Spin Liquid State in the 3D Frustrated Antiferromagnet $PbCuTe_2O_6$: NMR and Muon Spin Relaxation Studies

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$PbCuTe_2O_6$ is a rare example of a spin liquid candidate featuring a three-dimensional magnetic lattice. Strong geometric frustration arises from the dominant antiferromagnetic interaction that generates a hyperkagome network of Cu^{2+} ions although additional interactions enhance the magnetic lattice connectivity. Through a combination of magnetization measurements and local probe investigations by NMR and muon spin relaxation down to 20 mK, we provide robust evidence for the absence of magnetic freezing in the ground state. The local spin susceptibility probed by the NMR shift hardly deviates from the macroscopic one down to 1 K pointing to a homogeneous magnetic system with a low defect concentration. The saturation of the NMR shift and the sublinear power law temperature (T) evolution of the $1/T_1$ NMR relaxation rate at low T point to a nonsinglet ground state favoring a gapless fermionic description of the magnetic excitations. Below 1 K a pronounced slowing down of the spin dynamics is witnessed, which may signal a reconstruction of spinon Fermi surface. Nonetheless, the compound remains in a fluctuating spin liquid state down to the lowest temperature of the present investigation.

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Combining competing interactions and quantum fluctuations, maximized for low spin $S = 1/2$, is one major track followed in the past decade to discover novel disordered quantum states beyond the Landau paradigm of phase transitions with broken symmetries. One such long sought state is a quantum spin liquid (QSL), breaking no symmetries down to $T = 0$ but exhibiting macroscopic entanglement of strongly interacting spins and featuring exotic fractionalized excitations [1,2]. Much effort has been devoted towards low dimensional quantum antiferromagnets (AFM) where the low lattice coordination helps in further destabilizing classical ground states in favor of more exotic ones driven by quantum fluctuations [3]. A few spin liquid materials have been identified, either based on the highly frustrated kagome lattice—a weakly coordinated ($z = 4$) network made of corner-sharing triangles—including the celebrated Herbertsmithite mineral [4–6], or based on the less frustrated simple triangular lattices ($z = 6$) [7,8]. In three-dimensional (3D) systems quantum states are even more elusive. In the double perovskite Ba_2YMoO_6 compound featuring edge-shared tetrahedra ($z = 12$), the Mo^{5+} to host nearly pure spin $S = 1/2$, which quench partially into a valence bond glass state [9,10]. Further developments in this context arise from some rare-earth based pyrochlores where large spins with strong anisotropies decorate the corner-sharing tetrahedra ($z = 6$). The low energy physics can be mapped to a model of interacting effective spin $S = 1/2$ and may stabilize QSL states [11]. The hyperkagome structure—a 3D network of corner-sharing triangles ($z = 4$), offers an interesting alternative and indeed several exotic quantum phases relying on this geometry have been proposed [12]. At the origin of these studies is the $Na_4Ir_3O_8$ compound [13] where Ir^{4+} ions bear effective $J_{\rm eff} = 1/2$ spins and fail to order well below the exchange interaction energy although the ground state has recently been shown to be static [14,15]. Whether perturbation terms to the Heisenberg model, such as exchange anisotropies, or disorder in the interaction is responsible for the low T freezing is still an open issue. Remarkably, those spin liquid candidates in 3D are based on rather heavy ions where the applicability of a model of $S = 1/2$ Heisenberg spins is questionable.

Recently, some of us reported a quantum AFM $PbCuTe_2O_6$ (henceforth PCTO), which constitutes a strongly frustrated 3D network of Cu^{2+} ($S = 1/2$) spins. $PbCuTe_2O_6$ crystallizes in a cubic structure with a hyperkagome magnetic lattice if only the dominant second nearest neighbor (NN) interaction J is considered [16]. Additionally, weaker 1st NN (~$0.5J$) and 3rd NN (~$0.8J$) AFM interactions form isolated triangles and chains. The magnetic susceptibility χ exhibits a Curie-Weiss behavior with an AFM $\theta_{CW} \simeq -22$ K and no sign of a magnetic transition down to 2 K. The magnetic specific heat (C_m) shows a broad maximum at $T^{max} \simeq 0.05\theta_{CW} \simeq 1.1$ K, quite similarly as in $Na_4Ir_3O_8$, followed by a weak kink at 0.87 K of unclear origin. In magnetic fields larger than 8 T, the evolution of C_m with temperature is nearly quadratic at low T, in line with some theoretical predictions for the quantum hyperkagome model [17,18].

In this Letter, we present a comprehensive account of the local magnetic susceptibility and low temperature spin dynamics via NMR and muon spin relaxation measurements accompanied by low temperature magnetization studies on the highly frustrated 3D quantum antiferromagnet $PbCuTe_2O_6$. Muon spin relaxation data reveal no signature of long range magnetic ordering (LRO) down to 20 mK, a hallmark of a QSL state. The persistence of slow spin dynamics is confirmed by the NMR signal intensity being wiped out below 1 K and not being recovered down to our lowest temperature $T = 50$ mK. Before the signal is lost, the NMR shift saturates at a finite value pointing to a nonsinglet ground state.

The polycrystalline PCTO sample was synthesized by the method described in Ref. [16]. Figure 1 shows the T dependence of the magnetic susceptibility. The magnetic susceptibility ($\chi = M/H$) displays a Curie-Weiss behavior at high T and an enhancement at low temperature without any clear signature of LRO. A weak zero field cooled and field cooled (ZFC-FC) splitting is nonetheless observed at 0.87 K at the lowest applied field of 0.01 T. At higher magnetic fields the irreversibility is suppressed but a kink remains detectable, which slightly shifts towards lower T. This magnetic anomaly has to be connected to the kink in C_m at the same temperature (see the inset of Fig. 1). The relevance of this spin-glass-like transition for the bulk properties of PCTO is difficult to decide on the sole basis of the macroscopic measurements. In the following we use local probe measurements and clearly demonstrate that the 0.87 K anomaly is not a bulk transition but is attributed to the presence of a tiny amount of defects in the polycrystaline sample.

To gain further insights into the spin dynamics and ground state properties, we have performed muon spin relaxation measurements at the Paul Scherrer Institute. The zero field relaxation of the polarization of the muons stopped in the sample could be fitted to a single stretched exponential model $P_z(t) = \exp[-(\lambda t)^{\beta}]$ in the whole temperature range (see the Supplemental Material [19]). The monotonic decay of the polarization even at the lowest $T =$ 20 mK demonstrates the absence of a static internal field. In particular, the characteristic signatures of a frozen ground state, namely, (damped) spontaneous oscillations and for a powder sample a nonzero polarization at long times due to internal fields directed along the initial muon polarization, are not observed in PCTO. The transition to static magnetism seen at 0.87 K in bulk magnetization measurements should therefore be attributed to a minority spin fraction undetected in the muon spin relaxation experiment, i.e., below a few percent of the sample volume. As detailed below, the fact that bulk spins slow down on the verge of static magnetism in this same temperature range suggests nevertheless that the minority spin fraction does not constitute a separated impurity phase but could arise from some slightly disordered areas or grains in the polycrystalline sample.

The evolution of the relaxation rate λ and the stretched exponent β is shown in Fig. 2(b). The relaxation is close to exponential and hardly dependent on temperature above about 5 K indicating that the system is close to its paramagnetic limit [20]. At lower temperatures, the increase of the relaxation rate renders evidence for a slowing down of the spin dynamics likely resulting from the building up of short range correlations. Upon further cooling below about 1 K, the increase steeply accelerates as

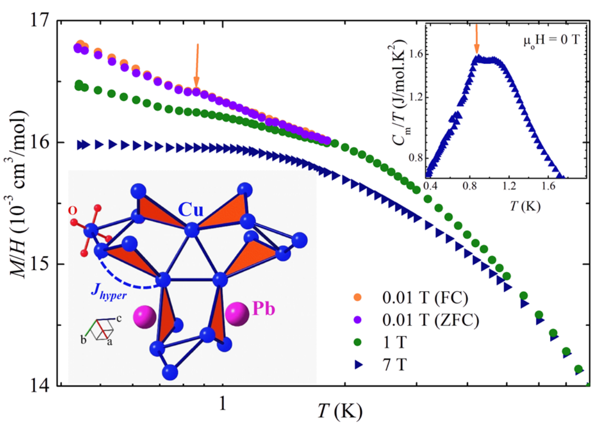

FIG. 1. Temperature dependence of the magnetic susceptibility in several applied fields. The bottom left inset shows a partial view of the crystal structure of $PbCuTe_2O_6$. The top right inset shows the T dependence of the magnetic specific heat by T (C_m/T) in 0 T (adapted from Ref. [16]).

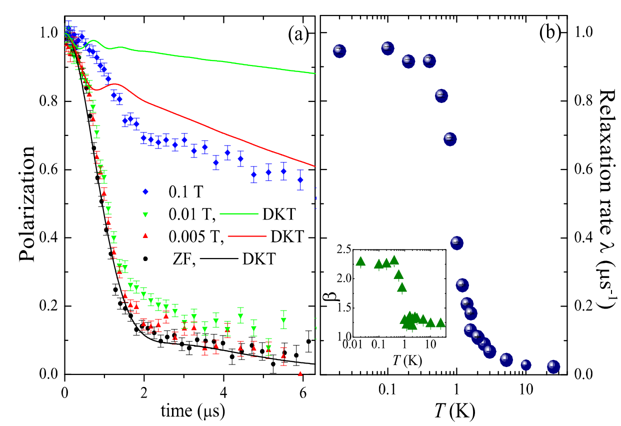

FIG. 2. (a) Field dependence of the muon polarization $P_z(t)$ at $T = 0.1$ K. The solid line corresponds to the dynamical Kubo-Toyabe model (DKT) as explained in the text. (b) T dependence of the relaxation rate obtained from the stretched exponential fit. The inset shows the T dependence of the stretched exponent.

if on the verge of a magnetic transition but then levels off below about 0.6 K. Such a saturation of λ is a common feature of highly frustrated magnets signaling the persistence of slow spin dynamics at $T \to 0$ in line with a QSL ground state.

The evolution of the relaxation shape from exponential ($\beta \sim 1$) to Gaussian ($\beta \sim 2$) across $\sim$1 K suggests that the electron spin fluctuations have slowed down substantially in the ground state at the limit of static magnetism. To quantify the level of fluctuations in the ground state, we have fitted the relaxation [see Fig. 2(a)] to the dynamical Kubo-Toyabe model [21] $P_{\rm DKT}(t, \Delta H, \nu, H_{\rm LF})$, which accounts for a Gaussian distribution of internal fields of width ΔH fluctuating at the rate ν, in a zero field or with an applied longitudinal field $H_{\rm LF}$. In a zero field, this model accounts well for the relaxation and gives $\Delta H = 1.1$ mT and $\nu = 0.7$ MHz. With a ratio $r = \gamma_\mu \Delta H/\nu \sim 1.3$ (where $\gamma_\mu = 2\pi \times 135.5$ Mrad/s is the muon gyromagnetic ratio), the Cu^{2+} spin fluctuations seem indeed to have slowed down to the quasistatic limit ($r \sim 1$) at the base temperature. However, keeping these zero-field parameters, the model fails to account for the field dependence. Indeed, in the case of (quasi)static magnetism one expects a strong reduction of the relaxation under an applied field of $\sim 5\Delta H \approx 5$ mT. Experimentally, a field at least 20 times larger is needed to reach a similar reduction, implying a more dynamical scenario [Fig. 2(a)]. Also surprising is the magnitude of the internal field, $\sim$1 mT, which corresponds to a tiny moment $\sim 0.065\mu_{\rm B}$ per Cu^{2+} ions obtained by estimating the dipolar field at the muon assumed to stop close to an oxygen site. These two features are strongly reminiscent of the "sporadic" model introduced to explain the "undecoupleable Gaussian shape" observed in the kagome bilayer chromates [22,23]. This model assumes that the relaxation in the spin liquid state arises mostly from deconfined spinon excitations that pass close to the muon for only a fraction of time ft while the background ground state is hardly magnetic, if not a singlet state, giving no sizeable relaxation for the remaining time fraction $(1 - f)t$. This results in a renormalization of the parameters of the dynamical Kubo-Toyabe $P_z(t) = P_{\rm DKT}(t, f\Delta H, fH_{\rm LF}, f\nu)$. From the field dependence of $P_z(t)$, we estimate $f \sim 1/10$. A detailed comparison calls for specific measurements versus field and temperature, which is beyond the scope of the present study, but gives a direction for further muon spin relaxation studies.

In complex systems such as frustrated magnets where static magnetism and persistent fluctuations are often found to coexist at low temperatures, the comparison of different techniques with different time windows is necessary to get a comprehensive understanding of the ground state properties. In addition to muon spin relaxation experiments, ^{207}Pb ($I = 1/2$, $\gamma_n/2\pi = 8.874$ MHz/T) NMR measurements were carried out. Shown in Fig. 3(a) are the field swept ^{207}Pb NMR spectra of PCTO at 63.5 MHz at different temperatures. The absence of major structural distortions or defects and a single ^{207}Pb nuclear site in the host lattice results in narrow spectra. This offers the opportunity to track the local magnetic susceptibility unambiguously. Shown in Fig. 3(b) is the integrated NMR signal intensity, after taking into account the spin-spin relaxation T_2 correction [19]. Remarkably, the intensity decreases drastically below 1.6 K, suggesting very fast relaxation times of the ^{207}Pb nuclei on the time scale of the NMR window, which is attributed to the slowing down of the Cu^{2+} spins at low T. Such a wipe out of the NMR signal has been observed in a few cases and usually the signal is recovered at low T, below a peak of $1/T_1$ at the transition temperature resulting from the critical slowing down of the spin dynamics [24–27]. At variance, here we did not recover the NMR signal intensity even at 50 mK, implying the persistence of slow spin dynamics at very low T. This is in perfect agreement with the muon spin relaxation data and confirms the dynamical nature of the ground state. The tiny broad signal detected at 0.7 K may then be related to the minority spin fraction undergoing the magnetic transition at 0.87 K. The Gaussian line shape of this remaining signal suggests a disordered, spin-glass-like state for these spins in line with the observed hysteresis of the magnetization—as one would expect a rectangular shaped powder average spectrum in a LRO phase [28]. From now on, we will concentrate on the NMR results in the T range $T > 1$ K where all of the bulk spins are probed.

At high temperature, the NMR line shift ^{207}K scales with the macroscopic susceptibility χ: $^{207}K = A_{\rm hf}\chi + K_0$, where $A_{\rm hf}$ is the hyperfine coupling constant and represents the hyperfine interaction between the Cu electron spin and ^{207}Pb, and K_0 is the T-independent chemical shift. We obtain $A_{\rm hf} = (1 \pm 0.05){\rm T}/\mu_{\rm B}$ and $K_0 = -0.05$ from a linear fit of ^{207}K vs χ. The T-dependent part of the NMR line shift, $K_{\rm spin}$, proportional to the spin part of the local susceptibility, is shown in Fig. 4(a). χ and $K_{\rm spin}$ are well reproduced by the high temperature series expansion (HTSE) and (7,7), (8,7) Padé approximants for the

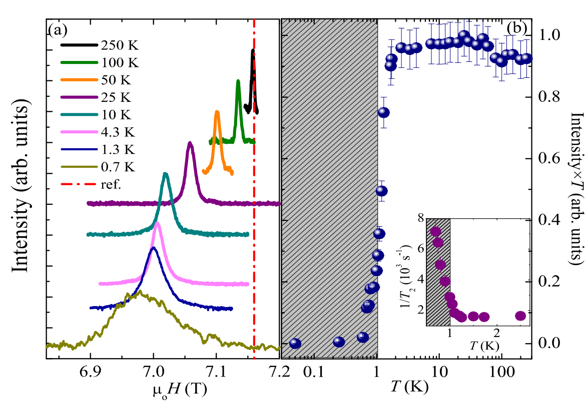

FIG. 3. (a) Temperature evolution of the field swept ^{207}Pb NMR spectra at 63.5 MHz. (b) Temperature dependence of the NMR signal intensity. The inset shows the T dependence of $1/T_2$ at 63.5 MHz.

Heisenberg model on the hyperkagome lattice with an AFM coupling strength of $J/k_B \approx (14 \pm 1)$ K between Cu spins [19,29]. Below about 10 K, the local susceptibility tracked by ${}^{207}K$ slightly deviates from the macroscopic one, pointing to the contribution of a tiny 0.4(3)% fraction of quasifree spin (or so called orphan spins) to the latter, and is almost constant down to 1 K [30]. The saturation at a finite and rather high value of the local susceptibility at low T is quite similar to the case of $Na_4Ir_3O_8$ and contrasts with many 2D frustrated AFMs where the local susceptibility exhibits a broad maximum at a fraction of J/k_B [5,31]. Furthermore, given that no large deviation is observed between the macroscopic χ and ${}^{207}K$ down to 1 K one can infer from the magnetization data (shown in Fig. 1) that the intrinsic susceptibility does not vary much either below 1 K. In particular, it seems unlikely that a spin gap larger than ~0.45 K ($\approx\theta/50$) opens up, which is confirmed by the existence of fluctuating local fields at temperatures as low as 50 mK.

Further insight into the spin correlations is provided by the ^{207}Pb spin-lattice relaxation T_1 measurements. As shown in Fig. 4(b) $1/T_1$ varies rather weakly with temperature, decreasing by a factor ~3 from its maximum at 300 K down to its minimum at 2 K, ruling out the possibility of a spin gap larger than 1 K in PCTO. Different T regimes can still be distinguished. Upon cooling from high T, $1/T_1$ progressively decreases down to ~20 K where it shows a marked kink and a steeper variation, which fits to a sublinear power law $T^{0.4}$. This change below $T \sim \theta$, corresponding to the saturation of the local susceptibility, has to be related to the emergence of short range spin correlations. This evolution can be compared to the one of the 2D spin liquid Herbertsmithite, $T^{0.7}$ [5], and to the theoretical prediction of power law behaviors for critical spin liquids [32,33]. However, contrary to these latter cases, the evolution of $1/T_1$ changes here again below about 2 K

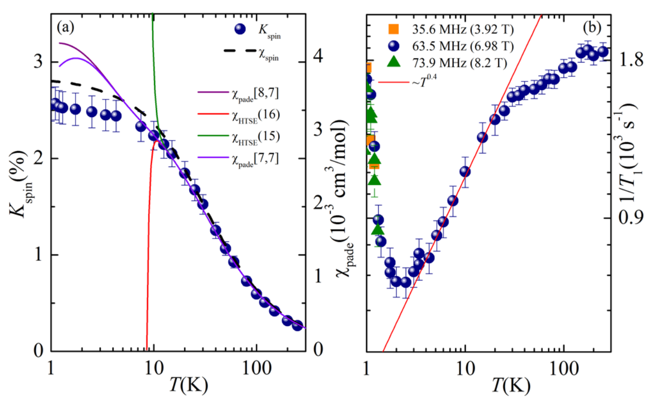

FIG. 4. (a) Temperature dependence of the ^{207}Pb shift and the magnetic spin susceptibility χ_{spin}. The solid lines correspond to the HTSE up to order 15 and 16 for the hyperkagome lattice and extrapolations using the Padé approximation (adapted from Ref. [29]). (b) T dependence of the spin-lattice relaxation rate at three frequencies. The solid line is a fit to T^α giving $\alpha = 0.4 \pm 0.05$.

where it sharply increases. The increase of $1/T_1$ below 2 K evidences a slowing down of the spin dynamics consistent with the muon spin relaxation results.

The compound $PbCuTe_2O_6$ appears as one rare example of a 3D AFM exhibiting a dynamical ground state, i.e., with no on-site frozen moments. This is all the more striking since first principles calculations suggest a high connectivity of the magnetic lattice ($z = 8$) resulting from three different AFM interactions of comparable strengths [16,34]. Whether these interactions compete and eventually enhance the magnetic frustration as, for instance, in kapellasite [35,36] or reduce the strong geometric frustration of the hyperkagome lattice generated by the dominant (NN) interaction requires a detailed study of the $S = 1/2$ Heisenberg model with all three interactions. Despite the complexity of the magnetic model, it is instructive to compare our results to the prototype material $Na_4Ir_3O_8$ for the 3D quantum hyperkagome model and related theories. Let us be reminded that in the case of the iridate hyperkagome lattice, spin-orbit coupling leads to an effective $J_{\mathrm{eff}} = 1/2$ Heisenberg model still under discussion, while such a model is the natural starting point in $PbCuTe_2O_6$. Also, the recent experimental work has shown that $Na_4Ir_3O_8$ experiences a magnetic transition below $T = 7$ K [14,15], at variance with $PbCuTe_2O_6$ where no freezing has been detected. Now, in the spin liquid phases of both compounds, the NMR shifts are found to saturate at a rather high value at low T, a feature that is best accounted for in a fermionic description of the magnetic excitations on the hyperkagome lattice leading to a spinon Fermi surface and a constant Pauli-like susceptibility [17,18]. The absence of a large spin gap in $PbCuTe_2O_6$ rules out the alternative possibilities of a valence bond crystal or a topological spin liquid ground state suggested for the hyperkagome model [12,37]. In the fermionic framework, the T^α ($\alpha \sim 2$ in a strong applied field) behavior of the heat capacity observed below ~0.6 K [16] is not predicted and requires an instability—namely a partial gap opening—of the spinon Fermi surface. The strong slowing down of the spin dynamics shown by the muon spin relaxation and NMR results at about 1 K could be the signature of such a crossover between two different spin liquids. Further, a partial gapping of the spinon Fermi surface at ~1 K resulting in a reduced density of spinon excitations may help in understanding the weak field dependence of the Gaussian-like muon spin relaxation, tentatively attributed to sporadic fluctuations below about 1 K.

To conclude, our investigations at low temperatures by magnetization, muon spin relaxation, and NMR reveal that $PbCuTe_2O_6$ is a promising 3D antiferromagnet with $S = 1/2$ where strong frustration leads to a spin liquid behavior. This rare case calls for an in-depth investigation of the appropriate magnetic Hamiltonian, including, for instance, the high temperature series expansion, together with theoretical developments in a fermionic approach. In this context our results, together with those in Ref. [16], give strong constraints on the possible ground states. In view of the relatively weak coupling strength, the effect of substitutions, the application of external pressure, and local probe experiments at higher magnetic fields might offer an appealing possibility to tune the magnetism of PCTO and to explore further insights into its magnetic properties.

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