Emergence of the spin polarized domains in the kagome lattice Heisenberg antiferromagnet Zn-barlowite (Zn\textsubscript{0.95}Cu\textsubscript{0.05})Cu\textsubscript{3}(OD)\textsubscript{6}FBr

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Kagome lattice Heisenberg antiferromagnets are known to be highly sensitive to perturbations caused by the structural disorder. NMR is a local probe ideally suited for investigating such disorder-induced effects, but in practice, large distributions in the conventional one-dimensional NMR data make it difficult to distinguish the intrinsic behavior expected for pristine kagome quantum spin liquids from disorder-induced effects. Here we report the development of a two-dimensional NMR data acquisition scheme applied to Zn-barlowite (Zn\textsubscript{0.95}Cu\textsubscript{0.05})Cu\textsubscript{3}(OD)\textsubscript{6}FBr kagome lattice, and successfully correlate the distribution of the low energy spin excitations with that of the local spin susceptibility. We present evidence for the gradual growth of domains with a local spin polarization induced by 5% Cu\textsuperscript{2+} defect spins occupying the interlayer non-magnetic Zn\textsuperscript{2+} sites. These spin-polarized domains account for ~60% of the sample volume at 2 K, where gapless excitations induced by interlayer defects dominate the low-energy sector of spin excitations within the kagome planes.

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INTRODUCTION

The quantum spin liquid (QSL) is a novel state of matter formed by entangled spin singlets, in which magnetic frustration effects prevent spins from undergoing magnetic long-range order\textsuperscript{1–5}. The last few decades have seen concerted efforts to identify model materials of the QSL. However, many of them undergo magnetic long-range order or spin freezing at low temperatures. Copper hydroxyhalide materials herbertsmithite ZnCu\textsubscript{3}(OH)\textsubscript{6}Cl\textsubscript{2}\textsuperscript{1,24} and Zn-barlowite ZnCu\textsubscript{3}(OH)\textsubscript{6}FBr\textsuperscript{21,24–30} are among the few exceptions without magnetic symmetry breaking even near absolute zero. As shown in Fig. 1, Cu\textsuperscript{2+} ions with electron spin-1/2 in Zn-barlowite form a corner-sharing triangular lattice known as the kagome lattice. The nearest-neighbor Cu\textsuperscript{2+}–Cu\textsuperscript{2+} antiferromagnetic super-exchange interaction is as large as J \textasciitilde 160 K\textsuperscript{1,23} and geometrically frustrated. While earlier studies point toward the realization of a proximate kagome QSL state in these materials\textsuperscript{6,8,11,12,15,17,19–21,24–27}, the structural disorder in these materials\textsuperscript{14,26} complicates the interpretation of the experimental results. Accordingly, the exact nature of the kagome planes has been highly controversial, necessitating a clear understanding of the influence of disorder on the kagome planes.

Recent work, including site-selective anomalous X-ray scattering experiments, established that the interlayer non-magnetic Zn\textsuperscript{2+} sites are occupied by extra Cu\textsuperscript{2+} defect spins with \textasciitilde15% probability in herbertsmithite\textsuperscript{14} and \textasciitilde5% probability in the most Zn-rich Zn-barlowite, synthesized as a powder\textsuperscript{26}. Accordingly, their actual chemical formula is (Zn\textsubscript{0.85}Cu\textsubscript{0.15})Cu\textsubscript{3}(OH)\textsubscript{6}Cl\textsubscript{2} for herbertsmithite and (Zn\textsubscript{0.95}Cu\textsubscript{0.05})Cu\textsubscript{3}(OH)\textsubscript{6}FBr for Zn-barlowite. We will use the acronym Zn\textsubscript{0.95} to represent Zn-barlowite hereafter. One important difference between Zn-barlowite and herbertsmithite is the location of the interlayer Cu\textsuperscript{2+} defects: in herbertsmithite, they occupy the centered, octahedral Zn\textsuperscript{2+} site, while in Zn-barlowite they occupy an off-center, trigonal prismatic site that is distinct from the octahedral Zn\textsuperscript{2+} site\textsuperscript{25,26}.

The extra interlayer Cu\textsuperscript{2+} defect spins in both of these materials could directly contribute to the magnetic response of the sample, such as enhanced bulk spin susceptibility $\chi_{\text{bulk}}$ at low temperatures. In addition, each interlayer defect spin interacts with the three nearest-neighbor (nn) kagome Cu\textsuperscript{2+} sites located in each of the two adjacent kagome planes. Furthermore, the structural distortion in the vicinity of the interlayer defects\textsuperscript{11,17,21,30} might enhance local spin susceptibility $\chi_{\text{local}}$ at low temperatures through Dzyaloshinskii-Moriya interaction\textsuperscript{9,10,13,19} and/or randomness introduced to the exchange interaction\textsuperscript{21–23}. On the other hand, the upper bound of the concentration of the non-magnetic Zn\textsuperscript{2+} inter-site defects diluting the magnetic Cu\textsuperscript{2+} sites within the kagome planes is \textasciitilde1% in both of these materials\textsuperscript{14,26}. This contradicts the persisting claim that as much as \textasciitilde5% of kagome Cu sites may be diluted by non-magnetic inter-site Zn\textsuperscript{2+} defects, which cause local spin singlets accompanied by oscillatory spin density induced in their vicinity\textsuperscript{12,20,21}.

Our earlier NMR measurements in the isotope-enriched single crystal samples of herbertsmithite successfully separated the main NMR peaks from those associated with the nn and the next nearest-neighbor (nnn) nuclei\textsuperscript{15} (nuclear spin I = 1)\textsuperscript{15} and $^1$O (nuclear spin I = 5/2)\textsuperscript{17} sites of the 15% interlayer Cu\textsuperscript{2+} defect spins. We demonstrated that the Knight shift of the main NMR peak arising from the defects far away from the interlayer defects decreases toward zero. The implication of the diminishing local spin susceptibility $\chi_{\text{local}}$ far from the defects has been the subject of an intense debate, i.e., whether the proximate kagome QSL realized in herbertsmithite and Zn\textsubscript{0.95} is gapped or gapless\textsuperscript{11,12,15,17,20,21,24}. On the other hand, the NMR Knight shift at the nn sites of the interlayer defects in herbertsmithite is negative and its magnitude grows with decreasing
temperature roughly in proportion to the bulk averaged spin susceptibility $\chi_{\text{bulk}}$ \cite{5,17}. This means that the interlayer defect moments, which are polarized by the external magnetic field $B_{\text{ext}}$, applied to conduct NMR measurements, induce a negative hyperfine magnetic field $B_{\text{hyp}}$ pointing in the opposite direction from $B_{\text{ext}}$. In principle, one can probe the spatial extent of the influence of interlayer Cu$^{2+}$ defects spins on the adjacent kagome planes by investigating the nn and further n$n$\texttext{a} and $^{17}$O sites. But we were unable to resolve these peaks at low temperatures, because the splitting between the multiple quadrupole-split NMR peaks is obscured by extreme magnetic line broadening with both positive as well as negative $B_{\text{hyp}}$.

Very recently, we used inverse Laplace transform (ILT) $T_1$ analysis technique \cite{21,34-41} to successfully deduce the density distribution function $P(1/T_1)$ of the nuclear spin-lattice relaxation rate $1/T_1$ in herbertsmithite and Zn$_{0.95}$ \cite{31}. The integral of $P(1/T_1)$ is normalized to 1, and $P(1/T_1)$ represents the probability for the nuclear spin to relax with a given value of $1/T_1$. In general, $1/T_1$ probes low-energy spin excitations in the form of the wave vector integral of the dynamical electron spin susceptibility at the NMR frequency $\omega (= 2\pi f)$,

\[
\frac{1}{T_1} = \frac{\gamma^2 k_B T}{\mu B \hbar^2} \sum_q |A_q|^2 \chi'(|\mathbf{q}, \omega|) \frac{1}{\omega},
\]

where $A_q$ is the $q$ dependent hyperfine form factor, and $\chi'(|\mathbf{q}, \omega|)$ is the imaginary part of the dynamical electron spin susceptibility (i.e., spin fluctuations at the resonance frequency $\omega$).

It turned out that the $^{63}$Cu nuclear spin-lattice relaxation rate $1/T_1$ in Zn$_{0.95}$ develops a bimodal distribution below $\sim$30 K due to the gradual emergence of spin singlets with inhomogeneous gap $\Delta$, which has a large distribution ranging from a few K to as high as $\Delta$ $\sim$30 K \cite{21}. These Cu sites involved in spin-singlet formation exhibit diminishing $1/T_1$ with decreasing temperature, and the absolute upper bound of their volume fraction is $F_{\text{singlet}}$ $\sim$50%. On the other hand, the remaining Cu sites with a fraction of $1 - F_{\text{singlet}}$ $\sim$50% or greater do not participate in the spin-singlet formation and remain correlated but paramagnetic. These paramagnetic Cu spins exhibit a large and roughly constant $1/T_1$ $\sim 10^{-3}$ s$^{-1}$, which is typical for gapless excitations of paramagnetic spins coupled by super-exchange interactions, but their origin was not clear.

The aim of this study is to probe the origin, nature, and fraction of these paramagnetic Cu sites based on the $^{19}$F NMR study of Zn$_{0.95}$. $^{19}$F has a nuclear spin $I = 1/2$, lacks nuclear quadrupole moment, and hence $^{19}$F NMR is immune from nuclear quadrupole interaction that splits and complicates $^{2}$D and $^{17}$O NMR lineshapes. $^{19}$F NMR, therefore, provides an avenue to probe the influence of interlayer defects on the kagome planes. Nonetheless, earlier $^{19}$F NMR studies based on the conventional one-dimensional NMR approach \cite{21,24} did not provide a clear-cut picture of the nature of defects in Zn$_{0.95}$, because the line broadening obscured the distinction between the intrinsic and defect-induced phenomena.

In this paper, we report the development of a two-dimensional NMR data acquisition scheme and its application to $^{19}$F NMR measurements in Zn$_{0.95}$. Instead of separately measuring the position by position variations of $\chi_{\text{local}}$ and low-energy spin excitations from the distributions of the Knight shift $K$ and $1/T_1$, respectively, we generate a two-dimensional correlation map $\chi_{\text{focal}}$ between them. In essence, this procedure allows us to count the number of $^{19}$F sites that have certain values of the Knight shift $K$ and $1/T_1$ (i.e., $\chi_{\text{focal}}$ and local spin excitations). We demonstrate that interlayer Cu$^{2+}$ defect spins induce distinct spin-polarized domains at low temperatures, in which $^{19}$F sites exhibit similar behavior as in antiferromagnetic barlowite Cu$_4$(OH)$_6$FBr with Néel temperature $T_N$ $\sim$15 K (abbreviated as Cu$_4$ hereafter) \cite{25,42-48}. The $^{19}$F sites in these domains of Zn$_{0.95}$ detect gapless spin excitations and enhanced $\chi_{\text{local}}$ induced by interlayer Cu$^{2+}$ defects spins. The volume fraction of these domains reaches as much as $F_{\text{para}}$ $\sim$60% at 2 K despite the low 5% concentration of

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**Fig. 1** Kagome lattice. a The crystal structure of Zn-barlowite “Zn$_{0.95}$” (Zn$_{0.95}$Cu$_{0.05}$)Cu$_4$(OD)$_6$FBr. For clarity, D-sites attached to O-sites are not shown in any of the panels. b A c-axis view of the kagome plane of Zn$_{0.95}$ and the interlayer Zn (cyan), Br (blue), and F (green) sites above and below the kagome plane. c A wider field of view of the kagome plane in Zn$_{0.95}$, without D, O, and Br sites. The Zn$^{2+}$ site surrounded by a black circle near the middle of the panel represents the Cu$^{2+}$ interlayer defect occupying one of the twenty Zn sites within this field of view with a 5% probability. The circle with orange-to-yellow shading represents the spin-polarized domains, which encompasses 12 of the 2019F sites in this field of view, corresponding to 60% as observed at 2 K in panel d. All the kagome Cu sites in this domain have polarized spins or interact with them. d Temperature dependence of the fraction $F_{\text{para}}$ of the $^{19}$F sites belonging to the spin-polarized domains estimated in this work. Blue shading depicts the freezing of the lattice distortion starting at $\sim$160 K and completing at $\sim$50 K \cite{21}.
the interlayer defects in Zn0.95, indicating the gradual spatial growth of these domains at low temperatures.

The rest of this article is organized as follows. We will begin the next RESULTS section with a presentation of the one-dimensional NMR data. We will explain how much one can learn from such conventional NMR data with the aid of ILT, and also its limitations. The following sub-section will develop the two-dimensional NMR data acquisition scheme, and discuss how one can de-convolute the 19F NMR Knight shifts 19K as determined from the deconvolution of C(1/T1T) based on double Gaussian fit. For comparison, we show 19F measured for the single peak observed for antiferromagnetic Cu4 (blue). The vertical error bars specify the maximum possible range of uncertainties. Using the right axis, we also show the bulk magnetization data of χbulk measured in 2.4 T for Zn0.95 (red) and Cu4 (blue).

where the summation goes over the twelve nn Cu sites of 19F nucleus with local spin susceptibility χlocal, Na is Avogadro’s number, Ahf is the positive hyperfine coupling with these nn Cu sites, and 19Kchem=0.01% is a very small and temperature-independent chemical shift.

In Fig. 3, we summarize 19Kpeak in comparison to χbulk. Our 19Kpeak results are similar to the earlier reports in ref. 24 and ref. 21; 19Kpeak begins to decrease below ~20 K toward zero. An earlier report fitted the results with an activation form 19Kpeak ~exp(−Δ/kBT) with a gap Δ=12, but we found that large experimental uncertainties of 19Kpeak caused by extremely broad lineshapes below 20 K make it rather difficult to rule out a linear temperature dependence expected for the gapless spin liquid picture based on Dirac Fermions.

We recall that 19Kpeak does not necessarily decrease to zero, unless all the 12 nn Cu sites of a given 19F site form spin singlets; but less than half of Cu sites are actually involved in spin-singlet formation in Zn0.95. In fact, 19Kpeak exhibits a temperature dependence analogous to that of χbulk only down to ~50 K, where the latter begins to grow. The broad 19F NMR lineshapes observed at low temperatures exhibit long tails stretching hundreds of kHz toward both higher and lower frequencies. This means that a majority of 19F sites sense large, distributed hyperfine magnetic fields B_{hf} with both positive and negative signs, and only a small fraction of 19F sites exhibit diminishing 19Kpeak below 20 K.

RESULTS
Conventional one-dimensional NMR data and their limitations

We first summarize the conventional one-dimensional 19F NMR results, and their limitations in elucidating the influence of defects. In Fig. 2a, we present the representative 19F NMR lineshapes observed for a deuterated, polycrystalline Zn0.95 sample of (Zn0.95Cu0.05)Cu3(OD)6FBr in an external magnetic field of 2.4 T. The full width at half maximum (FWHM) of the lineshape is as narrow as 26 kHz at 250 K owing to the small nuclear dipole moment of 2D. Upon cooling, the peak frequency 19fpeak of the lineshape slightly increases down to ~20 K, then decreases toward the bare resonance frequency 19f0 = 19γB_{ext} ≈ 96.02 MHz marked by the vertical dashed line. The resonant frequency expected in the absence of hyperfine interactions with electron spins in the lattice, and the nuclear gyromagnetic ratio of the 19F nucleus is 19γN/2π = 40.05 MHz/Tesla. We can summarize the change of 19fpeak using the NMR Knight shift 19Kpeak defined as

\[ 19K_{peak} = \frac{19f_{peak} - 19f_0}{19f_0} = \sum_{i}^{12} \frac{A_{hf}}{N_{A} \mu_{B}} \chi_{local} + 19K_{chem}. \]
If there is no magnetic inhomogeneity, we expect $X_{\text{local}} = X_{\text{bulk}}$ for all sites, and hence the NMR lineshape would remain narrow. In other words, the broadening of the lineshape indicates that $X_{\text{local}}$ develops a large distribution below ~50 K. Interestingly, this is the same temperature range, where the structural disorder freezes \(^3\) as evidenced by the broadening of the \(^{79}\text{Br}\) NQR lineshapes; the oscillation on the transverse relaxation measurements also uncovered the signature of structural dimer formation below ~50 K \(^3\).

We also measured $1/T_1$ at the peak frequency $^{19}\text{F}_{\text{peak}}$. The magnitude of $1/T_1$ develops a significant distribution below ~160 K, where the lattice freezing sets in \(^2\). Accordingly, we resorted to deduce the stretched-fit value of $1/T_{1,\text{str}}$ based on the conventional stretched fit of the recovery curve $M(t)$ as follows:

$$M(t) = M_0 - Ae^{-(t/T_{1,\text{str}})^\beta},$$

where $M_0$ is the saturated nuclear magnetization, $A$ is the change in the nuclear magnetization immediately after the inversion $\pi$ pulse or saturation comb pulses, and $\beta$ is the phenomenological stretched exponent. See Fig. 1g in ref. \(^2\) for the similar results of $M(t)$ and the fit. If magnetic inhomogeneity is negligibly small in Zn\(_{0.95}\), we expect $\beta = 1$. We emphasize that the stretched fit analysis of $M(t)$ is convenient but largely empirical, because it implicitly assumes a specific functional form for the density distribution function $P(1/T_1)$ of $1/T_{1,\text{str}}$. Strictly speaking, it is justifiable only if $P(1/T_1)$ may be represented with the modified Bessel function of the second kind \(^5\). Empirically, $1/T_{1,\text{str}}$ at various frequencies within the extremely broad lineshape. We summarize the representative results of the frequency dependence of $1/T_{1,\text{str}}$ and $\beta$ in Fig. 4c--e. $1/T_{1,\text{str}}$ at various frequencies within the extremely broad lineshape. We summarize the representative results of the frequency dependence of $1/T_{1,\text{str}}$ and $\beta$ in Fig. 4c--e. $1/T_{1,\text{str}}$ is larger at both lower and higher frequency sides of the peak. This suggests that the $1/T_1$ relaxation process at $^{19}\text{F}$ sites in the tailed sections of the broad lineshape is enhanced by low-energy spin excitations associated with the source of the hyperfine magnetic fields that gives rise to the line broadening. But we are unable to pinpoint their origin based on these measurements.

**Two-dimensional NMR data $C(f; 1/T_1)$**

Proximate quantum spin liquid materials that do not undergo magnetic long-range order are often structurally disordered and exhibit significantly distributed $1/T_1$. In our recent work, we overcame the difficulties in conventional NMR data acquisition protocols outlined in the previous section by using the ILTT analysis technique \(^3\). In the ILT analysis of the distributed $1/T_1$, one only assumes that $1/T_1$ has a spatial distribution, and each nuclear spin relaxes exponentially with the jth value $1/T_j$ with the probability density $P(1/T_j)$. Utilizing Tikhonov regularization, one can optimize the fit of the experimentally observed recovery curve $M(t)$ with a summation of single exponentials with gapped QSL. On the other hand, the power law behavior expected for the gapless QSL formed by Dirac Fermions is not observed, either. A key consideration in interpreting the $1/T_1$ results is that, again, $^{19}\text{F}$ sites are subjected to the fluctuations of the transferred hyperfine fields $B_{\text{hyp}}$, from 12 nn Cu\(^{2+}\) sites. Since the absolute upper bound of the fraction of spin singlets occupying the Cu sites is $F_{\text{singlet}} \approx 50\%$ in Zn\(_{0.95}\), many of the $^{19}\text{F}$ sites are under the influence of paramagnetic Cu spins that are not involved in spin singlets. This explains why the results for $1/T_{1,\text{str}}$ as well as $X_{\text{local}}$ do not meet the naive expectations for purely gapped or purely gapless QSL.

We also measured $1/T_{1,\text{str}}$ at various frequencies within the extremely broad lineshape. We summarize the representative results of the frequency dependence of $1/T_{1,\text{str}}$ and $\beta$ in Fig. 4c--e. $1/T_{1,\text{str}}$ is larger at both lower and higher frequency sides of the peak. This suggests that the $1/T_1$ relaxation process at $^{19}\text{F}$ sites in the tailed sections of the broad lineshape is enhanced by low-energy spin excitations associated with the source of the hyperfine magnetic fields that gives rise to the line broadening. But we are unable to pinpoint their origin based on these measurements.
These distribution of resonant frequency $19\text{f}$, measuring two sets of one-dimensional distributions separate and hence their population based on such a one-dimensional distribution function $P(1/T_1)$, as illustrated in Fig. 5. See refs. 36,38,39 for the details of the numerical ILT procedures.

For Cu$_2$, we observe a peak around $19\text{f}$ resonating around $1$/T$_1$ values of $1/300$ s$^{-1}$ caused by antiferromagnetic long-range order. We fixed the Tikhonov regularization parameter for ILT as $\beta = 0.72 T_{1,cg}$ of the $19\text{F}$ field at $19\text{F}$ sites transferred from the 12 nn Cu sites. For Cu$_2$, the peak still relax with the slower values of $1/300$ s$^{-1}$ above $160$ K for Zn$_{0.95}$ and above $77$ K for Cu$_2$, hence the apparent width of $P(1/T_1)$ in these regions is set primarily by the effective resolution of our ILT with fixed $\beta = 1$. (See Supplementary Materials of refs. 21,38 for details about the effective resolution of the ILT analysis.)

\[ M(t) = \sum_j M_0 \left[ 1 - 2 e^{-t/T_1} \right] P(1/T_1)_j, \]

where the summation of the probability $P(1/T_1)$ is normalized to 1. See refs. 36,38,39 for the details of the numerical ILT procedures.

In Fig. 5a, we summarize representative results of $P(1/T_1)$ at each frequency $19\text{f}_{\text{peak}}$ of the $19\text{F}$ NMR lineshapes observed for Zn$_{0.95}$. The integral of $P(1/T_1)$ is normalized to 1 (one). Corresponding results observed for Cu$_2$. Notice that the side peak of $P(1/T_1)$ observed for Zn$_{0.95}$ at $1/T_1$ $\approx 300$ s$^{-1}$ is absent for Cu$_2$. The large distribution observed at $1/2.4$ K is caused by antiferromagnetic long-range order. We fixed the Tikhonov regularization parameter for ILT as $\beta = 1$ to achieve the same effective resolution. The distributions of $1/300$ s$^{-1}$ in Zn$_{0.95}$ and above $T_{1,n o r m}$ is set primarily by the effective resolution of our ILT with fixed $\beta = 1$. (See Supplementary Materials of refs. 21,38 for details about the effective resolution of the ILT analysis.)

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Temperature dependence of $C(f; 1/T_1)$

In Fig. 7a–d, we summarize the representative results of $C(f; 1/T_1)$ observed for Zn$_{0.95}$ at various temperatures. See Supplementary Fig. 1 for the complete set of $C(f; 1/T_1)$ data and Supplementary Movie 1 for the movie summary of the evolution of $C(f; 1/T_1)$ as a function of temperature. Notice that $C(f; 1/T_1)$ has a nearly symmetrical oval shape around 250 K, because both $f$ and $1/T_1$ have only a minor distribution centered around their central value. This main peak remains fairly narrow along both the $f$ and $1/T_1$ axes, at least down to 10 K. But a distinct component emerges below ~120 K on the upper left-hand side of the main peak, and gradually splits off. In what follows, we call the emergent side peak with larger values of $1/T_1$ as the paramagnetic peak for the reasons to become clear below. The two-dimensional distribution of the paramagnetic peak continuously grows along the $f$ axis toward 2 K, but the growth of the distribution along the $1/T_1$ axis appears less significant at low temperatures.

In order to separate the contributions of the main and paramagnetic peaks, we deconvoluted $C(f; 1/T_1)$ into two separate two-dimensional Gaussian functions of $f$ and $1/T_1$ by conducting the least $\chi^2$ fit in the two-dimensional parameter space. See Supplementary Fig. 2 and Supplementary Fig. 3 for the details of the fit. We show the color contour map of the summation of these two Gaussian components in Fig. 7e–h. The two-component fit reproduces the experimental data in Fig. 7a–d fairly well. The paramagnetic side peak merges into the main peak at higher temperatures, and we were unable to clearly resolve them above 100 K. In Fig. 1d, we summarize the temperature dependence of the fraction $F_{\text{para}}$ of the $^{19}$F sites involved in the paramagnetic side peak estimated from the integral of the two-dimensional Gaussian peak in the $f$-$1/T_1$ space. $F_{\text{para}}$ gradually grows with decreasing temperature, and reaches as large as $F_{\text{para}} \approx 0.6$ at 2 K. We emphasize that the faint signature of the paramagnetic side peak seems to persist even at 150 K or above, as shown in Supplementary Fig. 1. It is consistent with our earlier finding that the $^2$D and $^{17}$O sites nn to the interlayer defects are distinct even at 295 K in herbertsmithite$^{15,17}$. On the other hand, the estimation of $F_{\text{para}}$ was difficult above 100 K due to the unstable nature of the two-dimensional fit of the small side peak involving a large number of free parameters.

From the central values of the two-dimensional Gaussian function for the paramagnetic peak, we estimated the central values of the distributed $^{19}K_{\text{para}}$ and $1/T_1^{\text{para}}$, whereas $^{19}K_{\text{main}}$ and $1/T_1^{\text{main}}$ were estimated from the two-dimensional Gaussian
function of the main peak; we summarize these results in Figs. 3, 8.

The paramagnetic peak is somewhat asymmetrical along the frequency axis with slightly more weight along the lower frequency side, but this does not significantly affect our estimation of the central value of $1/T_{1\text{par}}$. The central values of $1/K_{\text{par}}$ and $1/T_{1\text{main}}$ for the main peak are close to the nominal peak values of the one-dimensional data discussed in the previous section.

DISCUSSIONS

Our two-dimensional correlation maps and ILTT resolved $^{19}$F NMR lineshapes revealed that two distinct types of $^{19}$F sites exist in Zn$_{0.95}$ at low temperatures: (i) $^{19}$F sites with characteristic signatures of paramagnetic spins, i.e. enhanced Knight shift $^{19}$K$_{\text{para}}$ due to growing spin polarization, and large temperature-independent $1/T_{1\text{para}}$ induced by gapless low-energy spin excitations obeying $\chi \sim 1/T$. The volume fraction $P_{\text{para}}$ of these $^{19}$F sites reaches as much as ~60% at 2 K, indicating that spin-polarized domains gradually extends in space, as schematically shown in Fig. 1c. (ii) The main intrinsic $^{19}$F sites that are mostly immune from these effects, suggesting that they are spatially more distanced from the source of the spin polarization and more reflective of the intrinsic behavior of the kagome planes. These two different types of $^{19}$F sites become indistinguishable above ~120 K within our experimental resolutions.

Interestingly, the negative Knight shift $^{19}$K$_{\text{para}}$ of the paramagnetic peak shows qualitatively the same behavior as the negative Knight shift observed at the nn $^2$D and $^{17}$O sites of the 15% interlayer Cu$_2^{2+}$ defects occupying the Zn$_{2+}$ sites in herbertsmithite. This strongly suggests that the magnetic phase of Zn$_{0.95}$ with Cu$_2^{2+}$ defects of Zn$_{0.95}$. In order to test this scenario, we repeated two-dimensional $^{19}$F NMR measurements in a deuterated powder sample of barlowite Cu$_4$(OD)$_6$FBr. Cu$_4$ is the parent antiferromagnetic phase of Zn$_{0.95}$ with Cu$_2^{2+}$ spins occupying all the interlayer Zn$_{2+}$ sites in Zn$_{0.95}$ and undergoes a Neel transition into an antiferromagnetically ordered state at $T_N$ ~15 K.

We summarize the $^{19}$F NMR results of Cu$_4$ in Figs. 2b, 3, 5b, 8, 9 in comparison to the results for Zn$_{0.95}$. See Supplementary Fig. 4 for the complete set of C($f$, $1/T$) data of Cu$_4$ and Supplementary Movie 2 for the movie summary of the evolution of C($f$, $1/T$) as a function of temperature. Our one-dimensional NMR data for Cu$_4$ are similar to earlier $^{19}$F NMR measurements conducted in a limited temperature range below 100 K for a protonated powder sample of Cu$_4$. Notice that two-dimensional correlation maps C($f$, $1/T$) of Cu$_4$ in Fig. 9 show no signs of a split-off peak. Instead, Cu$_4$ exhibits only one type of $^{19}$F NMR peak in the entire paramagnetic state above $T_N$, this is consistent with the crystal structure of Cu$_4$, with a crystalllographically unique $^{19}$F site.

A striking finding here is that $^{19}$K$_{\text{para}}$ observed for Zn$_{0.95}$ shows nearly identical behavior as the unique $^{19}$F sites in antiferromagnetic Cu$_4$ above $T_N$, as shown in Fig. 3. This contrasts with the behavior of $^{19}$K$_{\text{main}}$ and reinforces our conclusion that the paramagnetic $^{19}$F sites observed for Zn$_{0.95}$ are in the close proximity with interlayer Cu$_2^{2+}$ defects occupying the Zn$_{2+}$ sites, where the structural and magnetic environment is locally similar to Cu$_4$’s. Since $X_{\text{bulk}}$ of Cu$_4$ shows strong enhancement below ~100 K, naturally, one expects analogous enhancement of the local spin susceptibility $X_{\text{local}}$ in the vicinity of Cu$_2^{2+}$ interlayer defects of Zn$_{0.95}$. The negative sign of the hyperfine magnetic field $b_{\text{hyp}}$ leads to a strongly negative $^{19}$K$_{\text{para}}$ in Zn$_{0.95}$. This further suggests that the conclusions from prior one-dimensional $^{19}$F NMR studies that neglect the effects of impurities should be reassessed.
While our $^{19}$F NMR measurements establish the gradual growth of spin-polarized domains induced in the vicinity of the Cu$^{2+}$ interlayer defects, our measurements do not reveal the exact spin configuration in these domains. The growth of staggering spin polarization within the kagome planes was previously proposed to account for the broadening of $^{17}$O NMR lineshapes in herbertsmithite, but it was attributed to the Zn$^{2+}$ anti-site defects within the kagome planes\textsuperscript{12,20}. Our findings here indicate that such spin vacancies within the kagome planes are not required to account for the NMR line broadening in these kagome materials; after all, Cu$_4$ has no Zn$^{2+}$ ions in its composition. Moreover, the upper bound of the Zn$^{2+}$ anti-site defect population is as little as \( \sim 1\% \)\textsuperscript{14,25}. At high temperatures (\( T > 160 \text{ K} \)) dominated by short-range spin fluctuations, it is striking that the behavior of Zn$_{0.95}$ clearly differs from Cu$_4$ (\( T_{N} \) and \( 1/T_1 \) increase upon cooling). This hints at an approach to two different ground states.

Another important point to emphasize is that the fraction of the paramagnetic $^{19}$F sites in Fig. 1d gradually grows below \( \sim 100 \text{ K} \) to as large as \( F_{\text{para}} \approx 60\% \) toward the base temperature of 2 K. In Fig. 1c, we use a circle with orange-to-yellow shading to schematically present the spin-polarized domain surrounding a Cu$^{2+}$ defect spin occupying the interlayer Zn$^{2+}$ site in the middle. Note that only \( \sim 40\% \) of such a volume remains at 2 K in Zn$_{0.95}$. Also shown (\( \circ \)) is the upper bound of the spin-singlet fraction \( F_{\text{singlet}} \) of Cu sites, estimated from the observable $^{63}$Cu NQR signals at the fixed pulse separation time \( \tau = 6 \mu \text{s} \)\textsuperscript{21}. (The lower error bars below 6 K represent the lower bound of \( F_{\text{singlet}} \) estimated based on the assumption that the $^{63}$Cu signal loss affects only the paramagnetic component. All other error bars correspond to the absolute maxima or minima of \( F_{\text{singlet}} \).) Blue shading schematically shows the temperature range where the freezing of the structural distortion sets in (\( \sim 160 \text{ K} \)) and completes (\( \sim 50 \text{ K} \)).

Fig. 9 Two-dimensional correlation map $C(f, 1/T_1)$ of Cu$_4$. a-d The two-dimensional correlation map $C(f, 1/T_1)$ observed for Cu$_4$ at representative temperatures. The $^{19}$F NMR lineshape gradually broadens below 250 K, as shown in Fig. 2b, toward \( T_N = 15 \text{ K} \), but the distribution of $1/T_1$ is always minimal and roughly symmetrical at all frequencies in the paramagnetic state. Unlike Zn$_{0.95}$, there is no hint of a distinct split-off peak above \( T_N \). The drastic change of $C(f, 1/T_1)$ at 4.2 K is due to antiferromagnetic long-range order.

Fig. 10 Volume fraction of paramagnetic and spin-singlet sites. \( 1 - F_{\text{para}} \) (\( \ast \), obtained from the results in Fig. 1d) represents the shrinking volume fraction of Zn$_{0.95}$ which is not within the spin-polarized domain and hence could exhibit intrinsic kagome spin liquid behavior without the perturbation caused by interlayer Cu$^{2+}$ defects occupying the Zn$^{2+}$ sites. Notice that only \( \sim 40\% \) of such a volume remains at 2 K in Zn$_{0.95}$. Also shown (\( \circ \)) is the upper bound of the spin-singlet fraction \( F_{\text{singlet}} \) of Cu sites, estimated from the observable $^{63}$Cu NQR signals at the fixed pulse separation time \( \tau = 6 \mu \text{s} \)\textsuperscript{21}. (The lower error bars below 6 K represent the lower bound of \( F_{\text{singlet}} \) estimated based on the assumption that the $^{63}$Cu signal loss affects only the paramagnetic component. All other error bars correspond to the absolute maxima or minima of \( F_{\text{singlet}} \).) Blue shading schematically shows the temperature range where the freezing of the structural distortion sets in (\( \sim 160 \text{ K} \)) and completes (\( \sim 50 \text{ K} \)).

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Turning our attention to the $1/T_1$ results in Fig. 8, $1/T_1^{\text{para}} \approx 100$ s$^{-1}$ observed for the paramagnetic peak of Zn$_{0.95}$ is nearly temperature-independent, and comparable to the high-temperature asymptotic value of $1/T_1$ observed for Cu$_6$. In contrast, Cu$_6$ exhibits a continuous enhancement of $1/T_1$, with decreasing temperature due to the growth of short-range order toward the long-range antiferromagnetic order at $T_N = 15$ K. According to Eq.(1), the local dynamical spin susceptibility in the vicinity of the interlayer Cu$^{2+}$ defects of Zn$_{0.95}$, therefore, grows slowly as $\chi \sim 1/T$. This means that gapless low-energy spin excitations exist locally in the vicinity of interlayer Cu$^{2+}$ defects. We emphasize, however, that these gapless spin excitations in Zn$_{0.95}$ are driven by the presence of interlayer defects and their influence on local magnetic and structural environments of the kagome planes, and should not be confused with the intrinsic gapless spin excitations expected for certain theoretical models of pristine kagome spin liquids.

In this context, it is worth recalling that some gapless spin liquid models predict a power law behavior in the temperature dependence of $1/T_1$. The recent $^{17}$O $1/T_1$ results as well as our initial $^{63}$Cu $1/T_1$ results for herbertsmithite, both deduced from the empirical analysis of $M(t)$ due to extremely large distributions of $1/T_1$, appeared to confirm such expectations of a power law behavior. However, our recent ILT analysis of $1/T_1$ observed here at paramagnetic $^{19}$F sites. This suggests that the paramagnetic $^{63}$Cu sites observed for both Zn$_{0.95}$ and herbertsmithite may be also located in the same spin-polarized domains observed here.

The absence of the signature of critical slowing down or spin freezing at 15 K for $1/T_1^{\text{para}}$ implies that the dimensions of the spin-polarized domain remain finite. Assuming that these domains are centered around 5% interlayer defect spins, $F_{\text{para}} \sim 60$% at 2 K implies that the domains grow in space but span only a few triangles from defects, as schematically shown in Fig. 1c. The significant fraction $F_{\text{para}} \sim 60$% at 2 K with strongly enhanced $1/T_1^{\text{para}}$ also implies that, as far as the low-energy spin excitations probed by NMR are concerned, one can expect to find the intrinsic kagome spin liquid behavior associated with spin-singlet formation only in $1-F_{\text{para}} \sim 40$% or less of the sample volume. In Fig. 10, we show the temperature dependence of $1-F_{\text{para}}$ together with the upper bound of the spin-singlet fraction $F_{\text{singlet}}$ as determined by $^{63}$Cu NQR measurements. Indeed the upper bound $F_{\text{singlet}}$ in Zn$_{0.95}$ is limited by the fraction of non-paramagnetic domains $1-F_{\text{para}}$ without spin polarization induced in the vicinity of interlayer Cu$^{2+}$ defects. We recall that $F_{\text{singlet}}$ is an upper bound and could easily be overestimated by a factor of $\sim 2$ due to difficulties in accounting for the transverse relaxation effects, but the magnitude of $F_{\text{singlet}}$ is still significant in comparison to $1-F_{\text{para}} \sim 40$%.

In conclusion, we have found two distinct magnetic signatures in the quantum spin liquid candidate Zn-barlowite, Zn$_{0.95}$. One signature arises from domains that are nearest to interlayer Cu$^{2+}$ impurities, and the local susceptibility and spin-lattice relaxation rate are similar to the paramagnetic state above $T_N$ of the antiferromagnetic parent compound barlowite, Cu$_6$. The other signature arises from regions far from the impurities and, therefore more closely reflects the intrinsic behavior of the kagome spins, where spin singlets gradually emerge with spatially inhomogeneous gaps. Finally, it may be also interesting to apply the one- and two-dimensional NMR techniques based on ILT to other kagome spin liquid and related materials, which are known to exhibit distributions in their NMR properties. Moreover, our approach might yield fresh insight into the distributions in local magnetic properties in unrelated disordered materials, such as diluted magnets and heavy Fermions.

METHODS

Samples

We synthesized the deuterated ($D = ^2$H) powder samples of ZnCu$_3$(OD)$_2$F$_2$ and Cu$_6$(OD)$_2$F$_2$ based on the procedures described in detail in ref. 23. We confirmed the sample quality based on powder X-ray diffraction measurements.

NMR

We conducted the spin echo $^{19}$F NMR measurements using standard pulsed NMR spectrometers. We conducted most of the $1/T_1$ measurements by applying saturation comb pulses prior to the spin echo sequence, and confirmed that the results are the same if we use an inversion pulse instead. The pulse separation time $\tau$ between the 90° and 180° pulses were 10 $\mu$s to ensure that we do not overlook any signals with faster transverse relaxation time. We carried out the inverse Laplace transform of the recovery curve $M(t)$ based on Tikhonov regularization using a fixed regularization parameter $\alpha = 1$ rather than optimizing at different temperatures and frequencies. This ensured that the effective resolution of ILT remains unchanged between different sets of measurements.

DATA AVAILABILITY

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

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REFERENCES

1. Balents, L. Spin liquids in frustrated magnets. Nature 464, 199–208 (2010).
2. Norman, M. R. Colloquium: Herbertsmithite and the search for the quantum spin liquid. Rev. Mod. Phys. 88, 041002 (2016).
3. Zhou, Y., Kanoda, K. & Ng, T.-K. Quantum spin liquid states. Rev. Mod. Phys. 89, 025003 (2017).
4. Broholm, C. et al. Quantum spin liquids. Science 367, eaay0668 (2020).
5. Imai, T. & Lee, Y. S. Do quantum spin liquids exist? Phys. Today 69, 30–36 (2016).
6. Shores, M. P., Nytko, E. A., Bartlett, B. M. & Nocera, D. G. A structurally perfect S = 1/2 kagomé antiferromagnet. J. Am. Chem. Soc. 127, 13462–13463 (2005).
7. Helton, J. S. et al. Spin dynamics of the spin-1/2 kagome lattice antiferromagnet ZnCu$_3$(OH)$_2$Cl$_2$. Phys. Rev. Lett. 98, 107204 (2007).
8. Mendels, P. et al. Quantum magnetism in the paratacamite family: towards an ideal kagome lattice. Phys. Rev. Lett. 98, 077204 (2007).
9. Rigol, M. & Singh, R. R. P. Magnetic susceptibility of the kagome antiferromagnet ZnCu$_3$(OH)$_2$Cl$_2$. Phys. Rev. Lett. 98, 207204 (2007).
10. Rigol, M. & Singh, R. R. P. Kagome lattice antiferromagnets and Dzyaloshinsky-Moriya interactions. Phys. Rev. B 76, 184403 (2007).
11. Imai, T., Nytko, E. A., Bartlett, B. M., Shores, M. P. & Nocera, D. G. $^{63}$Cu, $^{35}$Cl, and $^1$H NMR in the lattice in ZnCu$_3$(OD)$_2$Cl$_2$. Phys. Rev. Lett. 100, 087202 (2008).
12. Olarau, A. et al. $^{17}$O NMR study of the intrinsic magnetic susceptibility and spin dynamics of the quantum kagome antiferromagnet ZnCu$_3$(OH)$_2$Cl$_2$. Phys. Rev. Lett. 100, 087202 (2008).
13. Zorko, A. et al. Dzyaloshinsky-Moriya anisotropy in the spin-1/2 kagome compound ZnCu$_3$(OH)$_2$Cl$_2$. Phys. Rev. Lett. 101, 026405 (2008).
14. Freedman, D. E. et al. Site specific X-ray anomalous dispersion of the geometrically frustrated kagomé magnet, herbertsmithite, ZnCu$_3$(OH)$_2$Cl$_2$. J. Am. Chem. Soc. 132, 16185–16190 (2010).
15. Imai, T., Fu, M., Han, T. H. & Lee, Y. S. Local spin susceptibility of the S = 1/2 kagome lattice in ZnCu$_3$(OD)$_2$Cl$_2$. Phys. Rev. B 84, 020411 (2011).
16. Han, T.-H. et al. Fractionalized excitations in the spin-liquid state of a kagome-lattice antiferromagnet. Nature 492, 406–410 (2012).
17. Fu, M., Imai, T., Han, T. -H. & Lee, Y. S. Evidence for a gapped spin-liquid ground state in a kagome Heisenberg antiferromagnet. Science 350, 655 – 658 (2015).
18. Sherman, N. E., Imai, T. & Singh, R. R. P. Nuclear relaxation rates in the herbertsmithite kagome antiferromagnets ZnCu$_3$(OH)$_2$Cl$_2$. Phys. Rev. B 94, 140415 (2016).
Han, T.-H., Isaacs, E. D., Schlueter, J. A. & Singleton, J. Anisotropy: spin order and quantum spin liquids. Phys. Rev. B 118, 014406 (2022).

Takahashi, S. K. et al. Spin excitations of a proximate Kitaev quantum spin liquid. Phys. Rev. Lett. 127, 267202 (2021).

Wang, Y. et al. Heat transport in herbertsmithite: can a quantum spin liquid survive disorder? Phys. Rev. Lett. 127, 267202 (2021).

Feng, Z. et al. Gapped spin-1/2 spinon excitations in a new kagome quantum spin liquid compound Cu$_2$(OH)$_6$FBr. Phys. Rev. B 105, 041407 (2022).

Song, Y. Q. & Hurlimann, M. D. Solving Fredholm integrals of the first kind with tensor product structure in 2 and 2.5 dimensions. IEEE Trans. Sig. Process. 50, 1017–1026 (2002).

Kawamura, H. & Uematsu, K. Nature of the randomness-induced quantum spin liquids in two dimensions. J. Phys. Condens. Matter 31, 504003 (2019).

Singh, P. et al. Freezing of the lattice in the kagome lattice Heisenberg antiferromagnet Zn-barlowite and herbertsmithite. Nat. Phys. 17, 1109–1113 (2021).

Kumar, H. et al. Universal scaling of the specific heat in $S=1/2$ quantum kagome antiferromagnet herbertsmithite. Phys. Rev. B 106, 174406 (2022).

Kawamura, H. & Watanabe, K. Static and dynamical spin correlations of the S = 1/2 kagome antiferromagnets, Zn$_2$Cu$_3$O$_4$F$_2$Br. npj Quantum Mater. 5, 74 (2020).

Wei, Y. et al. Magnetic phase diagram of Cu$_3$Zn$_2$O$_4$F$_2$Br studied by neutron-diffraction and μSR techniques. Chin. Phys. Lett. 37, 107503 (2020).

Fu, Y. et al. Dynamic fingerprint of fractionalized excitations in single-crystalline Cu$_2$Zn(OH)$_6$FBr. Nat. Commun. 12, 3048 (2021).

Wang, L. et al. Universal scaling of the specific heat in $S=1/2$ quantum kagome antiferromagnet herbertsmithite. Phys. Rev. B 106, 174406 (2022).

Shimokawa, T., Watanabe, K. & Kawamura, H. Static and dynamical spin correlations of the S = 1/2 random-bond antiferromagnetic Heisenberg model on the triangular and kagome lattices. Phys. Rev. B 92, 134407 (2015).

Kimchi, I., Shekhtman, J. P., McQueen, T. M. & Lee, P. Scaling and data collapse from local moments in frustrated disordered quantum spin systems. Nat. Commun. 9, 4367 (2018).

Tustain, K. et al. From magnetic order to quantum disorder: a signature of the frustrated quantum antiferromagnet barlowite, Cu$_4$(OH)$_6$FBr. Phys. Rev. Lett. 127, 267202 (2021).

Smaha, R. W. et al. Materializing rival ground states in the barlowite family of kagome magnets: quantum spin liquids, spin ordered, and valence bond crystal states. npj Quantum Mater. 5, 23 (2020).

Smaha, R. W. et al. Site-specific structure at multiple length scales in kagome quantum spin liquid candidates. Phys. Rev. Mater. 4, 124406 (2020).

Tustain, K. & Smith, S. C. Anomalous isotope effects in the Zn-barlowite series of S = 1/2 kagome antiferromagnets, Zn$_2$Cu$_3$O$_4$F$_2$Br. npj Quantum Mater. 5, 74 (2020).

Watts and Cole-Davidson functions. J. Chem. Phys. 73, 3348–3357 (1980).

Itoh, M., Yasuoka, H., King, A. R. & Jaccarino, V. Decay of the nuclear magnetization in the randomly diluted antiferromagnets Fe$_2$Zn$_3$F$_7$ and Mn$_2$Zn$_3$F$_7$. J. Phys. Soc. Jpn. 55, 964–972 (1986).

Johnston, D. C. et al. Dynamics of magnetic defects in heavy fermion Li$_2$O$_3$ from stretched exponential $T_1$ Li NMR relaxation. Phys. Rev. Lett. 95, 176408 (2005).

Johnston, D. C. Stretched exponential relaxation arising from a continuous sum of exponential decays. Phys. Rev. B 74, 184430 (2006).

Mitrovic, V. F. et al. Similar glassy features in the $^{139}$La NMR response of pure and disorder induced Li$_2$Ba$_2$Zn$_4$Cu$_6$O$_{16}$. Phys. Rev. B 78, 014504 (2008).

Sun, B. & Dunn, K. Two-dimensional nuclear magnetic resonance petrophysics. Magn. Reson. Imaging 23, 259–262 (2005).

Liao, H. J. & Lai, G. Gapless spin-liquid ground state in the S = 1/2 kagome antiferromagnet. Phys. Rev. Lett. 118, 137202 (2017).

Kermarrec, E. et al. Spin dynamics and disorder effects in the S = 1/2 kagome Heisenberg spin-liquid phase of kagome. Phys. Rev. B 90, 205103 (2014).

Klanjesk, M. et al. A high-temperature quantum spin liquid with polaron spins. Nat. Phys. 13, 1130–1134 (2017).

Lu, F. et al. The observation of quantum fluctuations in a kagome Heisenberg antiferromagnet. Commun. Phys. 5, 272 (2022).

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AUTHOR CONTRIBUTIONS

T.I. and J.Y. planned the project. R.W.S., J. Wen, and Y.S.L. grew and characterized the samples. W.Y., J. Wang, P.M.S., and T.I. carried out NMR measurements and analyzed the data. T.I. and J. Wang wrote the manuscript with input from all authors.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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