Localized low-energy magnetic excitations in the kagomé Heisenberg quantum spin liquid candidate YCu$_3$(OH)$_6$Br$_{2.5}$

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The spin-1/2 kagomé Heisenberg antiferromagnet is generally accepted as one of the most promising two-dimensional models to realize a quantum spin liquid state. Previous experimental efforts were almost exclusively on only one archetypal material, the herbertsmithite ZnCu$_3$(OH)$_6$Cl$_2$, which unfortunately suffers from the notorious orphan spins problem caused by magnetic disorders. Here we turn to YCu$_3$(OH)$_6$Br$_{2.5}$, recently recognized as another host of globally undistorted kagomé Cu$^{2+}$ lattice free from the orphan spins, thus a more feasible system for studying the intrinsic kagomé quantum spin liquid physics. Our high-resolution low-temperature thermal conductivity measurements found vanishing small residual linear term of $\kappa/T$ ($T \to 0$), clearly rule out itinerant gapless excitations. Magnetic scattering of phonons grows exponentially with temperature, suggesting a gapped magnetic excitation spectrum. Additionally, the analysis of magnet field impact on the thermal conductivity reveals a field closing of the spin gap, while the excitations remain localized.

Quantum spin liquid (QSL) is an intriguing topic that has fascinated condensed matter physicists for decades. It is the ground state of certain magnetic systems where frustrations prevent the strongly correlated spins from forming a better understood magnetically ordered state, but leave them as quantum paramagnetic/disordered states that is featured by long range topological ordering, fractionalized quasiparticles, and gauge excitations [1–5]. Although appealing, our understanding of QSLs is still in its infancy. There is even no consensus whether QSLs really exist or not in solid-state materials. Apart from magnetic disorder effect, and structural imperfections of the kagomé lattice. They can cause spurious signals in experiments mimicking QSL features [19], and can also diminish the delicate sought-after signatures of QSL states [20].

The difficulties of extracting pristine information from herbertsmithite experiments lead to heated debates on many key issues, halting feedbacks to theoretic considerations of the KHA model [21–26]. What renders the situation even more intricate is that theoretical works searching for another representative material of the KHA model which are very close in energy 27–29. Needless to say, searching for another representative material of the KHA model is of paramount importance.

For these reasons, the importance of identification of the recently synthesized bromine compound YCu$_3$(OH)$_6$Br$_{2.5}$ (YCOB) as a new potential KHA material is obvious 27–29. As illustrated in Fig. 1, spin-1/2 Cu$^{2+}$ ions fully occupy the globally regular kagomé sites, free from site mixing with other nonmagnetic ions. The magnetic system of YCOB is dominated by large nearest neighbor coupling of an averaged value $J_1 \sim 60$ K, more than one order of magnitude larger than the further-neighbor and interlayer couplings 28. A certain exchange bond randomness is, however, to be expected because in between the Cu kagomé layers, the distribution of OH$^-$/Br$^-$ is not symmetric, pushing up to 70% of Y$^{3+}$ ions out of their ideal position 28. As a candidate for the KHA, no magnetic order was detected in YCOB by preliminary thermodynamic studies down to 50 mK (< $J_1$/1000) 27–29. In a word, YCOB appears to be the most promising realization of the kagomé QSL without.

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FIG. 1: (a) Lattice structure of YCOB. Although the anti-site mixing of OH$^{2-}$/Br$^{2-}$ pushes 70% of Y$^{3+}$ away from its ideal position and can cause quenched exchange randomness as illustrated in (b), the space group of $P\bar{3}m1$ and thus the globally regular kagomé lattice of Cu$^{2+}$ remains intact [25]. The black lines show the unit cell.

In this letter, low-temperature thermal conductivity ($\kappa$) measurements were performed on three single crystals of YCOB down to 70 mK. We firmly conclude that there is no residual linear term in the $T \to 0$ extrapolation of the $\kappa/T$ curve ($\kappa_0/T$), i.e. there are no itinerant spin excitations in the ground state. On the other hand, a clear deviation off standard phononic power-law $\kappa/T$ curve is observed at a quite low temperature $T^*$, implying that phonon-spin scattering persists down to mK range. Additionally, a clear magnetic field dependence of $\kappa$ is uncovered, revealing the field impact on the spin excitation spectrum of YCOB. Our analysis yields a spin gap $\Delta/k_B \approx 1.4$ K at zero magnetic field, which strongly reduces upon application of large magnetic fields.

Single crystals of YCOB were grown by the hydrothermal technique [27], followed by a recrystallization process to improve the crystal quality [25]. Three samples of roughly rectangular shape of $1.8 \times 0.24 \times 0.18$ (Sample#1), $0.85 \times 0.21 \times 0.053$ (Sample#2), and $2.2 \times 0.32 \times 0.24$ (Sample#3) were used for the heat transport measurements. Four silver wires were attached to the surfaces of the samples with silver paint, to let the heat flow in the $ab$-plane. Thermal conductivity was measured in a dilution refrigerator using a standard four-wire steady-state method, with two RuO$_2$ chip thermometers, which were in-situ calibrated against a reference RuO$_2$. Magnetic field was applied out of the $ab$-plane.

The thermal conductivity of the three YCOB samples without magnetic field, plotted as $\kappa/T$ vs $T$, is shown in Fig. 2(a). They are of very similar type. The minor difference of absolute values of the calculated $\kappa/T$ can be attributed to the uncertainty in the measurement of the sample geometry. The first key message of our work is the clear trend that all $\kappa/T$ curves going towards the origin of coordinates. This fact precludes itinerant quasiparticles as the excitations of the YCOB ground state, which otherwise should result a sizeable $\kappa_0/T$ like electrons in metals [30]. The data suggest that phonons are the only heat carrier in YCOB. Therefore, the fractionalized spin excitations, if existent in YCOB, must be localized or gapped.

Indeed, in the low-temperature limit $\kappa/T(T)$ obeys the expected power law dependence, as can be inferred from Fig. 2(b), where $\kappa/T(T)$ is plotted in log-log scale. However, as indicated by the dashed red line and marked with the red arrow, the curve deviates downward from the low-temperature power law above a critical temperature $T^*$.

FIG. 2: Low-temperature thermal conductivity of YCOB crystals without magnetic field. (a) $\kappa/T(T)$ curves of three single crystals. (b) $\kappa/T(T)$ curve of Sample#1 as a representative case, plot in the log-log scale. The dashed red line highlights its linear dependence at the low temperature limit. The data deviate downward from this linear behavior above a temperature $T^*$ marked by the arrow. (c) The fit parameters residual liner term $(\kappa_0/T$, left axis) and exponent $(\alpha$, right axis) of all three samples.
$T^* \sim 230$ mK. A power-law fit

$$\frac{\kappa}{T} = \frac{\kappa_0}{T} + b T^n$$  \hspace{1cm} (1)

to the data below $T^*$ results the exponent $n \approx 1.1$ and the residual linear term $\kappa_0/T = -5.66 \text{ mW K}^{-1} \text{ cm}^{-2}$. The vanishing small $\kappa_0/T$ is confirmed by the other two samples, as summarized in Fig. 2(c). As can be inferred from the same figure, the exponent $n$ is slightly sample dependent and varies between about 1.1 and 1.25. Such sample dependence of $n$ is characteristic for ballistic phonon heat transport where the phonons experience specular reflection on the sample surfaces [31, 32]. The reduced $\kappa/T$ above $T^*$ clearly indicates the breakdown of this ballistic transport and implies additional scattering of the phonons, the only source of which can be phonon–spin scattering. Actually, recent low-temperature heat transport studies on several quantum magnets revealed this type of scattering being important whenever magnetic fluctuations prevail [33, 34]. Hence, since below $T^*$ such scattering apparently freezes out in YCOB, without further analysis, our data imply an energy gap of the spin fluctuations.

To gain more information about the ground state properties of YCOB, $\kappa(T)$ was measured in various magnetic fields up to 16 T. The full set of results of Sample 1 is shown in Fig. 3 as a representative case. Apparently, all three samples share very similar behavior [37]. $\kappa(T)$ curves get further suppressed with increasing field, and $T^*$ is concomitantly pushed to lower temperatures. This sensitivity of $\kappa$ implies the field tunability of the magnetic excitations spectrum, underpinning the low energy nature of these excitations.

$\kappa(H)$ isotherms can provide information of the field impact on thermal transport from another perspective. As displayed in Fig. 3(b), a field of 16 T can reduce $\kappa$ by about 12.5% at higher temperatures. The field effect is less significant at lower temperatures, and is nearly indistinguishable at the lowest temperature investigated (101 mK, below $T^*$ at 16 T). It is worthwhile to notice that the magnetic specific heat $C_{\text{mag}}$ of YCOB increases in field [28, 29]. Such anticoherent $\kappa$ and $C_{\text{mag}}$ is hard to reconcile if they are contributed directly from the same (quasi)particles. Normally, for any entropy carrier, its contribution to $\kappa$ is related to its contribution to $C$ by simply multiply its velocity $v$ and its mean free path $l$, $\kappa \propto C_i v_i l_i$. The total thermal conductivity and specific heat are the sum of all components, $\kappa = \sum \kappa_i$ and $C = \sum C_i$. The contradicting trends of $\kappa$ and $C$ in field can only be reasonably explained by accepting that the field sensitive quasiparticle contributes differently to these two quantities. Field enhanced $C_{\text{mag}}$ means a proliferation of excitations, which reduce the phonon mean free path. That further corroborates our scattered phononic heat transport scenario proposed earlier to explain the zero-field $\kappa(T)$ behavior.

Having established that magnetic fluctuations do not directly contribute to the heat transport in YCOB but have a significant impact on the phononic transport beyond $T^*$ through scattering, we turn now to a more detailed analysis. According to Matthiessen’s rule, an additional magnetic scattering mechanism affects the total scattering time ($\tau_{\text{total}}$) in the form of

$$\tau_{\text{total}}^{-1} = \tau_p^{-1} + \tau_{p-s}^{-1}$$  \hspace{1cm} (2)

where $\tau_p$ stands for the intrinsic phonon scattering. A $\kappa(T)$ curve free from phonon–spin scattering, $\kappa_{\text{free}}(T)$, is estimated by the power-law fit to the zero-field $\kappa(T)$ curve below $T^*$ and its extension to the whole temperature range (dashed line in Fig. 2(b)). We seek to find a direct measure of the phonon–spin scattering rate $\tau_{p-s}^{-1}$. Our data provide access to it via the normalized reduc-

![Field impact on the thermal conductivity of YCOB.](image-url)

(a) The $\kappa(T)$ curves at different fields. Increasing magnetic field suppresses the $\kappa(T)$ curve monotonically, and this effect is discernible at lower temperatures in higher fields. (b) The closed color circles (left axis) represent the relative change of $\kappa$ according to the field change at different temperatures. For the $T = 820$ mK curve, data collected with field ramped up (larger red circles) and down (smaller magenta circles) match perfectly, excluding hysteresis effects. The open squares (right axis) show the relative field change of the magnetic specific heat, adapted from Ref. [28].

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FIG. 4: Exponential and power-law fits to the temperature dependence of $\tau_p/\tau_{p-s}$ (see text) for one sample at (a) zero field, and (b) high field. (c) The gap size estimated from the acceptable exponential fits at different fields of Sample#1 (■), Sample#2 (●), and Sample#3 (♦) [37]. The shaded region represents the temperature range over which the fit were performed. The dashed line is a guide to the eye.

In summary, by measuring the low-temperature thermal conductivity of YCOB, we managed to probe the excitations in this material realization of a modified KHA model. The absence of direct magnetic contribution to $\kappa$ firmly exclude itinerant spin excitation in this compound on top of its ground state. Furthermore, utilizing scattered phononic thermal conductivity as a probe, we found the magnetic excitations in YCOB persist down to very low temperature with a small spin gap. The gap size can be reduced by applying magnetic field. Our study highlight YCOB as a prime kagomé QSL candidate free from severe disorder problems, an ideal testbed for various QSL theories.

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See Supplemental Material for more data and analysis of all the samples, and a discussion on the κ(β) isotherms at higher temperatures.