Gapless Quantum Spin Liquid in the S=1/2 Anisotropic Kagome Antiferromagnet ZnCu$_3$(OH)$_6$SO$_4$

Supplementary information

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ZnCu$_3$(OH)$_6$SO$_4$ (#1), Zn$_{0.6}$Cu$_{3.4}$(OH)$_6$SO$_4$ (#2) and Cu$_4$(OH)$_6$SO$_4$ (#3) powder samples were prepared by hydrothermal synthesis from an aqueous suspension obtained from CuSO$_4$·5H$_2$O (#1: 1388 mg, 5.56 mmol. #2: 1198 mg, 4.8 mmol. #3: 1598 mg, 6.4 mmol), ZnSO$_4$·7H$_2$O (#1: 799 mg, 2.78 mmol. #2: 460 mg, 1.6 mmol. #3: 0 mg, 0 mmol) and NaOH (#1: 445 mg, 11.12 mmol. #2: 384 mg, 9.6 mmol. #3: 384 mg, 9.6 mmol) in 34 ml H$_2$O. The aqueous suspension was transferred into a 100 ml Teflon liner, which was capped and placed into a stainless steel pressure vessel. The vessel was heated at 170 °C for 4 days, and then cooled down to room temperature at a rate of 0.3 °C·min$^{-1}$. A blue-green polycrystalline powder was found at the bottom of the liner, then isolated from the liner by filtration, washed with high purity water, ethyl alcohol and acetone repeatedly and in succession, and dried over by a loft drier at 50 °C. By this procedure, 810 mg of ZnCu$_3$(OH)$_6$SO$_4$, 700 mg of Zn$_{0.6}$Cu$_{3.4}$(OH)$_6$SO$_4$ and 670 mg of Cu$_4$(OH)$_6$SO$_4$ were obtained. The corresponding yields are 96 %, 97 % and 93 % respectively, with respect to the starting material NaOH.
Figure S1. Synchrotron X-ray diffractions of ZnCu$_3$(OH)$_6$SO$_4$, Zn$_{0.6}$Cu$_{3.4}$(OH)$_6$SO$_4$ and Cu$_4$(OH)$_6$SO$_4$ with a incident light, $h\nu = 8639$ eV, $\lambda = 1.4352$ Å, at room temperature.
**Figure S2.** Anomalous scattering factors of ZnCu$_3$(OH)$_6$SO$_4$ obtained from synchrotron X-ray absorption fine structure (XAFS) around Cu K-edge (8680 ~ 9635 eV), at room temperature. Kramers-Kronig transformation based on the measured absorption spectrum was used [1].

**Figure S3.** Anomalous scattering factors of ZnCu$_3$(OH)$_6$SO$_4$ obtained from synchrotron XAFS around Zn K-edge (9361 ~ 10663 eV), at room temperature.
Figure S4. Synchrotron X-ray diffractions and combined Rietveld refinement of ZnCu$_3$(OH)$_6$SO$_4$ with incident lights, $h\nu = 8902$ eV, 8940 eV, 8979 eV (Cu K-edge), 9018 eV, 9058 eV, 9319 eV, 9570 eV, 9614 eV, 9659 eV (Zn K-edge), 9704 eV and 9750 eV respectively at room temperature. (a) Raw data. (b) Enlarged view of raw data around the strongest peaks. (c) Rietveld refinement data. (d) Enlarged view of refinement data around the strongest peaks. (e) Residuals between raw data and refinement data. (f) Enlarged view of residuals around the strongest peaks. The ratio of Zn:Cu ~ 1:3 measured by ICP and EDX, the above measured anomalous scattering factors of Zn and Cu around corresponding K-edges, and the theoretical anomalous scattering factors far away from the edges obtained from FPRIME [2] were used in the combined Rietveld refinements.
Figure S5. Synchrotron X-ray diffraction and combined Rietveld refinement of \( \text{ZnCu}_3\text{(OH)}_6\text{SO}_4 \) (Fig. S4) at Cu K-edge.
**Table S1.** Combined Rietveld refinement results of ZnCu$_3$(OH)$_6$SO$_4$. Space group: P 2$_1$/a, a = 13.0606(12) Å, b = 9.8697(10) Å, c = 6.0882(6) Å, $\beta$ = 103.6071(24)$^\circ$. A fixed positional parameter of proton is adopted due to its insignificant contribution to the x-ray scattering. $R_p$ = 2.15 %, $R_{wp}$ = 3.07 %, goodness of fit ($\chi^2$) = 1.805 in total.

| P 2$_1$/a | Fraction | x       | y       | z       | U$_{iso}$(×100) |
|-----------|----------|---------|---------|---------|-----------------|
| Cu1       | 0.895(20) | 0.2948(4)| 0.4854(5)| 0.5258(10)| 5.08(19)       |
| Zn1       | 0.105(20) | 0.2948(4)| 0.4854(5)| 0.5258(10)| 5.08(19)       |
| Cu2       | 0.925(24)| 0.2965(5)| 0.4908(5)| 1.0173(11)| 6.75(23)       |
| Zn2       | 0.075(24)| 0.2965(5)| 0.4908(5)| 1.0173(11)| 6.75(23)       |
| Cu3       | 0.957(18)| 0.1170(4)| 0.2605(4)| 0.1750(9) | 4.39(18)       |
| Zn3       | 0.043(18)| 0.1170(4)| 0.2605(4)| 0.1750(9) | 4.39(18)       |
| Cu4       | 0.221(3) | 0.1202(5)| 0.2613(4)| 0.6846(10)| 8.83(24)       |
| Zn4       | 0.779(3) | 0.1202(5)| 0.2613(4)| 0.6846(10)| 8.83(24)       |
| S         | 1.000    | 0.3880(5)| 0.2024(5)| 0.3240(14)| 7.14(17)       |
| O1        | 1.000    | 0.0857(10)| 0.1199(11)| 0.3967(22)| 1.06(40)       |
| O2        | 1.000    | 0.0960(13)| 0.1467(15)| 0.9132(28)| 5.29(56)       |
| O3        | 1.000    | 0.1463(12)| 0.3554(15)| 0.4529(35)| 7.19(60)       |
| O4        | 1.000    | 0.1569(8) | 0.3863(9) | 0.9604(24)| 0.53(35)       |
| O5        | 1.000    | 0.2674(12)| 0.5482(17)| 0.2526(46)| 16.25(73)      |
| O6        | 1.000    | 0.3712(16)| 0.3737(14)| 0.7913(30)| 6.94(65)       |
| O7        | 1.000    | 0.2751(6) | 0.1198(9) | 0.2976(19)| 0.83(31)       |
| O8        | 1.000    | 0.3636(15)| 0.3753(12)| 0.2748(24)| 5.23(53)       |
| O9        | 1.000    | 0.4389(9) | 0.1502(11)| 0.1148(21)| 1.60(40)       |
| O10       | 1.000    | 0.4251(11)| 0.1664(13)| 0.6455(15)| 5.06(58)       |
Figure S6. The ultraviolet/visible absorption spectrum of ZnCu$_3$(OH)$_6$SO$_4$ at 298 K. The spectrum gives an absorption edge energy which corresponds to a band gap $E_g$ [3], $\sim 4.2$ eV.

References

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[3] Tsunekawa S, Fukuda T and Kasuya A 2000 Blue shift in ultraviolet absorption spectra of monodisperse CeO$_{2-x}$ nanoparticles J. Appl. Phys. 87 1318