From Claringbullite to a new spin liquid candidate Cu₃Zn(OH)₆FCl

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The search for quantum spin liquid (QSL) materials has attracted significant attention in the field of condensed matter physics in recent years, but until now only a handful of them are considered as candidates hosting QSL ground state. Owning to their geometrically frustrated structure, Kagome materials are ideal system to realize QSL. In this study, we successfully synthesized a new kagome QSL candidate, Cu₃Zn(OH)₆FCl, and its parent compound Cu₄(OH)₆FCl (Claringbullite). X-ray diffraction (XRD) shows pure Cu₃Zn(OH)₆FCl is synthesized and chemical analysis show that the content of Zn²⁺ ions in the inter-kagome plane is about 0.7 per formula unit. Although some Cu²⁺ ions remain in the inter-kagome plane, structure analysis reveals that the prefect kagome plane is preserved and thermodynamic measurements show that magnetic order is completely suppressed in Cu₃Zn(OH)₆FCl, suggesting it is a new QSL candidate. On the other hand, Claringbullite develops magnetically ordered systems and QSL, in which the signatures of fractionalized anyonic excitations and other exotic properties of QSL could be revealed.

I. INTRODUCTION

In recent years, the search for quantum spin liquid (QSL) materials, usually realized in frustrated magnets, has attracted great interests due to the exotic anyonic excitations therein as well as their potential relation with quantum computation and unconventional superconductivity [1–6]. The common search ground for QSL but also a novel pathway of investigating the transition between QSL and magnetically ordered systems.

Among the discovered QSL candidates [10, 12, 13], herbertsmithite, ZnCu₃(OH)₆Cl₂ [14, 15], and Zn-doped barlowite, Cu₃Zn(OH)₆FBr [10, 11, 16] are the two well-known kagome QSL materials, and many related materials are also synthesized, such as Cu₃Mg(OH)₆Cl₂, Cu₃Cd(OH)₆(SO₄) [17, 22]. To synthesize a promising kagome QSL material, the perfect kagome structure must retain intact and the inter layer interaction shall be reduced, to optimize the perfect frustration in the 2D plane in order to suppress any magnetic order. Unfortunately most materials develop magnetic order at low temperatures which is usually accompanied by structure transitions that breaks the kagome lattice geometry.

In this study, we successfully synthesized a new kagome QSL candidate, Cu₃Zn(OH)₆FCl and its parent compound Cu₄(OH)₆FCl (Claringbullite). X-ray diffraction (XRD) shows pure Cu₃Zn(OH)₆FCl is synthesized and chemical analysis show that the content of Zn²⁺ ions in the inter-kagome plane is about 0.7 per formula unit. Although some Cu²⁺ ions remain in the inter-kagome plane, structure analysis reveals that the prefect kagome plane is preserved and thermodynamic measurements show that magnetic order is completely suppressed in Cu₃Zn(OH)₆FCl, suggesting it is a new QSL candidate. On the other hand, Claringbullite develops magnetically ordered systems and QSL, in which the signatures of fractionalized anyonic excitations and other exotic properties of QSL could be revealed.

II. CRYSTAL SYNTHESIS

Cu₄(OH)₆FCl and Cu₃Zn(OH)₆FCl were synthesized using a hydrothermal method. For Cu₄(OH)₆FCl, about 3 mmol Cu₂(OH)₂CO₃, 2 mmol CuCl₂ and 2 mmol NH₄F were mixed with about 20 mL deionized water in a 25 mL vessel. The sample was heated at 200 °C for one day and then slowly cooled to room temperature. A green powder was collected by drying the production. Cu₃Zn(OH)₆FCl was synthesized using ZnCl₂ instead of CuCl₂. But two impurities Cu₃Zn(OH)₆Cl₂, a poly-

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morph of herbertsmithite, and Zn(OH)F exist in the production. To avoid the production of Cu$_3$Zn(OH)$_6$Cl$_2$, the content of NH$_4$ was increased and HCl was added to the raw materials to prevent the formation of Zn(OH)F. Thus about 0.2 g concentrated hydrochloric acid (mass fraction about 35%) was mixed with about 3 mmol Cu$_2$(OH)$_2$CO$_3$, 4 mmol ZnCl$_2$ and 3 mmol NH$_4$F, producing pure Cu$_3$Zn(OH)$_6$FCl$_2$.

Cu$_3$Zn(OH)$_6$Cl$_2$ was characterized by powder XRD and no impurity peaks were found. The measured XRD data and the calculated pattern, refined by the Rietveld method using the program RIETAN-FP [23] are plotted in Fig. 1 (a). The refined structure parameters are listed in Table 1. The XRD measurement was performed at room temperature on a Rigaku Smartlab high-resolution diffractometer using Cu K$_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å). Two forms of chemical component analysis were used to determine the Zn content. First, energy-dispersive X-ray spectra were measured on a Hitachi S-4800 scanning electron microscope at an accelerating voltage of 15 kV, with an accumulation time of 90 s. Then, inductively coupled plasma atomic emission spectroscopy was performed using a Thermo IRIS Intrepid II instrument. These results show that the stoichiometric ratio of Cu and Zn ions is about 3:0.7.

The sample was pressed and cut into pieces about 1 mm$^2$ to perform the thermodynamic measurements. The magnetization data were measured using a superconducting quantum interference device magnetometer (Quantum Design MPMS). The specific heat data were measured in a physical property measurement system (PPMS) at zero magnetic field between 2 and 30 K. The specific heat below 2 K is measured using He-3 system.

### III. RESULT AND DISCUSSION

Cu$_3$Zn(OH)$_6$FCl crystallized in hexagonal lattice with space group P6$_3$/mmc (No. 194). The unit parameters are $a = b = 6.65377(11)$ Å, $c = 9.18896(11)$ Å. As shown in Fig. 1 Cu$_3$Zn(OH)$_6$FCl has a perfect kagome lattice at room temperature. The kagome planes show AA stacking and are separated by Zn$^{2+}$ ions. Table 1 provides detailed structure parameters of Cu$_3$Zn(OH)$_6$FCl. In Cu$_4$(OH)$_8$FCl, the interlayer Cu$^{2+}$ ions split from the equilibrium site and shows three equivalent positions [24]. In Cu$_3$Zn(OH)$_6$FCl, the interlayer Zn ions sit on the ordered site. The XRD pattern was refined using splitting model while the interlayer Zn$^{2+}$ ions sit at (1/3, 2/3, 1/4) which is an equilibrium site. The occupancy on each of three equivalent Zn site is 0.319, indicating some Cu ions sit on the inter layer.

Fig. 2 (a) shows the temperature dependence of magnetic moment of Cu$_3$Zn(OH)$_6$FCl and Cu$_4$(OH)$_8$FCl at 1 Koe below 50 K. The vertical coordination is in logarithmic scale to highlight the salient difference. The moment of Cu$_4$(OH)$_8$FCl increases abruptly at about 17 K, which is its magnetic phase transition temperature reported in previous study [24], while Cu$_3$Zn(OH)$_6$FCl shows no obvious magnetic order transition down to 2 K. The $1/\chi$ data between 300 K and 2 K of Cu$_3$Zn(OH)$_6$FCl at 10 Koe in zero-field-cooling (ZFC) and field-cooling (FC) conditions are shown in the inset of Fig. 2 (a). Curie-Weiss law ($\chi = c/(T + \theta_{cw})$) was used to fit the data between 150 K and 300 K and gave rise to $\theta_{cw} = -223$ K. The value of $\theta_{cw}$ (19.2 meV) indicates a strong antiferromagnetic interaction between Cu$^{2+}$ ions in the kagome layer, suggesting strong frustration in the system. The Curie constant is 1.556 K-emu-mol$^{-1}$. Assuming $S = 1/2$ and using the typical g factor value in kagome lattice for Cu ions $g = 2.3 \pm 0.1$ [20, 25], the Cu content can be calculated, 3.28 $\pm$ 0.14 per formula unit. This gives that Zn content is 0.72 $\pm$ 0.14 per formula unit which is consistent.
with the chemical analysis discussed above.

Fig. 2 (b) shows the field dependence of magnetization of Cu$_3$Zn(OH)$_6$FCl and Cu$_4$(OH)$_6$FCl at 2 K. Cu$_4$(OH)$_6$FCl shows obvious ferromagnetic behavior with the magnetization jump about 0.0865 μB/Cu, while Cu$_3$Zn(OH)$_6$FCl shows no visible hysteresis. Comparison between Cu$_4$(OH)$_6$FCl and Cu$_3$Zn(OH)$_6$FCl demonstrates the disappearance of magnetic order in the latter, although the Zn content is not equal to 1. A linear function $M = A + B \times H$ is used to fit the magnetization at high field as shown in Fig. 2 (b). Similar fitting analysis has been performed in Cu$_{4-x}$Zn$_x$(OH)$_6$FBr and the Zn content dependence (doping dependence) of $B(x)$ has been obtained in Fig. 6(b) in Ref. 10. Compared with the fitting results in Fig. 2 (b) here, we find very consistent value in the $x$-dependence of the Zn content. For Cu$_4$(OH)$_6$FCl, we obtain $B = 0.035$ emu-mol$^{-1}$, almost the same as that in Cu$_4$(OH)$_6$FBr; and for Cu$_3$Zn(OH)$_6$FCl, we obtain $B = 0.02$ emu-mol$^{-1}$, this value is very close to the $x = 0.7$ value in Cu$_{4-x}$Zn$_x$(OH)$_6$FBr, again suggesting the success of doping process and Cu$_3$Zn(OH)$_6$FCl may be a new QSL candidate.

Moreover, our results are consistent with a previous study on Cu$_4$(OH)$_6$FCl, in which a magnetic transition at around 15 K was reported [24]. Recent neutron scattering and NMR studies reveal that Cu$_4$(OH)$_6$FBr change its structure at low temperature [16, 26] and such structural change gives rise to magnetic order. It is possible that a similar process happened in Cu$_4$(OH)$_6$FCl as well. Further neutron scattering experiment, similar to that performed on Cu$_4$(OH)$_6$FBr [11, 16], will reveal this process.

Fig. 3 (a) shows the specific heat of Cu$_3$Zn(OH)$_6$FCl at...
zero field from 0.8 K to 30 K and the inset shows the specific heat below 5 K at different fields. Fig. 3 (b) shows the $C_p/T$ between 2 K and 30 K for Cu$_3$Zn(OH)$_6$FBr and Cu$_4$(OH)$_6$FCl. Consistent with the magnetic measurements, the specific heat data above 0.8 K in Fig. 3 (a) show that Cu$_3$Zn(OH)$_6$FCl do not have any magnetic phase transition. As for Cu$_4$(OH)$_6$FCl, the magnetic order transition arises at about 15 ~ 17 K, which is manifested in the high temperature peak in $C_p/T$ in Fig. 3 (b). Further reduce the temperature, $C_p/T$ of Cu$_4$(OH)$_6$FCl shows another peak at 5 K, and $C_p/T$ of Cu$_3$Zn(OH)$_6$FCl shows another peak at around 3 K. These low temperature peaks, have also been seen in Cu$_{4-x}$Zn$_x$(OH)$_6$FBr [16] and previous study of Cu$_4$(OH)$_6$FCl [24], as well as in ZnCu$_3$(OH)$_6$Cl$_2$ [12, 27], share the same property that they are all significantly affected by magnetic field, as exemplified in the inset of Fig. 3 (a) for Cu$_3$Zn(OH)$_6$FCl and the inset of Fig. 2 (c) for Cu$_3$Zn(OH)$_6$FBr in Ref. [16]. The current understanding of such behavior is that these are the contribution from inter kagome layer Cu ions [10, 16], which have very weak interactions among themselves and are easily polarized by external field.

Even in the presence of inter kagome layer Cu, one can still obtained the information of the kagome QSL specific heat from the current data. First one needs to estimate the background of specific heat, to this end, the formula $C_{bg} = aT^2 + bT^3$ was used to fit the specific heat data between 20 K and 30 K in zero field. For Cu$_4$(OH)$_6$FCl, we obtain $a = 0.0246$ J-K$^{-3}$-mol$^{-1}$ and $b = 1.508 \times 10^{-4}$ J-K$^{-4}$-mol$^{-1}$ and for Cu$_3$Zn(OH)$_6$FCl, $a = 0.0152$ J-K$^{-3}$-mol$^{-1}$ and $b = 5.182 \times 10^{-5}$ J-K$^{-4}$-mol$^{-1}$. Obviously the $T^2$ term dominates in $C_{bg}$ which comes from the spin correlations above 20 K in two dimensional structure. The $T^3$ term, on the other hand, comes from the three dimensional lattice contribution [25]. By subtracting the low-temperature background contribution $C_{bg}$ from the measured specific heat data, the magnetic specific heat and the magnetic entropy are obtained for these two materials. At 25 K, their magnetic entropy both reach corresponding maximal values. For Cu$_4$(OH)$_6$FCl, its magnetic entropy is about 4.15 J-mol$^{-1}$-K$^{-1}$, very close to that of Cu$_4$(OH)$_6$FBr [16] while for Cu$_3$Zn(OH)$_6$FCl, the value is about 2.39 J-mol$^{-1}$-K$^{-1}$, similar with that in Cu$_3$Zn(OH)$_6$FBr system [16]. These results suggest that Cu$_4$(OH)$_6$FCl is very close to Cu$_4$(OH)$_6$FBr with possibly the same magnetic structure, and Cu$_3$Zn(OH)$_6$FCl is close to Cu$_3$Zn(OH)$_6$FBr with QSL ground states.

IV. CONCLUSION

To summarize, in this work we have successfully synthesized a new QSL candidate material Cu$_3$Zn(OH)$_6$FCl and its parent material Claringbullite Cu$_4$(OH)$_6$FCl and performed comprehensive thermodynamic measurements on them. We find Cu$_3$Zn(OH)$_6$FCl a highly frustrated kagome material and do not show magnetic order down to 0.8 K and hence is a good candidate for kagome QSL, whereas Cu$_4$(OH)$_6$FCl is magnetically ordered below 17 K. The possible structure change in Cu$_4$(OH)$_6$FCl accompanied with the development of magnetic order is yet to be revealed by elastic neutron scattering. It will also be very interesting to further explore the similarity of the Cu$_4$-Zn$_x$(OH)$_6$FBr family with that of the Cu$_4$-Zn$_x$(OH)$_6$FBr family.

Nevertheless, the pathway from Cu$_4$(OH)$_6$FCl to Cu$_3$Zn(OH)$_6$FCl provides an example of chemical control of the interlayer Zn ions in kagome materials, and offers the opportunity to investigate the transition between magnetically ordered systems to QSL state. Such investigations will have very significant theoretical impact. As the material realization of topological order, possible kagome QSL in Cu$_3$Zn(OH)$_6$FCl and its transition to the magnetically order Claringbullite Cu$_4$(OH)$_6$FCl, could potentially help to understand the novel phenomena such as the different types of Ising gauge field structures in kagome QSLs [25], the existence of fractionalized anyonic excitations and their symmetry fractionalization in the symmetry enriched topological orders, proposed for Z$_2$ QSL in kagome systems from static signature in magnetic edge states [29] and dynamical signature in inelastic neutron scattering [30, 31]. If any of these signatures could be discovered in real material such as Cu$_4$(OH)$_6$FCl and Cu$_3$Zn(OH)$_6$FCl presented in this work, it will greatly encourage the further development of the field of topological orders as the new paradigm of condensed matter physics.

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