The observation of quantum fluctuations in a kagome Heisenberg antiferromagnet

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The search for the experimental evidence of quantum spin liquid (QSL) states is critical but extremely challenging, as the quenched interaction randomness introduced by structural imperfection is usually inevitable in real materials. YCu3(OH)6.5Br2.5 (YCOB) is a spin-1/2 kagome Heisenberg antiferromagnet (KHA) with strong coupling of \( \langle J_1 \rangle \sim 51 \) K but without conventional magnetic freezing down to \( 50 \) mK \( \sim 0.001 \langle J_1 \rangle \). Here, we report a Br nuclear magnetic resonance (NMR) study of the local spin susceptibility and dynamics on the single crystal of YCOB. The temperature dependence of NMR main-line shifts and broadening can be well understood within the frame of the KHA model with randomly distributed hexagons of alternate exchanges, compatible with the formation of a randomness-induced QSL state at low temperatures. The in-plane spin fluctuations as measured by the spin-lattice relaxation rates \( (1/T_1) \) exhibit a weak temperature dependence down to \( T \sim 0.03 \langle J_1 \rangle \). Our results demonstrate that the majority of spins remain highly fluctuating at low temperatures despite the quenched disorder in YCOB.

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Quantum spin liquid (QSL) is a state of matter that exhibits exotic fractional excitations and long-range entanglement without symmetry breaking\(^1\)\(^4\). Since Anderson’s proposal of the prototype, i.e., resonating-valence-bond (RVB) state, in 1973\(^5\), QSL has been attracting researchers for decades, due to its key role in understanding high-temperature superconductivity\(^6\) and the possible realization of the topological quantum computation\(^7\). Experimentally, many prominent two-dimensional QSL candidate compounds have been extensively studied (the one-dimensional scenario of QSL is qualitatively different\(^8\)), including the kagome-lattice ZnCu\(_3\)(OH)\(_6\)Cl\(_2\) (herbstsmithite)\(^9\)\(^10\), triangular-lattice \(\kappa\)-(ET)\(_2\)Cu\(_2\)(CN)\(_3\)\(^11\)\(^12\), EtMe\(_3\)Sb[Pd(dmit)\(_2\)]\(_2\)\(^13\)\(^14\), YbMgGaO\(_4\)\(^15\)\(^16\), etc., all of which generally exhibit gapless QSL behaviors\(^17\)\(^18\)\(^19\)\(^20\)\(^21\)\(^22\)\(^23\)\(^24\), but without evident magnetic thermal conductivity\(^25\)\(^26\)\(^27\)\(^28\).

Despite the progress, the existing experimental evidence for QSL remains circumstantial and strongly depends on theoretical interpretation. The root cause lies in the quenched interaction randomness introduced by structural imperfection that is inevitable in all real materials\(^29\)\(^30\)\(^31\)\(^32\). Therefore, great efforts are being devoted to exploring for ultrahigh-quality candidate materials, which is extremely challenging\(^33\). On the other hand, disorder-free QSL, even the KHA can lead to a valence bond glass ground state (GS)\(^34\). Despite the growing interest in theory, the key issue is the appearance of gapless spin excitations\(^35\)\(^36\). Unlike other magnetic ordering nor spin-glass freezing was observed down to \(T \sim 0.03\)\((J_1)\) despite the quenched exchange randomness, thus supporting the survival of strong quantum fluctuations in YCOB.

**Results**

**NMR spectra.** Figure 2a shows the \(^{81}\)Br NMR spectra measured on the crystal \(S_1\) (Supplementary Fig. 1) at \(\mu_B H_c \sim 10.75\) T \((\sim 0.14(J_1))\). Two well-separated peaks are observed, originating respectively from two different Wyckoff positions of 2d (Br1) and 1a (Br2). Above \(-15\) K, the ratio between the integrated intensities of these two peaks \(I_{Br2}/I_{Br1} \sim 0.2\) is well consistent with the stoichiometric ratio of Br2 and Br1 determined by single-crystal x-ray diffraction (XRD) \(j_{Br2}/j_{Br1} = 0.22(1)\)\(^34\) (see inset of Fig. 2b). Below 15 K, the weight of Br1 NMR line decreases drastically and \(I_{Br2}/I_{Br1}\) increases sharply, due to the reduced spin-spin relaxation times (Supplementary Note 4 and Supplementary Fig. 5)\(^35\). Neither Br1 nor Br2 peak splits down to 1.7 K, suggesting the absence of conventional magnetic ordering within the ability of our resolution.

The NMR shift of Br1 (\(K_1\)) detecting three \((z = 3)\) equidistant spins of each triangle on the kagome lattice (Fig. 1a), follows the bulk susceptibility \(\chi_B\) measured at the same magnetic field strength in the full temperature range (Fig. 2b), compatible with the absence of defect orphan spins in YCOB. In contrast, the NMR shift of Br2 (\(K_2\)) shows an obvious deviation from the bulk susceptibility below \(\sim 100\) K \(- 2(J_1)\). Generically, the NMR shift consists of a \(T\)-dependent term proportional to the local susceptibility and a \(T\)-independent term \((K_0)\). Above 100 K, the NMR line broadening is insignificant (Fig. 2) and the calculated local magnetization is nearly spatially homogeneous (Fig. 3a), and thus one expects a scaling law \(K = A_{hf} q^4 + K_0\) where \(A_{hf}\) presents the hyperfine coupling between Br (Br1 or Br2) nuclear and Cu\(^{2+}\) electronic spins. By fitting the experimental data (see inset of Fig. 2c), we obtain \(A_{hf1} = -0.68(2)\ T/\mu_B\), \(K_0 = -0.015(7)\%\) and \(A_{hf2} = 0.55(3)\ T/\mu_B\), \(K_0 = 0.02(1)\%\). The presence of both positive and negative hyperfine couplings of the same nuclear species is surprising, and the underlying mechanism must be complex, including both the positive and negative contributions.

The NMR shift of Br2 probes spins of hexagons on the kagome lattice (Fig. 1b, c), but is obviously smaller than \(A_{hf2} q^4\) \((K_2 < K_0)\) below 100 K (Fig. 2c). In fact, the formation energy of the optimized nonsymmetric Br2-OH2 stacking sequence (Fig. 1b) \((-37.8\ eV/\text{FU})\), is \(\sim 2.5 \times 10^4\ K/\text{FU}\) lower than that of the symmetric Br2-Br2 configuration (Fig. 1c) \((-35.7\ eV/\text{FU})\). Therefore, Br2 ions actually prefer the nonsymmetric local environments, and Br2 nuclear spins mainly probe the symmetric hexagons with alternate exchanges \((J_{1a} > J_{1c})\) as illustrated in Fig. 1b. Intuitively, the nonsymmetric hexagon tends to locally release the frustration and form three nonmagnetic singlets along the stronger couplings \(J_{1a}\) (Fig. 3e), which accounts...
for the relatively smaller Br2 shifts observed below 100 K (Fig. 3a). Moreover, the Br1 line detects the site susceptibility/magnetization of all the Cu\(^{2+}\) spins with exchange couplings \(J_{1a}, J_{1b},\) and \(J_{1c}\), whereas the Br2 line mainly probes the hexagons of spins only with \(J_{1a}\) and \(J_{1c}\). The Br2 line probes less kinds of Cu\(^{2+}\) spins, and thus is narrower than the Br1 line.

Quantitatively, the temperature dependence of both Br1 and Br2 shifts can be reproduced by the average magnetization of all

\[
\langle S_z \rangle = \frac{M}{H_x}\n
\]

The principal axes of the electric field gradient calculated by density functional theory at the Br1 (a) and Br2 (b) sites are displayed by arrows scaled by the modulus of the tensor element, \(\nu_{zz}\). In our measurements, the external magnetic field is always applied along the \(z\) axis, and thus the second-order quadrupole shifts of the main NMR lines are negligibly small. d The crystal structure determined by the single-crystal x-ray diffraction. The thin lines mark the unit cell.

**Fig. 1** Crystal structure of YCu\(_3\)(OH)\(_6\).5Br\(_2.5\) around the kagome layer of Cu\(^{2+}\). The Br1 nuclear (\(^{81}\)Br or \(^{79}\)Br) spin detects three equidistant Cu\(^{2+}\) electronic spins of each triangle on the kagome lattice (a), and the inset defines the coordinate system for the spin components. Whereas, the Br2 nuclear spin mainly probes the nonsymmetric hexagon of spins with alternate exchanges (b), instead of the symmetric hexagon with almost uniform exchange (c). The formation energies of b and c stacking sequences are listed, and the different exchange paths of Cu-O-Cu (\(J_{1a}, J_{1b},\) and \(J_{1c}\), depending on the bond angles) are marked.

**Fig. 2** Nuclear magnetic resonance spectra of YCu\(_3\)(OH)\(_6\).5Br\(_2.5\). a Frequency-sweep spectra measured on the sample \(S_1\) at a field \(\mu_0 H = 10.75\) T (the reference frequency \(f_0 = 81\gamma n\mu_0 H = 123.64\) MHz). The shifts of two lines, \(K_1\) and \(K_2\), are marked by solid and hollow triangles, respectively. Temperature dependence of \(K_1\) (b) and \(K_2\) (c), with the bulk magnetization \(\langle S_z \rangle\) measured at \(\mu_0 H = 10.75\) T for comparison. The inset of b shows the ratio between the integrated intensities of \(^{81}\)Br2 and \(^{81}\)Br1 lines, as well as the stoichiometric ratio from x-ray diffraction. Inset of c displays \(K_1\) and \(K_2\) shifts vs bulk susceptibility \(\chi\) (i.e. \(M/H\)). The red bars display the normalized frequency regions where the intensity is larger than half of the maximum value in b and c, and error bars on \(I_{Br2}/I_{Br1}\) show a standard error from the fit.
the triangles and nonsymmetric hexagons on the kagome lattice, viz. $K_1 \sim A_{11} K_1 (S_i^z/S_i^z/\mu_n H_n)$ and $K_2 \sim A_{12} K_2 (S_i^z/S_i^z/\mu_n H_n)$, respectively (Fig. 3a), with $J_{1a} = 89$ K, $J_{1b} = 48$ K, and $J_{1c} = 16$ K ($J_2 \approx 51$ K) experimentally determined by bulk susceptibilities (Supplementary Note 1 and Supplementary Fig. 2). Taking all the triangles and nonsymmetric hexagons into account, we are able to simulate the broadening of both Br1 and Br2 lines by introducing the distributed density $\propto d_{\text{dist}}(S_i^z)/d(S_i^z)$ (Fig. 3b, c), where $d_{\text{dist}}(S_i^z)$ is the number of triangles or nonsymmetric hexagons with the local magnetization (per site) ranging from $\langle S_i^z \rangle$ to $\langle S_i^z \rangle + d(S_i^z)$. $\langle S_i^z \rangle$ is thermally averaged, so the distributed density is a function of $T$.

The simulations also enable us to revisit the correlation functions $(S_i \cdot S_j)$ in this KHA system with randomness. Compared to the ideal case (Fig. 3f), a small fraction (~3/54) of well-defined singlets with $(S_i \cdot S_j) \sim -0.7 \rightarrow -0.75$ are frozen at low $T$ in YCOB (Fig. 3e), which is a signature of releasing frustration due to the quenched randomness. These local singlets might confine the mobile spinons to the kagome lattice, with the well-known ZnCu$_3$(OH)$_6$Cl$_2$ [28, 29], EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ [30, 31], etc. However, the majority of antiferromagnetic interactions remain not fully satisfied at low $T$ (Fig. 3d, e), and the GS wavefunction should be represented by a superposition of various pairings of spins. It is worth to mention that the weights of different pairings should be different due to the quenched randomness. The survival of strong frustration in the $S = 1/2$ random KHA speaks against the product GS wavefunction of randomly distributed singlets, and may still give rise to strong quantum fluctuations. To test this, we turn to the spin dynamics of YCOB mainly probed by the spin-lattice relaxation rates as follow.

Spin dynamics. The representative spin-lattice relaxation data measured on YCOB are displayed in Fig. 4a and b, which can be well fitted to the single-exponential function for the central transition of $I = 3/2$ nuclear spins, i.e.,

$$M(t) = M_0 - 2M_0 F \left( \frac{1}{10} e^{-\frac{t}{\tau}} + \frac{9}{10} e^{-\frac{t}{\tau}} \right),$$  \hspace{1cm} (1)

where $M_0$ and $F$ are scale parameters for intensity. Alternatively, the relaxation data may be fitted with the stretched-exponential one,

$$M(t) = M_0 - 2M_0 F \left[ \frac{1}{10} e^{-\left(\frac{t}{\tau}\right)^\beta} + \frac{9}{10} e^{-\left(\frac{t}{\tau}\right)^\beta} \right].$$  \hspace{1cm} (2)

Here, the stretching exponent $\beta$ slightly decreases at low temperatures (see inset of Fig. 4b), but remains large down to the...
lowest temperature of 1.7 K, $\beta \approx 0.8$. Moreover, the fit to the single $T_1$ function (i.e. $\beta = 1$) is still good even at 1.7 K (Fig. 4b), with the adj. $R^2 = 0.997^{53}$. The inclusion of the additional fitting parameter $\beta$ only slightly improves the fit (the adj. $R^2$ increases to 0.998), and even makes the standard error on $T_1$ larger. Therefore, all the following $T_1$ data are obtained with the single-exponential fits.

Figure 4c shows the results of Br1 nuclear spin-lattice relaxation rates ($1/T_1$). Br1 $1/T_1$ is highly sensitive to the electronic spin fluctuations perpendicular to the applied magnetic field on the kagome layer via the hyperfine coupling $39,44-46$.

$$\frac{1}{T_1} \sim T \frac{1}{h} \sum_{q} |\chi(q,F_0)| \sim \frac{\pi J_{0}^{2} M_{0}^{2} q^{2}}{Z} \sum_{q,m,m'} e^{-\frac{2}{m}} \times |\langle q | S_{m}^{+} | m \rangle|^{2} \delta \left( f_0 - \frac{E_{m} - E_{m'}}{h} \right) \tag{3}$$

where the $q$ dependence of $A_{hy}$ is neglected, $f_0 = \gamma_{P} H_{ll}$ ($\ll k_B T/h$) → 0 presents the NMR frequency, $S_{q}$ is the Fourier transform of $S_{1}^{z}$ over all triangles, and $Z = \sum_{m} \exp(-E_{m}/k_B T)$ the partition function. In our simulation of $1/T_1$, the delta function is replaced by a Gaussian distribution with narrow width $\sim 10^{-3}(f_{0}/h)^{3,56}$.

At high temperatures ($T \gg \langle J_{1} \rangle$), the Moriya paramagnetic limit yields the $T$-independent $1/T_{1,hy} = (2\pi)^{-1} \frac{S(S+1)}{3} 2z/\langle J_{1} \rangle \approx 300 \text{s}^{-1}$, reasonably comparable with the observation (Fig. 4c), where $v_{c} = \langle J_{1} \rangle \sqrt{2z S(S+1)/3} / h$ is the exchange frequency with the coordination number $z = 4^{35,37,38}$. Upon cooling, $1/T_1$ slightly decreases first and then rises at $T \sim \langle J_{1} \rangle$. These features are qualitatively reproduced by the random KHA model of YCOB (Fig. 4c). It is challenging to precisely simulate $1/T_1$, possibly due to the neglecting of the $q$ dependence of $A_{hy}$. At $T = 15 K \sim 0.3\langle J_{1} \rangle$, a weak anomaly (kink) of $1/T_1$ is observed, coinciding with the saturation of local nearest-neighbor correlations ($S_{1} \cdot S_{1}$) (Fig. 3d). This is possibly attributed to the emergence of short-range spin correlations, as seen in $\kappa$-(ET)$_{2}$Cu$_2$(CN)$_{3}$, PbCuTe$_2$O$_6$, etc. $50,59-61$.

Discussion

As $T$ further decreases below $\sim 10 K \sim 0.2\langle J_{1} \rangle$, $1/T_1$ exhibits a weak enhancement, $1/T_1 \sim T^{-\alpha}$ with $\alpha = 0.20 \pm 0.02$, at least down to 1.7 K $\sim 0.03\langle J_{1} \rangle$. This weak enhancement of $1/T_1$ is well reproducible between different single-crystal samples, nuclear spin probes ($^{81}$Br and $^{79}$Br), and applied magnetic fields ($\mu_B H_0 = 10.75$ and 11.59 T), as shown in Fig. 4. It is necessary to mention that the similar slowing down of spin fluctuations was also reported in other quantum disordered spin systems $62,63$. Such a behavior of $1/T_1$ suggests the spin system of YCOB may be proximate to a gapless/critical QSL state or highly dynamic valence bond glass with long-range fluctuating singlets. First, such a temperature dependence of $1/T_1$ is inconsistent with conventional glassy spin freezing. Glassy freezing is typically observed by NMR as a broad peak in $1/T_1$ vs $T$ when the inverse correlation time matches the NMR frequency, and such a peak ($T_2$ minimum) defines the freezing temperature $T_{f}$. Moreover, $1/T_1$ is usually expected to increase by more than one order of magnitude at $T_2$ from that above $T_{f}$. However, such a robust peak in $1/T_1$ vs $T$ is absent in YCOB, as shown in Fig. 4c. Other NMR quantities, line width and $1/T_2$ (Supplementary Fig. 6), also exhibit the common features of well-reported QSL candidates $15,20,30,60,67,68$, and speak against the existence of well-defined $T_{f}$ in YCOB (Supplementary Note 5). Note that other experiments, including magnetic and thermodynamic measurements $44-46$, also have precluded the possibility of...
conventional magnetic transition. Thereby, the formation of short-range spin correlations (i.e., $\langle S_i \cdot S_j \rangle < 0$) should be responsible for the broadening of NMR lines and enhancement of $1/T_1$ and $1/T_2$ observed at low temperatures in YCOB.

Second, classical spin fluctuations are driven by thermal energy $k_B T$, and cease at low temperatures, $T \ll \langle J \rangle^2$. A real example can be the system $S = \frac{5}{2}$ KHA LiFe$_2$(PO$_4$)$_2$(PO$_4$)$_2$, where the slowing down of classical spin fluctuations, $1/T_1 \sim T^{-1}$, observed just above the antiferromagnetic transition temperature $T_{\text{N}}$ increases much faster than that seen in YCOB, upon cooling. Therefore, the observation of $1/T_1 \sim T^{-0.20\pm0.02}$ suggests that quantum fluctuations must play an important role at low temperatures ($T \approx 0.1 \langle J \rangle$) in YCOB.

Third, below $T = 0.1 \langle J \rangle$, the calculated local nearest-neighbor correlations (Fig. 3d) for the spin system of YCOB level off, manifesting that the observed quantum critical slowing down of spin fluctuations (i.e., $1/T_1 \sim (T - T_c)^{-\alpha}$ with $T_c \approx 0 K$) are associated with a gapless nature of the spin excitations. This is further supported by the nearly quadratic $T$ dependence of specific heat (C − $T^2$) at low temperatures (i.e. quantum fluctuations)\textsuperscript{24,54,63,67}. Since $1/T_1$ only weakly depends on temperature in the full temperature range between 1.7 and 300 K, $1/T_1(T) \propto \sum \chi^{abc}(q) f_0$ (see equation (3)) follows a Curie behavior diverging towards $T = 0 K$, as shown in Fig. 4d. We also fit the data with the critical function, $1/(T_1T) \sim (T - T_c)^{-\alpha}$ in the full temperature range, and find $T_c \approx 0.1 \pm 0.4$ K $\approx 0.11(5)$ (see the green lines in Fig. 4d). The dynamical susceptibility ($\sum \chi^{abc}(q) f_0$) relates to the second derivative of the free energy, and thus the observation of $T_c \approx 0 K$ (Fig. 4d) indicates a quantum critical behavior. In the paramagnetic limit ($T \rightarrow \infty$), the spin fluctuations including the extremely strong thermal fluctuations ($\alpha T$, see ref. 1) take huge values for an arbitrary spin system. In YCOB, nearly the same Curie behavior, $1/(T_1T) \propto \sum \chi^{abc}(q) f_0 \propto 1/T$, persists from 300 K $\gg \langle J \rangle$ down to 1.7 K $\approx 0.03\langle J \rangle$ (Fig. 4d), thus supporting the survival of strong spin fluctuations toward zero temperature (i.e. quantum fluctuations). All together, these features are in line with the spin dynamics of the putative gapless/critical QSL or dynamical valence bond glass with long-range fluctuating singlets.

We have investigated the local spin susceptibility and dynamics by Br NMR measurements on the high-quality single crystals of YCOB whose randomness has been quantified. The quenched exchange randomness gives rise to the spatially inhomogeneous susceptibility, which accounts for the different $T$ dependencies of Br1 and Br2 main line shifts, as well as broadening. Despite a small fraction of frozen random singlets, the majority of spins of YCOB evade conventional magnetic ordering and remain highly fluctuating, as evidenced by the weak power-law $T$ dependence of $1/T_1$ down to $T \approx 0.03\langle J \rangle$. Our work highlights the role of quantum fluctuations to the gapless QSL behaviors generally observed in relevant materials with inevitable randomness.

**Methods**

**NMR measurements.** Two single-crystal samples of YCOB ($S_i$ and $S_j$ with $\approx 6.2$ and $15.2$ mg, respectively) used in NMR measurements were grown by a recrystallization in a temperature gradient\textsuperscript{44}. The $^{81}$Br ($R_{2}^{81} = 11.4989$ MHz/T) and $^{79}$Br ($R_{2}^{79} = 10.6675$ MHz/T) NMR measurements were performed using standard spin echo sequences at external magnetic fields $\approx 10.75$ and 11.59 T aligned to the c axis, between 300 and 1.7 K (the base temperature of our setup). Main NMR shifts of Br1 and Br2 are derived from the central transitions recorded by a stepped frequency sweep ranging 121–125 MHz wherein no satellite transitions from Br can be observed due to the large nuclear quadrupole frequency $\nu_0 > 20$ MHz (Supplementary Note 2 and Supplementary Fig. 3). However, the element of the electric field gradient (EFG) tensor $V_{zz}$ is nearly parallel to the external field, and thus the second-order quadrupole shift is negligibly small (Supplementary Note 6 and Supplementary Figs. 7 and 8). Spin-lattice (1/T$_1$/T) and spin-spin (1/T$_2$) relaxation rates are investigated on Br1 site, measured in inversion recovery and Hahn spin-echo decay methods, respectively (Supplementary Note 3 and Supplementary Fig. 4). The error bars on $T_1$ come from the standard nonlinear curve fits by using the Origin program, as shown in Fig. 4.

**Simulations.** We conducted the finite-temperature Lanczos diagonalization simulations of the random KHA model\textsuperscript{34} for the NMR lines shifts and broadening, local magnetization and correlation, as well as 1/T$_1$. No significant finite-size effect of the calculation was observed down to $T = 0.1 \langle J \rangle$.\textsuperscript{44} The formation energy (Fig. 4) is calculated as $E(YCOB)_{\text{YCOB}} - E(YCOB)_{\text{Br}}$ and $\gamma(T) = \chi(T) - 3\langle \mu(C) \rangle - (6 + x)\langle \mu(\text{OH}) \rangle - (3 + x\langle \mu(Br) \rangle)$, where the total energy is obtained from the previous density functional theory calculation\textsuperscript{44}, and $\gamma(T)$, $\langle \mu(C) \rangle$, $\langle \mu(\text{OH}) \rangle$ and $\langle \mu(Br) \rangle$ are the chemical potentials of the constituents. The international system of units is used throughout this paper, and $\mu$ presents thermal and sample average.

**Data availability**

The data sets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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