^{63}Cu, ^{35}Cl, and ^{1}H NMR in the $S = \frac{1}{2}$ Kagome Lattice $ZnCu_3(OH)_6Cl_2$

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$ZnCu_3(OH)_6Cl_2$ ($S = \frac{1}{2}$) is a promising new candidate for an ideal Kagome Heisenberg antiferromagnet, because there is no magnetic phase transition down to ~50 mK. We investigated its local magnetic and lattice environments with NMR techniques. We demonstrate that the intrinsic local spin susceptibility *decreases* toward $T = 0$, but that slow freezing of the lattice near ~50 K, presumably associated with OH bonds, contributes to a large increase of local spin susceptibility and its distribution. Spin dynamics near $T = 0$ obey a power-law behavior in high magnetic fields.

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A major challenge in condensed matter physics today is identifying a model material for investigating *spin liquid* [1,2]. Searching for exotic electronic states without magnetic long range order, such as Kagome Heisenberg antiferromagnets, constitutes a common thread in a wide range of research fields, from high temperature superconductivity to low dimensional quantum magnetism. Over the last decade, many candidate materials have been investigated as model systems for a Kagome lattice [3–6]. However, they mostly exhibit a magnetically ordered or spin-glass-like state at low temperatures. A recent breakthrough in the hunt for a spin liquid state [2] is the successful synthesis [7] and characterization [8] of $ZnCu_3(OH)_6Cl_2$ (herbertsmithite), a chemically pure spin $S = \frac{1}{2}$ Kagome lattice. As shown in Fig. 1, three Cu^{2+} ions form a triangle, and a network of corner-shared triangles form a Kagome lattice. The $S = \frac{1}{2}$ spins on Cu sites are mutually frustrated by antiferromagnetic superexchange interaction $J \sim 170$ K [8,9], hence the possibility of a spin liquid ground state.

Recent measurements of $ZnCu_3(OH)_6Cl_2$ with bulk magnetic susceptibility, χ_{bulk} [8], specific heat [8], neutron scattering on powders [8], μSR [10,11], and ^{35}Cl NMR [10] have established that $ZnCu_3(OH)_6Cl_2$ remains paramagnetic down to at least ~50 mK with no evidence of magnetic long range order. These findings indeed point towards the possible realization of a frustrated spin liquid state with the Kagome symmetry. However, very little is known beyond the paramagnetic nature of the ground state. For example, the bulk-averaged susceptibility, χ_{bulk}, reveals a mysterious sharp *increase* below ~50 K [8]. This clearly contradicts the predictions of various theoretical calculations: series expansions predict a *decrease* of χ_{bulk} below $T \sim J/6$ with a gap [12,13], while the recent Dirac Fermion model predicts linear behavior in T towards $T = 0$ [14]. Does this apparent contradiction mean that $ZnCu_3(OH)_6Cl_2$ is not a good Kagome model system after all, or that extrinsic effects other than Kagome Heisenberg interaction, such as mixing of Zn ($S = 0$) into Cu ($S = \frac{1}{2}$) sites [15,16] and Dzyaloshinsky-Moriya (DM) interactions [9,17], simply mask the intrinsic Kagome behavior below ~50 K? What about spin dynamics? Do spin fluctuations slow down toward a critical point, or are they gapped [12–14]?

In this Letter, we report a ^{63}Cu, ^{35}Cl, and ^{1}H NMR investigation of $ZnCu_3(OH)_6Cl_2$ for a broad range of magnetic fields and frequencies. Taking full advantage of the local nature of NMR techniques, we uncover hitherto unknown properties of $ZnCu_3(OH)_6Cl_2$. First, from the observation of the broadening of ^{35}Cl NMR line shapes, we will demonstrate that local spin susceptibility, χ_{loc}, has a large distribution throughout the sample. Moreover, the smallest components of χ_{loc} actually *saturate* and even *decrease* with T below $T \sim 0.2J$, even though the bulk averaged χ_{bulk} increases as $\sim 1/T$. The observed decrease of χ_{loc} is precisely what the intrinsic spin susceptibility of a Kagome Heisenberg antiferromagnet is expected to show. Second, from the comparison of ^{1}H and ^{35}Cl nuclear spin-lattice relaxation rates, $^{1,35}(1/T_1)$, we present unambiguous evidence for slow freezing of the lattice near ~50 K, most likely due to orientational disorder of OH bonds. We suggest that this subtle freezing of lattice distortion enhances the DM interactions, and is key to understanding the aforementioned upturn of bulk-averaged spin susceptibility, χ_{bulk}, below ~50 K that masks the intrinsic Kagome behavior of χ_{loc}. Third, we demonstrate from the measure-

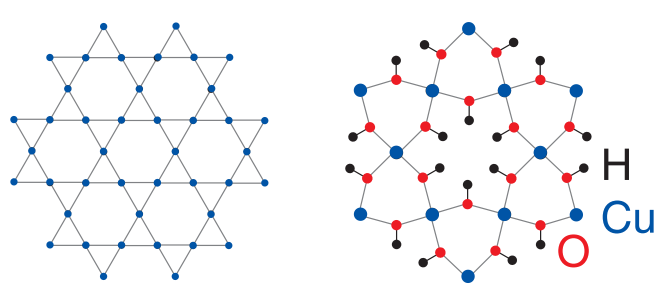

FIG. 1 (color online). Left: A Kagome lattice. Right: Cu^{2+} Kagome layer in $ZnCu_3(OH)_6Cl_2$. Cl^- site is above or below the middle of the Cu^{2+} triangles.

ments of the ^{63}Cu nuclear spin-lattice relaxation rate, $^{63}(1/T_1)$, that in the presence of a high magnetic field the low frequency Cu spin fluctuations *grow* without a gap below ~30 K satisfying a simple power law.

In Fig. 2, we show representative ^{35}Cl NMR line shapes. For these measurements, we cured a powder sample in glue in a magnetic field of 9 T. From powder x-ray diffraction measurements, we confirmed that approximately 20% of the powder is uniaxially aligned along the c axis. In fact, we observe a sharp c-axis central peak near 35.02 MHz (marked as $B//c$ in Fig. 2) arising from particles oriented along the c-axis. The "double horns" marked as #1 and #2 are split by the nuclear quadrupole interaction, and arise from the randomly oriented portion of the powder (i.e., 80% of the sample) [10]. Notice that the whole ^{35}Cl NMR line shape begins to tail-off toward lower frequencies below ~50 K. The resonance frequency of the sharp c-axis central peak and its distribution depends on the NMR Knight shift, ^{35}K, induced by $\chi_{\rm loc}$. Hence the observed line broadening implies that $\chi_{\rm loc}$ varies depending on the location within the sample below ~50 K.

In Fig. 3, we summarize the ^{35}Cl NMR Knight shifts ^{35}K and $^{35}K_{1/2}$ deduced from the line shapes, together with $\chi_{\rm bulk}$ as observed by SQUID. ^{35}K corresponds to the central peak above ~45 K as determined by FFT techniques. Below ~45 K, where the central peak is smeared out by line broadening, we determined ^{35}K as the higher frequency edge of the central peak from point-by-point measurements; i.e., ^{35}K represents the smallest component of the distributed $\chi_{\rm loc}$. $^{35}K_{1/2}$ corresponds to the half-intensity position of the central peak on the lower frequency side of the spectrum. Quite generally, $^{35}K = A_{\rm hf}\chi_{\rm local} + {}^{35}K_{\rm chem}$, where $A_{\rm hf}$ is the magnetic hyperfine interaction between ^{35}Cl nuclear spin and nearby Cu electron spins, and $^{35}K_{\rm chem}$ is a very small, temperature independent chemical shift. In the present case, from the comparison with $\chi_{\rm bulk}$, we can estimate $A_{\rm hf} \sim -3.7 \pm 0.7$ kOe$/\mu_B$. The negative sign of $A_{\rm hf}$ makes the overall sign of ^{35}K negative. Accordingly, we have inverted the vertical scale of Fig. 3.

We wish to comment on two important aspects of Fig. 3. First, ^{35}K follows Curie-Weiss behavior all the way from 295 K down to ~25 K. This clearly differs from $\chi_{\rm bulk}$ which begins to deviate from Curie-Weiss behavior below temperatures as high as ~150 K [8]. On the other hand, series-expansion calculations indicate that the Kagome lattice follows Curie-Weiss behavior down to $T \sim J/6 \sim$ 25 K [12]. Our Knight shift data demonstrate that $\chi_{\rm local}$ of some ideal segments of the Cu^{2+} Kagome lattice in this material indeed show such behavior. Theoretical models also predict that below $T \sim J/6 \sim 25$ K, $\chi_{\rm bulk}$ begins to decrease exponentially with a small gap [12], or linearly [14]. As shown in Fig. 2, the ^{35}Cl NMR line shape begins to transfer some spectral weight to higher frequencies below 25 K. Recalling that $A_{\rm hf}$ is negative, this is consistent with vanishing spin susceptibility, $\chi_{\rm local}$, near $T = 0$ for some parts of the Kagome lattice. After the initial submission of this Letter, Olariu *et al.* also observed a similar decrease of ^{17}O NMR Knight shift and arrived at the same conclusion [18].

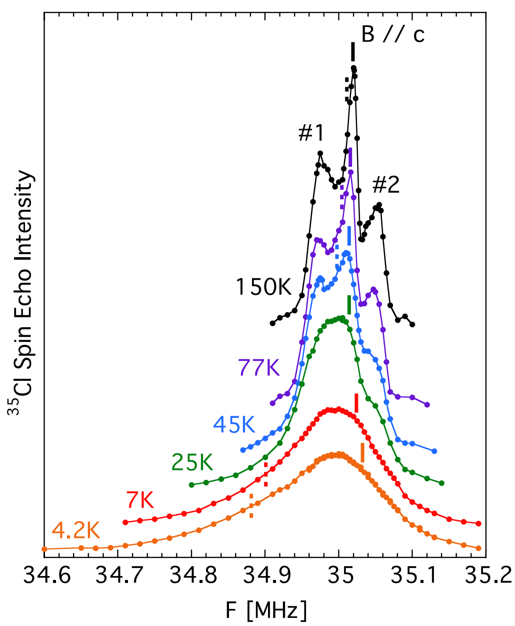

FIG. 2 (color online). ^{35}Cl NMR line shapes of the $I_z = +\frac{1}{2}$ to $-\frac{1}{2}$ central transition in 8.4 Tesla in a partially (~20%) uniaxially aligned powder sample. The sharp peak near 35.02 MHz marked as "$B//c$" originates from the particles whose c axis is aligned along the external magnetic field. Vertical lines specify the c-axis peak and edge corresponding to ^{35}K. Vertical dashed lines specify the frequency corresponding to $^{35}K_{1/2}$.

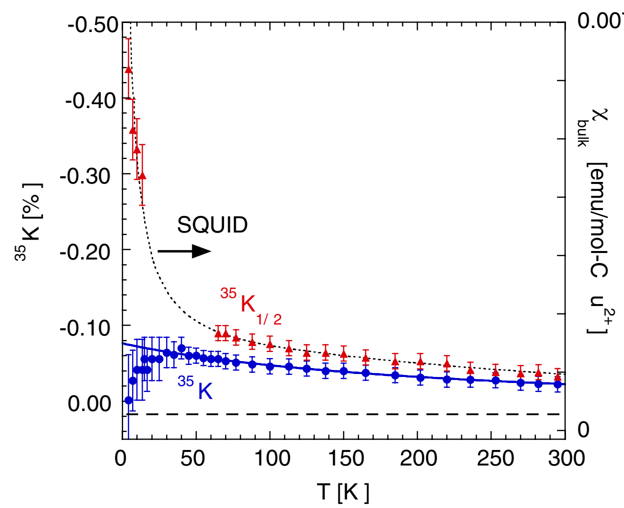

FIG. 3 (color online). ^{35}Cl NMR Knight shift (left scale). ^{35}K (blue circles). $^{35}K_{1/2}$ (red triangles). The blue solid line is a fit to Curie-Weiss behavior, $^{35}K = (22 \pm 7)/(T - \theta_{\rm CW}) + {}^{35}K_{\rm chem}$, where $\theta_{\rm CW} = -240 \pm 80$ K. The constant background $^{35}K_{\rm chem} = 0.018\%$ is shown by a dashed line. $\chi_{\rm bulk}$ measured by SQUID (dotted line) is also overlaid (right scale).

Another important aspect of Fig. 3 is that $^{35}K_{1/2}$ begins to deviate from the aforementioned Curie-Weiss fit in a manner similar to $\chi_{\rm bulk}$, as the ^{35}Cl NMR line gradually broadens to lower frequencies. It is important to realize that $^{35}(1/T_1)$ also begins to increase in the same temperature range below $\sim$150 K (see Fig. 4). Below 50 K, where $^{35}(1/T_1)$ shows a peak, the ^{35}Cl NMR line shows a dramatic broadening to lower frequencies. Figure 2 and 3 establish that $^{35}K_{1/2}$ follows the same trend as $\chi_{\rm bulk}$; i.e., some segments of the Kagome lattice have large and distributed local spin susceptibility $\chi_{\rm local}$, and their temperature dependence is different from the smaller $\chi_{\rm local}$ as represented by ^{35}K. $\chi_{\rm bulk}$ simply represents a bulk average of $\chi_{\rm local}$.

In passing, we recall that earlier μSR Knight shift $K_{\mu{\rm SR}}$ measurements by Ofer *et al.* [10] showed identical behavior between $K_{\mu{\rm SR}}$ and $\chi_{\rm bulk}$. They concluded that the upturn of $\chi_{\rm bulk}$ below 50 K is not caused by impurity spins but is a bulk phenomenon. Our new results in Fig. 3 do not contradict these μSR data. $K_{\mu{\rm SR}}$ was deduced by assuming a Gaussian distribution of $\chi_{\rm local}$; hence by default $K_{\mu{\rm SR}}$ represents the central value of the presumed Gaussian distribution. That explains why $K_{\mu{\rm SR}}$ shows behavior similar to $\chi_{\rm bulk}$ and $^{35}K_{1/2}$.

Next, we turn our attention to the dynamics of lattice and spin degrees of freedom. Figure 4 shows the temperature dependence of the ^{35}Cl nuclear spin-lattice relaxation rate, $^{35}(1/T_1)$, measured at the central peak frequency in various magnetic fields, B. We also plot $^{1}(1/T_1)$ for ^{1}H NMR in 0.9 T, and $^{63}(1/T_1)$ for ^{63}Cu NMR in 8 T. We have overlaid $^{1,63}(1/T_1)$ on $^{35}(1/T_1)$ measured in comparable magnetic fields by scaling the vertical axis.

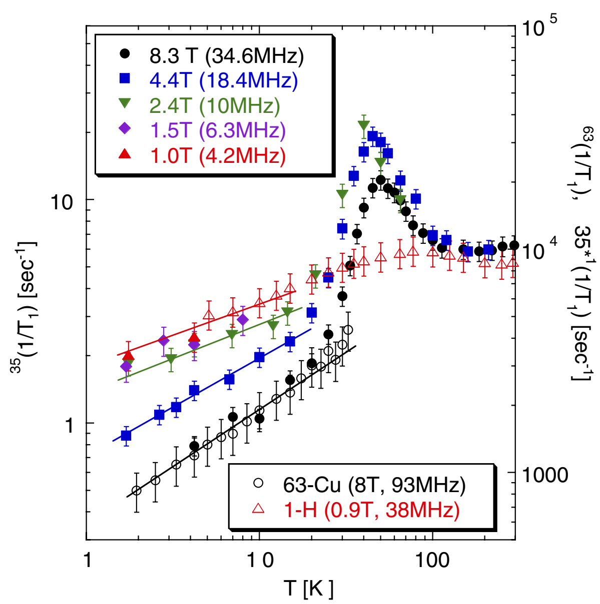

FIG. 4 (color online). Temperature dependence of ^{35}Cl NMR spin-lattice relaxation rate $^{35}(1/T_1)$ at various magnetic fields (filled symbols). Solid line represents a fit to a power law, $^{35}(1/T_1) = T^{\eta}$ with $\eta = 0.47$ (8.3 T), 0.44 (4.4 T), 0.2 (2.4 T and 1.0 T). ^{1}H relaxation rate in low field (0.9 T), $^{1}(1/T_1)$, and ^{63}Cu relaxation rate in high field (8 T), $^{63}(1/T_1)$, are also superposed on $^{35}(1/T_1)$ measured in comparable magnetic field.

We can draw a number of conclusions from Fig. 4. First, let us focus on T and B independent results of $^{35}(1/T_1)$ above $\sim$150 K. This high temperature regime is easily understandable within Moriya's theory for the exchange narrowing limit of Heisenberg antiferromagnets, where we should expect $^{35}(1/T_1)_{\rm exc} \sim A_{\rm hf}^2/J = {\rm const}$ for $T > J \sim 170$ [19]. If we assume $J \sim 170$ K and $A_{\rm hf} \sim -4$ kOe$/\mu_B$, we can estimate $^{35}(1/T_1)_{\rm exc} \sim 4$ sec^{-1}. This is in excellent agreement with our result.

Another important feature is that $^{35}(1/T_1)$ begins to increase below $\sim$150 K and peaks near $\sim$50 K. Since ^{35}Cl is a quadrupolar nucleus with nuclear spin $I = \frac{3}{2}$, the observed enhancement may be caused by slow fluctuations of the lattice via nuclear quadrupole interactions, as well as by Cu spin fluctuations. To discern the two possibilities, we show $^{1}(1/T_1)$ of ^{1}H measured at 0.9 T for comparison. The $^{1}(1/T_1)$ data nicely interpolate $^{35}(1/T_1)$ in the field-independent regime above $\sim$150 K and $^{35}(1/T_1)$ measured at a comparable magnetic field (1 T) at low-temperatures, without a peak near $\sim$50 K. Since ^{1}H has $I = \frac{1}{2}$, $^{1}(1/T_1)$ has no contributions from lattice fluctuations. Therefore we conclude that the peak of $^{35}(1/T_1)$ near $\sim$50 K arises from enhancement of lattice fluctuations at the NMR frequency. The peak of $^{35}(1/T_1)$ shifts to progressively lower temperatures as we lower the ^{35}Cl NMR frequency, from 50 K (34.6 MHz at 8.3 T), 46 K (18.4 MHz at 4.4 T) to 40 K (10 MHz at 2.4 T). This means that the typical frequency scale of lattice fluctuations is 35 MHz at 50 K, 18 MHz at 46 K, and 10 MHz at 40 K, and the Kagome lattice becomes static below 40 K. Given that no structural phase transition has been detected by x-ray and neutron scattering techniques, the observed freezing of the lattice near $\sim$50 K must be a very subtle effect. In fact, our careful measurements of the quadrupole split $\pm\frac{1}{2}$ to $\pm\frac{3}{2}$ satellite transitions of ^{35}Cl NMR did not detect any noticeable changes, either. All pieces put together, we suggest that the lightest elements in the lattice, i.e., OH bonds, must be freezing with random orientations, with only subtle effects on heavier atoms.

Regardless of the exact nature of the freezing of the lattice, our observation provides a major clue to understanding the mysterious behaviors of $\chi_{\rm bulk}$ and $\chi_{\rm local}$. Recent structural studies revealed that up to 6% of Cu sites may be occupied by Zn to create unpaired defect spins [15]. There is no doubt that such antisite disorder would enhance $\chi_{\rm bulk}$ and contribute to the large distribution of $\chi_{\rm local}$ at low temperatures. However, it is important to realize that $\chi_{\rm bulk}$ begins to deviate from high temperature Curie-Weiss behavior below $\sim$150 K [8], exactly where $^{35}(1/T_1)$ begins to grow due to slowing of lattice fluctuations toward $\sim$50 K. Furthermore, the crossover between the two different Curie-Weiss behaviors of $\chi_{\rm bulk}$ and $^{35}K_{1/2}$

takes place precisely when the lattice fluctuations die out below $\sim$50 K [8]. Evidently, the anomaly of the lattice correlates well with that of the spins, suggesting it must be playing a major role in the deviation of spin susceptibility from the theoretically expected behavior of ideal Kagome Heisenberg antiferromagnets. In fact, recent numerical simulations by Rigol and Singh showed that DM interactions can enhance spin susceptibility below $\sim$50 K [9,17]. Our experimental finding naturally fits with their theoretical picture: when OH bonds freeze with random orientation, the hexagonal symmetry of the Kagome lattice slightly breaks down locally; this would progressively enhance the DM interaction from $\sim$150 K to $\sim$50 K, hence leading to an enhancement of χ_{bulk} and $^{35}K_{1/2}$, as well as a large distribution of χ_{local}.

Finally, let us focus on the low temperature regime below 20 K, where only spin fluctuations contribute to $(1/T_1)$. $^{35}(1/T_1)$ at $\sim$4 K is independent of magnetic field from $B \sim 0.9$ T up to $B \sim 2$ T, but larger magnetic fields suppress $^{35}(1/T_1)$. This suggests that unpaired paramagnetic spins are fluctuating in low magnetic fields, but applied magnetic field decouples the weak coupling between them. The exact origin of these paramagnetic spins is not clear, but one obvious possibility is unpaired free spins induced in the near neighbor sites of Zn ($S = 0$) ions occupying the Cu sites, i.e., antisite disorder [15,16]. In fact, after the initial submission of the present work, Olariu *et al.* reported that approximately 30% of the integrated intensity of ^{17}O NMR signals is split off from the main line, which they attributed to the contribution of the 4 nearest neighbor O sites of Zn ions occupying the Cu sites [18]. Our observation of field dependence is also consistent with a recent report that the application of $B \sim 8$ T suppresses defect contributions to dc spin susceptibility in the low T regime [16].

All the $^{63,35,1}(1/T_1)$ data measured at various magnetic fields and frequencies decrease towards the zero temperature limit. That is, we observe no hint of critical slowing down of spin fluctuations towards $T \sim 0$; hence any magnetic critical point, if it exists, is still very far from our temperature region. This is in agreement with an earlier report based on a limited set of ^{35}Cl NMR data [10], but in remarkable contrast with earlier NMR works on frustrated spin systems with Kagome or triangular lattice geometry, where $(1/T_1)$ data always show evidence for a magnetic long range order or freezing [6]. At $B \sim 8$ T, both $^{35}(1/T_1)$ and $^{63}(1/T_1)$ decrease toward $T = 0$, obeying a simple power law, $^{63}(1/T_1) = T^{\eta}$ with $\eta \sim 0.5$. Since the slope of the log-log plot of $(1/T_1)$ increases somewhat at higher fields, $\eta \sim 0.5$ may be somewhat underestimated. We note that spin fluctuation susceptibility is proportional to $^{63}(1/T_1T) = T^{\eta-1}$; hence spin fluctuations *grow* toward $T = 0$. This is inconsistent with the exponential decrease expected for a gapped Kagome lattice in some theoretical scenarios. On the other hand, recent field theoretical calculations based on the Dirac Fermion model predicted a power law, $^{63}(1/T_1) = T^{\eta}$, with unknown critical exponent η [14]. We note that the issue of power-law behavior of spin dynamics is at the focus of the field theoretical approach toward spin liquid systems. It remains to be seen if the Dirac Fermion model would be consistent with $\eta \gtrsim 0.5$.

To summarize, we have presented a site-by-site picture of the new Kagome material $ZnCu_3(OH)_6Cl_2$ using NMR techniques. Our NMR data revealed that both local spin susceptibility and spin dynamics (in high magnetic fields) show aspects that are consistent with theoretical conjectures for ideal Kagome antiferromagnets, despite perturbations from lattice freezing and paramagnetic defects.

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