Field-Induced Freezing of a Quantum Spin Liquid on the Kagome Lattice

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We report ^{17}O NMR measurements in the $S = 1/2\,(Cu^{2+})$ kagome antiferromagnet Herbertsmithite $ZnCu_3(OH)_6Cl_2$ down to 45 mK in magnetic fields ranging from 2 to 12 T. While Herbertsmithite displays a gapless spin-liquid behavior in zero field, we uncover an instability toward a spin-solid phase at sub-Kelvin temperature induced by an applied magnetic field. The latter phase shows largely suppressed moments $\lesssim 0.1\mu_B$ and gapped excitations. The $H - T$ phase diagram suggests the existence of a quantum critical point at the small but finite magnetic field $\mu_0 H_c = 1.55(25)$ T. We discuss this finding in light of the perturbative Dzyaloshinskii-Moriya interaction which was theoretically proposed to sustain a quantum critical regime for the quantum kagome Heisenberg antiferromagnet model.

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Quantum spin liquids (QSL) are appealing states of matter which do not break any symmetry of the spin Hamiltonian. While QSL behaviors are well established for one-dimensional spin systems, their existence in higher dimensions remains questionable. The quantum kagome Heisenberg antiferromagnet (QKHA) is considered as the best candidate to stabilize such a QSL phase in two dimensions [1–3]. The specificity of this model relies on the unique combination of strong quantum fluctuations enhanced by low spins $S = 1/2$ and high geometrical frustration of the lattice of corner-sharing triangles. Early numerical studies have shown, despite finite size limitations, that the ground state of the QKHA model does not support any simple order parameter [4–6] and have evidenced an original excitation spectrum with dense sets of low energy excitations in all spin sectors [5,6]. A recent state-of-the-art calculation [7] favors a QSL ground state with a small gap much like the resonating-valence-bond state [8,9]. Other recent proposals with similar ground-state energies encompass large unit-cell valence-bond crystals [10] as well as gapless "critical" spin liquids with algebraic spin correlations [11,12]. Clearly, the exact ground state of the QKHA remains a challenging and highly debated issue [13,14]. In this respect, studying the effect of perturbation, such as disorder, anisotropies, or external field, is not only necessary to compare to real materials but also proves to be efficient to discriminate between the competing ground states—critical QSL are expected to be easily destabilized [15,16] while gapped ones should be more robust.

To confront theories, a significant step was achieved with the synthesis [17] of the first "structurally perfect" QKHA, $ZnCu_3(OH)_6Cl_2$, called Herbertsmithite. The electron spin moments of Cu^{2+} ions ($S = 1/2$) form undistorted kagome planes, well separated from each other by diamagnetic Zn^{2+} triangular planes which ensure the quasi-two-dimensionality of the magnetic net (Fig. 1). Despite a sizable antiferromagnetic superexchange $J = 180(10)$ K, Herbertsmithite develops no on-site magnetization [18,19] and remains in an unfrozen, fluctuating state under zero field with short-ranged spin correlations down to at least 50 mK ($\simeq J/4000$), as expected for a liquid state [18,20]. Inelastic neutron scattering [18] and nuclear magnetic resonance (NMR) [21,22] investigations consistently point to the absence of a spin gap larger than $\sim J/200$ and evidence a peculiar power-law temperature dependence of the spin dynamics, a possible hint of quantum criticality. At such a low energy scale, small perturbations to the ideal nearest neighbor Heisenberg model may become relevant and determine the properties of the ground state. First, intersite Cu^{2+}/Zn^{2+} mixing defects are known to be

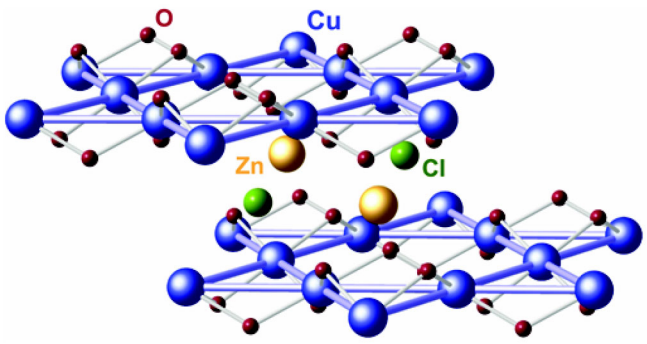

FIG. 1 (color online). Structure of Herbertsmithite. In this ideal structure, Cu and O atoms each occupy one crystallographic site.

present at the level of 5%–10% [18,23] which could stabilize a gapless valence-bond glass [24]. More fundamentally, the lack of inversion center of the magnetic bonds on the kagome lattice allows for Dzyaloshinskii-Moriya (DM) interaction of spin-orbit origin. In Herbertsmithite, the DM magnitude is estimated to be $D \sim 0.04J - 0.08J$ [25,26], not far from a theoretically expected quantum critical point at $D_c \sim 0.1J$ [27].

In this Letter, we report the spin dynamics of Herbertsmithite in a magnetic field down to very low temperature, $T \simeq J/4000$, probed by ^{17}O NMR, in order to uncover the ultimate ground-state properties and test for criticality. The location of oxygen on the superexchange path between two adjacent Cu ions in the kagome lattice confers on the oxygen nucleus a dominant coupling to the magnetic properties of the kagome plane (Fig. 1). This site selectivity is decisive in the context where the low-T thermodynamic properties and the response of less-coupled local probes are dominated by interplane defects [28,29]. We uncover a field-induced transition to a frozen phase for applied fields higher than $\mu_0 H_c = 1.55(25)$ T and draw the $H - T$ phase diagram.

NMR measurements were performed on the powder sample of ^{17}O-enriched Herbertsmithite used in Ref. [21]. The spin echo was obtained with the standard pulse sequence, $\pi/2 - \tau - \pi$. The NMR spectra were obtained by recording the integrated echo intensity, point by point, while sweeping the external magnetic field with a fixed rf frequency [30]. The spin-lattice relaxation rate, $1/T_1$, was obtained by saturation-recovery method. The absolute values of T_1 were obtained by scaling the recovery curves to previous results at 6.8 T [21,30].

In Fig. 2, we display our $1/T_1$ results as a function of temperature down to 45 mK in four different magnetic fields. At $\mu_0 H = 6.8$ T, in contrast to the known modest sublinear T dependence of $1/T_1 \sim T^{0.73}$ above 1 K [21], we find a 3 orders of magnitude decrease of $1/T_1$ below $T_c = 520(30)$ mK. Both the marked onset and the magnitude of the drastic slowing down of the underlying dynamics indicate a transition from the high-T spin-liquid phase to a low-T solidlike phase. This drastic change of the dynamics is detected not only in the vicinity of the peak of the NMR spectrum but also at various positions on the wings, which points to a homogeneous transition. The $1/T_1$ data taken at 2.0, 3.1, and 12.0 T display a similar drop below a temperature T_c which is found to increase with the applied field. The corresponding phase diagram is drawn in Fig. 3. By extrapolation to still lower fields, it seems that T_c vanishes at some small but finite critical field H_c. This is in line with the absence of freezing in zero field evidenced with μSR [19]. Fitting the data to a phenomenological expression $T_c \propto (H - H_c)^{\delta}$ yields a quantum critical point at $\mu_0 H_c = 1.55(25)$ T and $\delta = 0.6(1)$. Note that removing the 12 T data point, which may be too far away from the critical regime, improves

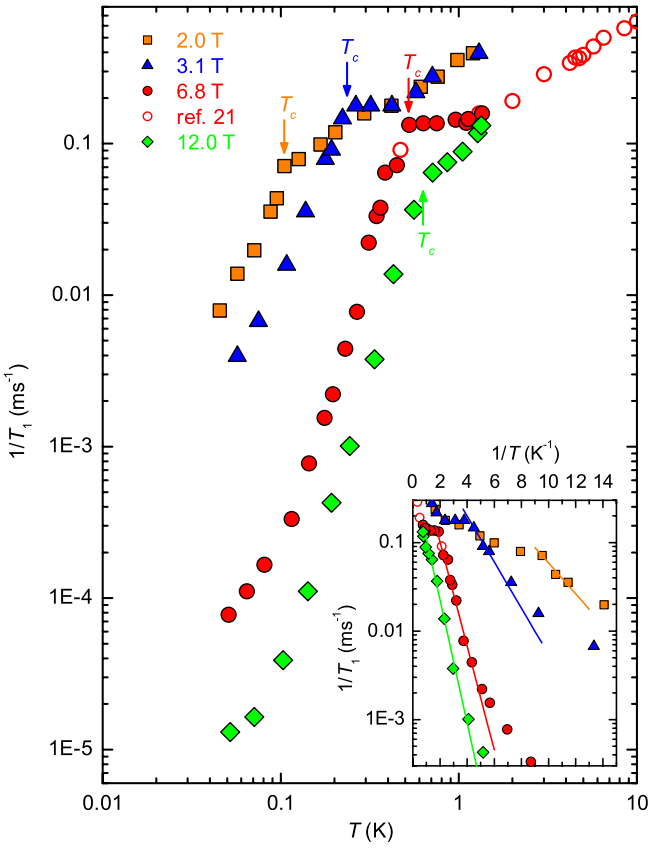

FIG. 2 (color online). ^{17}O nuclear spin-lattice relaxation rate, $1/T_1$, as a function of T in Herbertsmithite down to 45 mK. Inset: solid line represents the initial slope below T_c.

significantly the quality of the fit (see dashed line in Fig. 3). The Zeeman energy $\mu_B H_c \sim J/180$, where μ_B is the Bohr magneton, is quite small on the scale of J which underlines the fragility of the zero-field spin-liquid state of Herbertsmithite.

The inset of Fig. 2 shows an Arrhenius plot of $1/T_1$ versus $1/T$. The linear behavior below T_c, evident at 6.8 and 12.0 T, strongly supports the existence of a gap in the spin dynamics. This gap in the spin-solid phase likely reveals some magnetic stiffness arising from the DM anisotropic interaction. For $T \lesssim 200$ mK, the relaxation originates from a residual contribution which is marginal at high fields but sizeable at $\mu_0 H = 2.0$ and 3.1 T. This residual relaxation may be attributed to the interplane Cu defects which behave like nearly free $S = 1/2$ spins with a small antiferromagnetic coupling of $\sim$1 K [23]. Their contribution is expected to decrease as the field increases, i.e., as their magnetization gets saturated. From the initial slope of the $1/T_1$ curves just below T_c (Fig. 2, inset), discarding the lowest T data points, we extract the gap Δ. The inset of Fig. 3 displays the values obtained for Δ and their comparison to T_c. Within error bars, Δ increases linearly with T_c with the slope $\alpha = \Delta/k_B T_c = 2.3(3)$ [31].

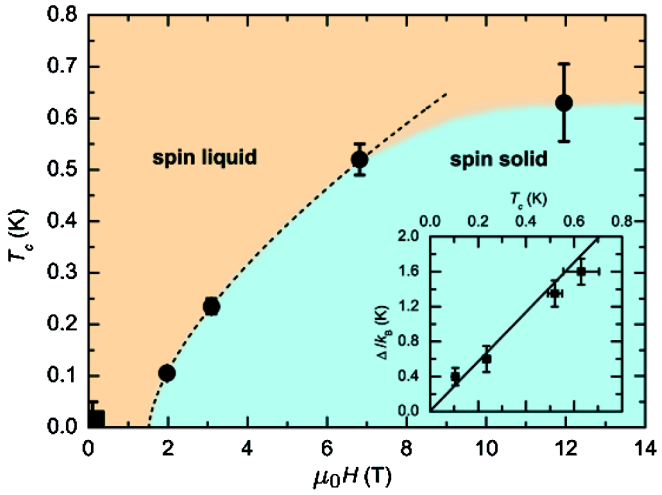

FIG. 3 (color online). $H - T$ phase diagram of Herbertsmithite from this study (black circles) and from the absence of spin freezing at least down to 50 mK in μSR experiment (black square) [19]. T_c separates the spin-liquid phase from the spin-solid phase characterized by strongly suppressed fluctuations. The dashed line is a plot of $(H - H_c)^{\delta}$ with $\mu_0 H_c = 1.53$ T and $\delta = 0.65$ (see text). Inset: Δ versus T_c.

We now turn to the NMR spectra which reflect the distribution of local magnetization around the probe nuclei. For $H > 3$ T and for $T \gtrsim T_c$, we find that the spectrum width is both field and temperature independent (see Fig. 4). This is in agreement with an earlier study at $\mu_0 H \sim 7$ T [21] which demonstrated a sizeable broadening of the spectra with $1/T$ at high temperature and a saturation below 5 K. It suggests that the width is related to the interplane defects above T_c. The smaller width observed at 2 T and $T = 0.2$ K is in agreement with this picture when the defects are becoming less saturated. At this smallest field, the width cannot be measured reliably above $T > 0.2$ K because of inhomogeneous, strong spin-spin relaxation processes. Spectra at 12 T, where the longer spin-spin relaxations do not affect the line shape, are displayed in Fig. 5. Below T_c, the increase of the width, much like that of an order parameter, contrasts sharply with the absence of variation observed above T_c. This points clearly to a static magnetization which develops in the kagome plane in the spin-solid phase. The Gaussian-like line shape implies a random static phase whereas, in the case of an ordered phase, the well-defined internal field at the O site would yield a rectangular shape for a powder averaged spectrum [32]. Given the hyperfine constant 3.5 T/μ_B, and independently from any model, we can extract a typical moment value $\mu_{\mathrm{Cu}} \sim 0.1\mu_B$, an order of magnitude smaller than the full moment for a spin 1/2. This small value likely reflects a renormalization of the moment by strong quantum fluctuations. The absence of any clear broadening below T_c for the lower fields suggests even weaker Cu moments, in line with an enhanced quantum reduction in the vicinity of the critical point H_c.

We now aim to discuss which model could best account for a weak-field-induced transition in the context of quantum criticality. The algebraic (critical) spin-liquid model [12] captures both the absence of a gap in zero field and the instability under an applied field. A transition to an XY long-range ordered phase and an accompanying on-site magnetization $M \propto H^{\alpha}$ was predicted to occur at $T_c \propto H$ [16]. This is not consistent with our data which suggest a finite critical field. Also, the presence of a sizeable DM interaction in Herbertsmithite should induce long-range order already in zero field in this model [15].

A different approach using exact diagonalization [27] or Schwinger boson techniques [33,34] consists, on the contrary, of including the DM interaction in the Heisenberg

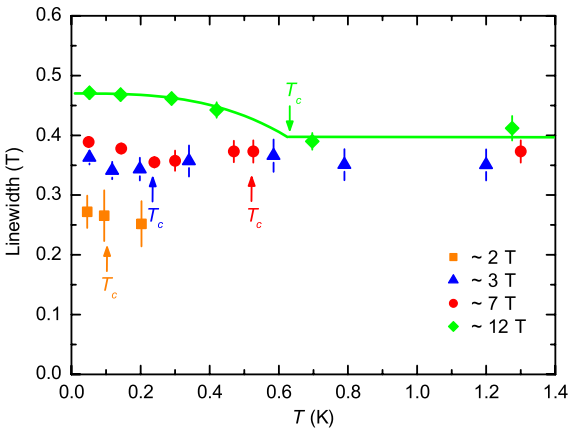

FIG. 4 (color online). Linewidth (full-width at half-maximum) of the ^{17}O NMR spectra vs T for the different fields investigated here, after correction for inhomogeneous spin-spin relaxation effect.

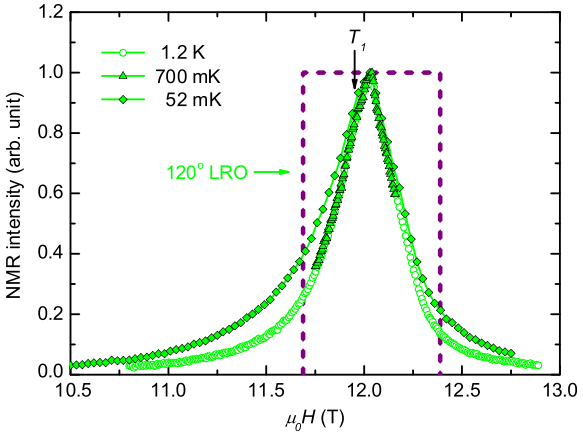

FIG. 5 (color online). ^{17}O NMR spectra normalized to their maximum intensity in ~12 T at different T. The vertical arrow shows the location at which $1/T_1$ measurements were performed. The dashed rectangle represents the expected spectral shape for 120° long-range-ordered (LRO) phase with $0.1\mu_B$ static moments.

model as a starting point. Although the QKHA model may be gapped [7], the DM perturbation might naturally account for the gapless zero-field phase of Herbertsmithite by admixing singlet and triplet states. Also in this framework, Herbertsmithite lies close to a quantum critical point that is in fact sustained by DM anisotropy. A quantum critical region is expected to open at finite temperatures within a finite range of a control parameter around its critical value [35], which could in this case be the magnetic field. From the point of view of symmetry-breaking, the effects of the DM and Zeeman terms may in essence not be very different. Such an interplay between these two terms was established for $S = 1/2$ Heisenberg antiferromagnetic chains, a canonical example of a QSL state in one dimension [36]. Then, Herbertsmithite could be driven from a QSL to a spin-solid phase by a moderate field, $H_c \sim D_c - D$. In this framework, the smallness of the moment expresses the weakness of the order parameter in the vicinity of the quantum critical point [27]. Moreover, the quantum critical region is characterized by the absence of energy scale other than temperature which can explain the power-law behavior of spin correlations [18,20–22]. It is then interesting to compare the results with other kagome compounds of different D/J, e.g., vesignieite, with possibly $D/J > 0.1$, shows an unusual heterogeneous ground state where spin-liquid and frozen moments coexist [37,38].

Our results share certain features with the field-induced transition recently reported for the organic triangular quantum antiferromagnets $\kappa - (\mathrm{BEDT-TTF})_2\mathrm{Cu}_2(\mathrm{CN})_3$ and $\mathrm{EtMe}_3\mathrm{Sb}[\mathrm{Pd(dmit)}_2]_2$ which lie close to Mott transition and show a QSL ground state [39,40]. As in Herbertsmithite, small magnetic fields induce the freezing of the zero-field QSL ground state toward a spin-solid phase with strongly suppressed moments. In NMR measurements, no critical divergence in $1/T_1$ nor critical broadening in the spectra are detected [40–42], similarly to Herbertsmithite as shown here. This similarity is quite intriguing since the two lattices, triangular and kagome, have been believed for long to yield very different ground states and excitation spectra according to numerical studies [2,5,6].

In conclusion, the QSL ground state of Herbertsmithite appears quite fragile against external magnetic fields. However, in Herbertsmithite, the observed spin freezing likely results from the combination of both a finite applied field and sizeable DM interaction which eventually suggests that the QSL ground state of pure QKHA itself is somewhat robust against perturbations. It opens up the possibility for a spin gap in the pure QKHA in accordance with most recent calculations [7]. The field-induced frozen phase that we evidenced here calls for further investigation. Experiments in higher magnetic fields that saturate the interplanar defect contributions and induce larger moments within the kagome plane are desirable. Our finding along with the results reported for the quantum triangular antiferromagnets, prompts a comparative study of the growing class of QSL materials to understand their generic behavior in a broader context of frustration and quantum criticality.

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