Instabilities of spin-liquid states in a quantum kagome antiferromagnet

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The emergent behavior of spin liquids that are born out of geometrical frustration makes them an intriguing state of matter. We show that in the quantum kagome antiferromagnet $\text{ZnCu}_3(\text{OH})_6\text{SO}_4$ several different correlated yet fluctuating states exist. By combining complementary local-probe techniques with neutron scattering, we discover a crossover from a critical regime into a gapless spin-liquid phase with decreasing temperature. An additional unconventional instability of the latter phase leads to a second, distinct spin-liquid state that is stabilized at the lowest temperatures. We advance such complex behavior as a feature common to different frustrated quantum magnets.

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In recent years, the intense search for quantum spin liquids (SLs)—collective highly entangled states in which long-range magnetic order is suppressed by quantum fluctuations—has unveiled states with exotic fractional excitations and, frequently, with topological order [1]. The case of the geometrically frustrated two-dimensional (2D) Heisenberg quantum kagome antiferromagnet (QKA) is a prime example [1,2]. For this model, after numerous theoretical studies proposed a multitude of different ground states, a gapped SL state has been lately advocated [3–5] and also experimentally indicated [6]. However, its exact nature, as well as its topological classification, remains unclear [4,5,7–9]. Moreover, fierce competition seems to exist among candidate SL ground states of the QKA [10,11]. Therefore, the true ground state could be very sensitive to perturbations, leaving room for unconventional instabilities such as nontrivial symmetry breaking [12] or topological ordering. Recently, an instability of this kind has indeed been observed experimentally, but on the related 2D triangular lattice [13].

To explore possible instabilities of the kagome lattice, we focus on $\text{ZnCu}_3(\text{OH})_6\text{SO}_4$, a compound with intriguing magnetic properties [14] that has recently joined a small number of QKA systems with a possible SL ground state [15–18]. Notwithstanding theoretical predictions claiming the contrary, the majority of these systems appears to be gapless [14,17,18]. Therefore, in-depth experimental studies of new QKA candidates that reveal common features as well as subtle differences among the studied materials are very important. One particularly relevant issue is the role of impurities in the magnetism of QKAs [19–23]. This has been experimentally extensively studied in herbertsmithite [24–27], $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, which is recognized as the best realization of the QKA model so far, despite substantial (5–10%) Cu-Zn intersite disorder [28]. In this compound, such impurities were found to dominate bulk magnetic excitations at low temperatures and low energies ($\lesssim 0.8$ meV) [26,27]. The

compound investigated here closely resembles herbertsmithite in the degree of the Cu-Zn intersite disorder (6–9%; Ref. [14]). However, the two crystal structures are notably different, as in $\text{ZnCu}_3(\text{OH})_6\text{SO}_4$ the Zn^{2+} site lies within the kagome planes, while it is positioned between the kagome layers in herbertsmithite. Consequently, $\text{ZnCu}_3(\text{OH})_6\text{SO}_4$ features well-isolated 2D kagome planes, where three nonequivalent Cu^{2+} sites are coupled with an average intrakagome exchange interaction of $J = 65$ K [14]. Bulk susceptibility (χ_b) and heat capacity (C_p) measurements failed to detect any sign of magnetic ordering down to temperatures T three orders of magnitude below J [14]. Moreover, a T -independent intrinsic kagome susceptibility χ_k [see Fig. 1(b)] and a linearly increasing magnetic C_p , which are both characteristic of spinon excitations with a pseudo-Fermi surface, were observed after subtraction of quasi-free-defect contributions from both quantities. Surprisingly, these two features signifying a gapless SL state were found in two T regions, between 5 and 15 K (which we call SL1) as well as at $T < 0.6$ K (SL2) [14]. Such an intricate, two-state SL behavior, which appears unique among QKA representatives, clearly requires further verification and deeper understanding.

Here we provide a unique experimental viewpoint on the stability of the SL states in $\text{ZnCu}_3(\text{OH})_6\text{SO}_4$ that is related to the general issue of the QKA ground state, by combining inelastic neutron scattering (INS) with two local-probe spectroscopic techniques employing different coupling mechanisms, nuclear magnetic resonance (NMR) and muon spin relaxation (μSR). The temperature- and field-dependent NMR and μSR spin-lattice relaxation ($1/T_1$) measurements, supported by INS experiments that yield complementary information on the spatial and temporal spin correlations, expose various distinct fluctuating regimes. μSR , performed down to 21 mK, gives evidence of a fluctuating SL ground state, while NMR discloses another state with characteristics of a gapless SL at higher temperatures. In combination with INS, the NMR $1/T_1$ measurements reveal that this high- T SL state is followed by a critical region at even higher temperatures, where the scaling of the dynamical susceptibility

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FIG. 1. (a) The μ^+ polarization in $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$ (Cu_3D) in a LF of 8 mT (symbols) and the corresponding fits from a stretched-exponential model (lines; see text for details). In the inset the low- T data of Cu_3D are compared to 1.6 K data of $\text{Cu}_4(\text{OD})_6\text{SO}_4$ (Cu_4D) in the same LF and in zero field. (b) The longitudinal muon relaxation rate $1/T_1^\mu$ compared to the intrinsic kagome susceptibility χ_k measured at 0.1 T [14]. The two different SL regimes are denoted by SL1 and SL2.

with ω/T is obeyed over several decades in frequency ω . This complex sequence of correlated electronic states suggesting SL instabilities is likely a more general feature of frustrated antiferromagnets.

μSR is a particularly powerful technique for detecting even the smallest magnetic fields B_μ , of either nuclear or electronic origin, at the muon stopping site and for quantifying their dynamics [29]. The measurements were performed on the general Purpose Surface-Muon (GPS) and Low Temperature Facility (LTF) instruments, Paul Scherrer Institute (PSI), Switzerland, and on the EMU instrument at the ISIS Facility, Rutherford Appleton Laboratory, United Kingdom. The time decay of the muon spin polarization $P(t)$ is driven by the Zeeman coupling of the muon magnetic moment with B_μ . It is presented in Fig. 1(a) for a longitudinal field (LF) of 8 mT, which isolates the relaxation due to fluctuating Cu^{2+} electronic moments [30]. The background-subtracted [30] data could be modeled with the stretched-exponential form $P_{\text{str}}(t) = e^{-(t/T_1^\mu)^{\beta_\mu}}$, with the stretching exponent $\beta_\mu = 0.86(6)$. As T decreases from 150 K, the muon relaxation rate $1/T_1^\mu$ first increases gradually, but then gets substantially enhanced below 5 K [Fig. 1(b)]. Since the LF is small compared to the frequency ω_e of fluctuating B_μ ($\gamma_\mu B_{\text{LF}} \ll \omega_e \sim k_B J/\hbar$; $\gamma_\mu = 2\pi \times 135.5 \text{ MHz/T}$, k_B and $\hbar$ denote the muon gyromagnetic ratio, the Boltzmann constant, and the reduced Planck constant, respectively), the standard exponential decay of the field autocorrelation function yields the muon relaxation rate $1/T_1^\mu \propto (\gamma_\mu \Delta B_\mu)^2/\omega_e$ [29]. The observed increase of $1/T_1^\mu$ below 5 K is thus a sign of pronounced slowing down of electronic fluctuations and/or enlarged local-field distribution width ΔB_μ . It coincides with the low- T increase of the intrinsic χ_k [Fig. 1(b)]. $1/T_1^\mu$ levels off below $\sim 0.6 \text{ K}$ [Fig. 1(b)], signaling persistent dynamics of B_μ below this temperature. The low- T increase of $1/T_1^\mu$ and the relaxation plateau are both features common

FIG. 2. The ^2D NMR relaxation rate $1/T_1^{\text{NMR}}$ measured at 2.35 T on the left spectral maximum of $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$ (arrow in the lower inset, showing the NMR spectrum at 80 K), obtained from the model of magnetic relaxation (see the text). The straight line points out the region where $1/T_1 \propto T^\eta$. The upper inset depicts the T dependence of the stretching exponent β , also showing a power-law dependence below 100 K.

to different kagome antiferromagnets [16–18,31,32]. The unchanged shape of $P(t)$ unquestionably reveals that any kind of electronic freezing is absent in $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$ at least down to 21 mK, that is $T/J \geq 1/3000$. This stands in sharp contrast to the related magnetically ordered $\text{Cu}_4(\text{OD})_6\text{SO}_4$, where an oscillatory $P(t)$ is observed below its Néel temperature of 7.5 K [33]. In that compound the first local minimum occurs at $t = \frac{\pi}{\gamma_\mu B_\mu} = 0.062 \mu\text{s}$ at 1.6 K [inset in Fig. 1(a)] and corresponds to a static $B_\mu = 60 \text{ mT}$.

Further insight into the spin fluctuations in $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$ is provided by ^2D NMR spin-lattice relaxation. These measurements were performed on the lower-frequency spectral maximum (lower inset in Fig. 2; details on static NMR properties are given in Ref. [30]). The relaxation rate $1/T_1^{\text{NMR}}$ is determined by fluctuating local magnetic fields, as the experimental magnetization inversion-recovery curves are explained well with the magnetic-relaxation model for spin-1 nuclei [34], $M(t) = M_0[1 - (1+s)(\frac{1}{4}e^{-(t/T_1)^\beta} + \frac{3}{4}e^{-(3t/T_1)^\beta})]$, with $s < 1$ due to imperfect inversion of broad NMR lines and with β denoting the stretching exponent. $1/T_1^{\text{NMR}}$ is set by spin fluctuations at the Larmor frequency ω_L ,

$$\frac{1}{T_1^{\text{NMR}}} \propto \gamma^2 T \sum_{\mathbf{Q}} |A_{\mathbf{Q}}|^2 \frac{\chi''(\mathbf{Q}, \omega_L)}{\omega_L}, \quad (1)$$

where $\chi''(\mathbf{Q}, \omega_L)$ stands for the wave-vector dependent dynamical susceptibility and $A_{\mathbf{Q}}$ is the coupling between the ^2D nuclear and Cu^{2+} electronic moments. In a paramagnetic regime a temperature-independent relaxation rate is expected [35]. In $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$, deviations from such a behavior are already found at room T and are substantially enhanced below 200 K (Fig. 2). The observed decrease of $1/T_1^{\text{NMR}}$ is a robust sign of developing spin correlations and is accompanied by a significant increase of the T_1 -distribution width, evidenced by β decreasing from 0.93(3) at 300 K to

0.53(3) at 1.6 K (upper inset in Fig. 2). Such a T -dependent broadening of the T_1 distribution is often observed in frustrated antiferromagnets [13,36–38] and is generally recognized as a fingerprint of correlated disordered states. On the contrary, a trivial reduction of β imposed by impurities that lead to a distribution of A_Q 's is T independent [38].

Between 200 and 40 K, we find $1/T_1^{\text{NMR}} \propto T^\eta$ with $\eta = 0.30(2)$. A similar power-law behavior was previously observed in a number of 2D SL candidates, where it was attributed to gapless excitations [39–43]. $1/T_1^{\text{NMR}} \propto T^\eta$ is theoretically expected for a Dirac U(1) SL on the kagome lattice [41,44]; however, for such a state the theory predicts $\chi \propto T$ and $C_p^{\text{ZF}} \propto T^2$, which both contradict the experimental observations in $\text{ZnCu}_3(\text{OH})_6\text{SO}_4$ [14]. Alternatively, a gapped Z_2 SL in the quantum-critical region close to an antiferromagnetically ordered state of a triangular lattice also exhibits power-law NMR relaxation [45]. Moreover, $1/T_1^{\text{NMR}} \propto T^\eta$ is well established in one-dimensional (1D) spin systems [46]. There, it is considered a hallmark of quantum criticality emerging at $T \lesssim J$ and η ranges from positive to negative values as the magnetic field is tuned across the quantum critical region. With the universality of quantum-critical spin fluctuations [47], the observed power-law dependence in $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$ may well be a signature of criticality. In such a case, the energy scale is determined solely by temperature and is independent of the microscopic characteristics of the Hamiltonian. Therefore, one expects a scaling of the form $\chi''(\omega) \propto |\omega|^\nu F(\hbar\omega/k_B T)$ [47].

In order to verify this interesting possibility in $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$, we performed powder INS measurements. The data were collected on the FOCUS instrument at PSI, Switzerland. After using an innovative method for the subtraction of background we developed in Ref. [30], the magnetic contribution to the scattering intensity, $S(\omega)$, was obtained by Q integration ($0.35 \text{ \AA}^{-1} \leq Q \leq 1.4 \text{ \AA}^{-1}$). From $S(\omega)$ the imaginary part of the dynamical susceptibility, $\chi''(\omega) = S(\omega)[1 - e^{-\hbar\omega/k_B T}]$, was derived (Fig. 3). Interestingly, above

FIG. 3. (a) The magnetic contribution to the neutron-scattering intensity, $S(\omega)$, in $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$, where Q integration was performed over wave vectors $0.35 \text{ \AA}^{-1} \leq Q \leq 1.4 \text{ \AA}^{-1}$, and (b) the related dynamical susceptibility $\chi''(\omega)$. Solid lines are a guide to the eye.

FIG. 4. Scaling of the dynamical susceptibility with the reduced energy following a power law $\chi'' \propto (\hbar\omega/k_B T)^\alpha$ above ~ 40 K. Lower inset: the $1/T_1^{\text{NMR}} \propto B^{-\eta}$ field dependence of the ^2D NMR relaxation rate at 40 K. Upper inset: a schematic $T-g$ phase diagram with a quantum critical point between SL and some other phase at the critical tuning parameter value g_c and the associated quantum critical region (yellow). The SL instability that leads to two distinct SL phases is indicated by the dashed line.

40 K, $\chi''(\omega)$ was found to scale with reduced energy as $\chi''(\omega) \propto (\hbar\omega/k_B T)^\alpha$, where $\alpha = 0.6(1)$ (Fig. 4). Such a scaling law leads, according to Eq. (1), to $1/T_1^{\text{NMR}} \propto (T/\omega)^\eta$ with $\eta = 1 - \alpha = 0.4(1)$. This is in good agreement with $\eta = 0.30(2)$ obtained from the NMR data. Moreover, the predicted power-law field dependence $1/T_1^{\text{NMR}} \propto \omega^{-\eta} \propto B^{-\eta}$ is also observed experimentally, with $\eta = 0.25(5)$ (lower inset in Fig. 4), thus providing additional verification of the proposed criticality. We note that similarly B -dependent $1/T_1^{\text{NMR}}$ is found in quantum-critical 1D systems [46], while impurities would typically yield a more pronounced dependence, with $1/T_1^{\text{NMR}} \propto B^{-1}$ [48]. The astonishing feature that emerges when combining NMR and INS results on $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$ in the T range 40–200 K is that the $\chi''(\omega)$ scaling observed in the INS data in the energy range 0.3–2 meV extends to several orders of magnitude lower energies, as $\hbar\omega_L = 0.06 \text{ \mu eV}$ in NMR. Such a broad range of universal fluctuation indeed appears to be a fingerprint of criticality. Scale-free intrinsic kagome-lattice correlations that persist to high T at high energies were also observed in herbertsmithite [24]. There, the impurity contribution to $\chi''(\omega)$ is limited to $T < 10$ K [26] and $\hbar\omega < 0.8 \text{ meV}$ [27]. As the effective low- T Curie-Weiss temperature of the impurity spins is approximately -1 K in $\text{ZnCu}_3(\text{OH})_6\text{SO}_4$ [14] as well as in herbertsmithite [28] and the amount of impurities in both compounds is very similar, we exclude any role of quasifree impurities in the scaling presented in Fig. 4. On the other hand, any observed scaling at low T and ω [49] could be biased by impurity contributions.

Below 40 K, the high- T scaling of the dynamical susceptibility is not valid, as the $\chi''(\omega, T)$ data sets from different temperatures no longer overlap (Fig. 4). At the same temperature, the power-law dependence of $1/T_1^{\text{NMR}}$ (Fig. 2) starts to flatten. It exhibits a shallow minimum at ~ 15 K and a maximum at

~ 5 K (Fig. 2). In sharp contrast, β evolves monotonically, proving that such behavior of $1/T_1^{\text{NMR}}$ is intrinsic. The $1/T_1^{\text{NMR}}(T)$ dependence remains qualitatively unchanged even if we use a fixed β to fit the data. The essentially T -independent region of $1/T_1^{\text{NMR}}$ between the shallow minimum and the maximum coincides with the temperature-independent region of intrinsic susceptibility [Fig. 1(b)] and the linearly dependent heat capacity [14]. It can thus be attributed to a correlated SL state of the system below ~ 15 K. We note that the flattening of $1/T_1^{\text{NMR}}$ below 40 K cannot be attributed to weakly interacting impurities, as the measured NMR-line shift is driven by intrinsic kagome spins at least down to 10 K [30], which differs from the situation encountered in herbertsmithite [50].

The dynamical properties of the magnetic state in $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$ change again below 5 K, as a steady decrease of $1/T_1^{\text{NMR}}$ is observed once more upon cooling (Fig. 2). Such a rich T dependence clearly reflects multiple diverse states that the system goes through with changing temperature. At the same time, no anomalies are observed in the static properties of the NMR spectra [30]. Interestingly, a qualitatively similar behavior of $1/T_1^{\text{NMR}}$ with two different power-law correlated regimes and a flat T region in between was found in organic triangular-lattice SL candidates [13,36]. In $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$, such an intricate behavior was attributed to a symmetry breaking and/or a topological instability of a gapless SL phase [13]. Based on our $1/T_1^{\text{NMR}}$ data, we propose that a similar crossover between different SL1 and SL2 phases is at work in $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$.

This crossover is further witnessed by the muon relaxation rate $1/T_1^\mu$ [Fig. 1(b)], which suddenly starts to increase below 5 K, after exhibiting a very gentle T dependence between 15 and 5 K, being in line with the high- T SL1 phase. We note that μSR yields a somewhat different, more indirect viewpoint on the spin dynamics than NMR. Namely, the μSR experiment was performed in a small external field ($B_{\text{LF}} \ll B_\mu$), and therefore Eq. (1), which is derived using time-dependent perturbation theory in the limit of large external fields, is not directly applicable [51]. Moreover, in μSR , contrary to NMR, the long-range dipolar interactions typically overshadow the contact hyperfine interaction in magnetic insulators [29]. Therefore, in $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$, the effective spatial averaging of the dipolar interaction makes the muon relaxation due to the relatively dense impurity spins dominant at low temperatures, where $\chi_k \ll \chi_b$ [14]. The same behavior was indeed observed in herbertsmithite, where the low- T $1/T_1^\mu$ scaled linearly with the quantity of Cu^{2+} impurities on the Zn site [31]. The increase of $1/T_1^\mu$ below 5 K can in our case then be ascribed to evolving correlations between impurity and intrinsic kagome spins. Judging from the relaxation plateau, these correlations saturate within the low- T SL2 state below 0.6 K, suggesting that an effective impurity coupling is established. Because of a finite T -independent χ_k and linear $C_p(T)$ below 0.6 K [14] the SL2 state appears to be gapless, with any gap smaller than $J/3000$ as evidenced by persisting muon relaxation observed down to at least 21 mK.

From a theoretical standpoint, a gapped SL ground state, possibly of Z_2 type, is expected for the isotropic Heisenberg QKA model [3–5]. The weight of magnetic excitations could, however, be considerably shifted towards zero energy due to a proximate valence bond solid (VBS) state [8], as was proposed from experimental observations on herbertsmithite [25]. Alternatively, quantum criticality between the Z_2 SL and an antiferromagnetically ordered state can be induced by the Dzyaloshinskii-Moriya interaction [52,53], which is known to be sizable in other Cu-based QKA representatives [54,55] and could also justify a gapless state [56]. Such a magnetic anisotropy that acts as a tuning parameter, being slightly off its critical value g_c , may explain the scaling behavior observed in $\text{ZnCu}_3(\text{OD})_6\text{SO}_4$ around $T \sim J$ and the selection of the gapless high- T SL1 state around 15 K ($T/J \sim 0.23$), in the sense of the schematic phase diagram shown in Fig. 4. It is intriguing that the crossover from this state into the SL2 state is stabilized at even lower temperatures, that is below 0.6 K ($T/J \sim 0.01$).

With two clearly distinguishable SL regimes the investigated compound is unique among QKAs. The crossover between the two regimes observed in NMR and μSR relaxation is not reflected in the static NMR properties. Hence, the distinction between the two SL states must originate from spin excitations. Therefore, this crossover may well be of a topological character or due to nontrivial symmetry breaking. In fact, for gapless SL states with a spinon pseudo-Fermi surface various spinon-pairing instabilities can be expected at low temperatures [12,57,58]. Alternatively, impurities due to the Cu-Zn intersite disorder inherent to the investigated system that are strongly coupled to the kagome lattice could pin spinons at low temperatures and thus provide a spinon-instability mechanism. While such a premise calls for further theoretical investigations, we note that the intriguing instability of the SL observed in $\text{ZnCu}_3(\text{OH})_6\text{SO}_4$ appears to be a more general feature of geometrically frustrated antiferromagnets, common to 2D kagome and organic triangular lattices [13] that possess a much smaller quantity of impurities, and possibly even to the 3D hyperkagome lattice [59]. We expect that such an emergent behavior of SLs is a fingerprint of particular type of low-energy excitations, common to various geometrically frustrated spin lattices.

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