibility at $B = 3$ T. Figure 3(b) shows that the Knight shift drops quickly below $\sim 30$ K. At high temperatures ($\sim 100$ K), Knight shift $^{19}K$ has a systematic variation as a function of magnetic field, whose origin is unclear at present and left for future investigation, but we note that such a behavior would not change our results at low temperatures below 30 K. The Knight shift at low fields (0.914 T and 3
We therefore believe that Cu$_3$Zn(OH)$_6$FBr has a gapped QSL ground state, consistent with results in herbertsmithite [29] and unambiguously manifest the spin-1/2 quantum number of spinons. It reflects the spin fractionalization in a QSL state when spin rotation symmetry meets topology. Within minimal symmetry (e.g. time reversal symmetry and translational symmetry) assumptions, a gapped kagome QSL should be $Z_2$-gauge type [11][12] (i.e. toric code type [5]) according to the theoretical constraints [45].

In conclusion, we have successfully synthesized a new kagome compound Cu$_3$Zn(OH)$_6$FBr and its quantum spin liquid ground state is verified in our thermodynamical measurements. Our $^{19}$F NMR data reveals a gapped spin-liquid ground state for Cu$_3$Zn(OH)$_6$FBr, similar to previous $^{15}$O NMR results on herbertsmithite. Most importantly, we provide experimental evidence for spin-1/2 quantum number for spin excitations, i.e. spinons. We therefore believe that Cu$_3$Zn(OH)$_6$FBr provides a promising platform for future investigations of the topological properties of quantum spin liquid states.

We acknowledge Yongqing Li for discussions on the magnetic susceptibility measurements. We thank Xi Dai and Zhong Fang for useful discussions. We acknowledge fundings from the National Key Research and Development Program of China under Grant Nos. 2016YFA0300502, 2016YFA0300503, 2016YFA0300604, 2016YF0300300 and 2016YFA0300802, the National Natural Science Foundation of China under Grant Nos. 11421092, 11474330, 11574359, 11674406, 11374346 and 11674375, National Basic Research Program of China (973 Program) No. 2015CB921304, the National Thousand-Young-Talents Program of China, the Strategic Priority Research Program (B) of the Chinese Academy of Sciences under Grant No. XDB07020000, XDB07020200 and XDB07020300. The work in Utah is supported by DOE-BES under No. DE-FG02-04ER46148.

---

1. Philip W Anderson, “The Resonating Valence Bond State in La$_2$CuO$_4$ and Superconductivity.” Science 235, 1196–8 (1987).
2. X.G. Wen, Quantum Field Theory of Many-Body Systems: From the Origin of Sound to an Origin of Light and Electrons. Oxford Graduate Texts (OUP Oxford, 2004).
3. Alexei Kitaev and John Preskill, “Topological Entanglement Entropy,” Phys. Rev. Lett. 96, 110404 (2006).
4. Michael Levin and Xiao-Gang Wen, “Detecting Topological Order in a Ground State Wave Function,” Phys. Rev. Lett. 96, 110405 (2006).
5. A. Yu. Kitaev, “Fault-tolerant quantum computation by anyons.” Ann. Phys. (N.Y.) 303, 2–30 (2003).
6. D. C. Tsui, H. L. Stormer, and A. C. Gossard, “Two-Dimensional Magnetotransport in the Extreme Quantum Limit,” Phys. Rev. Lett. 48, 1559–1562 (1982).
7. R. B. Laughlin, “Anomalous Quantum Hall Effect: An Incompressible Quantum Fluid with Fractionally Charged Excitations,” Phys. Rev. Lett. 50, 1395–1398 (1983).
8. R. de Picciotto, M. Reznikov, M. Heiblum, V. Umansky, G. Bunin, and D. Mahalu, “Direct observation of a fractional charge,” Nature 389, 162–164 (1997).
9. Steven A. Kivelson, Daniel S. Rokhsar, and James P. Sethna, “Topology of the resonating valence-bond state: Solitons and high-Tc superconductivity,” Phys. Rev. B 35, 8865–8868 (1987).
10. N. Read and B. Chakraborty, “Statistics of the excitations of the resonating-valence-bond state,” Phys. Rev. B 40, 7133–7140 (1989).
11. N. Read and Subir Sachdev, “Large-N expansion for frustrated quantum antiferromagnets,” Phys. Rev. Lett. 66, 1773 (1991).
12. X. G. Wen, “Mean-field theory of spin-liquid states with finite energy gap and topological orders,” Phys. Rev. B 44, 2664–2672 (1991).
13. Patrick A. Lee, “An End to the Drought of Quantum Spin Liquids,” Science 321, 1306–1307 (2008).
14. Leon Balents, “Spin liquids in frustrated magnets.” Nature 464, 199–208 (2010).
15. M. R. Norman, “Colloquium: Herbstsmithite and the search for the quantum spin liquid.” Rev. Mod. Phys. 88, 041002 (2016).
16. Matthew P Shores, Emily A Nytko, Bart M Bartlett, and Daniel G Nocera, “A structurally perfect S= 1/2 kagome antiferromagnet,” J. Am. Chem. Soc. 127, 13462–13463 (2005).
17. J. S. Helton, K. Matan, M. P. Shores, E. A. Nytko, B. M. Bartlett, Y. Yoshida, Y. Takano, A. Suslov, Y. Qiu, J.-
