Spin Liquid Ground State in the Frustrated Kagome Antiferromagnet MgCu$_3$(OH)$_6$Cl$_2$

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We report $\mu$SR experiments on Mg$_x$Cu$_{4-x}$(OH)$_6$Cl$_2$ with $x \sim 1$, a new material isostructural to Herbertsmithite exhibiting regular kagome planes of spin $\frac{1}{2}$ ($\text{Cu}^{2+}$), and therefore a candidate for a spin liquid ground state. We evidence the absence of any magnetic ordering down to 20 mK ($\sim 4 \times \mu_0 J/10^4$). We investigate in detail the spin dynamics on well characterized samples in zero and applied longitudinal fields and propose a low $T$ defect based interpretation to explain the unconventional dynamics observed in the quantum spin liquid phase.

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Quantum magnetism in frustrated networks has been acknowledged for a long time as the ideal playground to stabilize new quantum phases. Since the proposal of an RVB state by P.W. Anderson,$^1$ advances in theory has led to the emergence of a rich variety of spin liquid phases, including algebraic and gapped spin liquids.$^2,3$ On the experimental side, Herbertsmithite, ZnCu$_3$(OH)$_6$Cl$_2$, is among the best materials to explore such quantum states, as it combines the highly frustrated two-dimensional kagome lattice and quantum spins $\frac{1}{2}$ of Cu$^{2+}$. No magnetic freezing has been detected down to 50 mK $\sim J/4000$,$^2,4$ and spin-spin correlations are found to be short ranged and dynamical as expected for a liquid state.$^4$

Nevertheless, this material deviates from the “perfect” image since it has sizable level of Cu-Zn intersite mixing. The replacement of non-magnetic Zn$^{2+}$ ions at the interlayer position by magnetic Cu$^{2+}$ causes almost free spin $\frac{1}{2}$ defects that correspond to $5-10\%$ of the total Cu content, as determined from various techniques (see$^5$ for a review). The exact amount of the complementary defect, where a Zn$^{2+}$ non-magnetic impurity induces a spin vacancy in the kagome plane, remains difficult to evaluate quantitatively, due to similar x-ray scattering factors of Cu and Zn and the absence of a straightforward magnetic response. As a result, it varies with samples and experimental techniques from a quasi absence of $1\%$ from anomalous x-ray scattering to a non negligible $5\%$ value from NMR.$^6$

Very recently, the new series, the Mg-paratracamites Mg$_x$Cu$_{4-x}$(OH)$_6$Cl$_2$ isostructural to Zn-paratracamite, has been successfully synthesized. The similar ionic radii of Mg$^{2+}$ and diamagnetic Zn$^{2+}$ ions leads to a minimal difference of the crystal structure and hence exchange pathway, resulting in comparable coupling $J \sim 190$ K,$^6$ evaluated by high-temperature series expansion$^7$. If Cu/Mg mixing is still expected, the difference in their x-ray scattering factors now enables reliable x-ray structure analysis. Authors of Ref.$^7$ succeeded to synthesize materials for $x < 0.75$ where they found a ferromagnetic component in macroscopic susceptibility under $T_C = 4$ K, attributed to a 3D coupling via interlayer Cu$^{2+}$, similar to the Zn case. A minimal Mg$^{2+}$ substitution within the kagome planes ($\leq 3\%$) was determined through x-ray diffraction. A different synthesis was recently reported which led to samples with $0.93 \leq x \leq 0.98$.$^8$, these correspond to the Herbertsmithite analogues and correspondingly to model quantum kagome antiferromagnets. A small ferromagnetic fraction at $T_C \simeq 4 - 5$ K was tentatively ascribed to an impurity phase.

In this Letter, we first report the $\mu$SR local probe investigation down to 20 mK in the Mg$_x$Cu$_{4-x}$(OH)$_6$Cl$_2$ Herbertsmithites with $x \sim 1$ which evidences a spin liquid ground state with no sign of spin freezing. We also study the sub-Kelvin spin dynamics of both atacamites (Mg, Zn) where an $x$-dependent plateau of $1/T_1$ appears with unconventional dynamics. We argue that this relaxation is driven by interlayer Cu$^{2+}$ ions and discuss its origin.

The experiments were carried out on Mg atacamite powder samples close to the idealized Herbertsmithite structure, $x = 0.84, 0.92$, and 1.21, synthesized following a hydrothermal route described elsewhere$^9$, as well as on the $x = 1$ Zn atacamite sample from$^7$. The ratio of Cu/Mg and Cu/Zn was determined by ICP-AES (Table I). Refinements of x-ray diffraction data for the Mg compounds give separately the Cu ($n$) and Mg ($p$) occupancies of the interlayer and the kagome sites corresponding to the formula $\text{(Cu}_{1-p}M_p)\text{M}_{n}\text{Cu}_{3-n}$(OH)$_6$Cl$_2$ (M=Mg, Zn) and thus an independent determination of $x = 3p - n + 1$ (Table II). $\mu$SR experiments were performed at the ISIS and PSI facilities in zero and longitudinal applied field configurations down to 20 mK. We also measured DC magnetic susceptibility on a standard Quantum Design SQUID magnetometer in the 1.8 – 300 K $T$-range.
TABLE I: Chemical composition determined through ICP, x-ray refinements and saturated magnetization for (Cu1−pMg)p(M1−xCu)x(OH)yClz where M=Mg, Zn. Each site occupancy is constrained to unity.

| Element | Mg | Mg | Zn | Mg |
|---------|----|----|----|----|
| ICP analysis | x = 0.84 | x = 0.92 | x = 1 | x = 1.25 |
| x-ray analysis | x = 0.83 | x = 0.91 | - | x = 1.21 |
| p | 0.04 | 0.06 | - | 0.12 |
| n | 0.29 | 0.27 | - | 0.15 |

Magnetization

| n | 0.266(4) | 0.217(5) | 0.186(4) |

FIG. 1: Interlayer Cu$^{2+}$ contribution $M_{\text{def}}$ extracted from magnetization measurements and normalized by $M_{\text{sat}} = N_A g \mu_B S = 6143$ emu. The saturation value gives n, the amount of interlayer Cu$^{2+}$ per formula unit. The lines reproduce a Brillouin fit with an interacting scale of $\theta = 0.8$ K. Inset: Normalized magnetization at $T = 1.75$ K up to 14 T. Lines are fits for the linear component.

and magnetization at 1.75 K up to 14 T with a Cryogenic Vibrating Sample Magnetometer.

In order to reveal the magnetic response of the interplane defects we measured the magnetization of the Mg ($x = 0.92$ and $x = 1.21$) and Zn ($x = 1$) samples at low $T = 1.75$ K and up to 14 T. Following the analysis in Ref. [14], we divide the total magnetization into two contributions, a Brillouin-like component arising from the quasi-free interlayer Cu$^{2+}$ and a linear term coming from the strongly coupled Cu$^{2+}$ of the kagome planes (Fig.1). By subtraction of the latter one, we have access to the saturated magnetization $M_{\text{def}} = nN_A g \mu_B S$ of the interlayer Cu$^{2+}$. Taking $g = 2.2$ from Ref. [12], we determine $n$ which agrees reasonably well with the refinements for the Mg samples and provides a value for the Zn sample otherwise inaccessible by structural studies (Table I). These results confirm quantitatively the existence and the quasi-free behavior of the interplane defects in the Mg and Zn Herbertsmithites.

We now turn to the local $\mu$SR investigations. $\mu$SR is very sensitive to any small magnetic field (down to $\sim 0.1$ G) and is therefore a powerful tool to detect any frozen moment. The muon is implanted inside the volume and, as a positive charged particle, will stop in the vicinity of a negative environment, i.e. either near OH$^-$ (80 %) or Cl$^-$ (20 %). The polarizations from 0 (ZF) to 2500 G longitudinal applied field (LF) are reported in Fig.2. Our experiments demonstrate a similar magnetic behavior of the Mg and Zn compounds, as expected due to their crystallographic similarities. Following the former work of Ref. [3], the ZF polarization is fitted on a high statistics run at 50 mK by $P(t) = P_{\text{nucl}}(t)e^{-(\lambda)t}$. $P_{\text{nucl}}(t)$ depends only on static fields from surrounding nuclei and $\lambda$ stands for a small dynamical relaxation. The well defined oscillation of $P_{\text{nucl}}(t)$ is due to the formation of a $\mu$-O-H complex [16], and from the field experienced by the muon, $H_{\mu-OH} = 7.8$ G, one estimates a distance of 1.5 Å to hydrogen [17]. The ZF polarization is found identical in the extended $T$-range 0.05 – 20 K, except for a slight variation of $\lambda$. Therefore, we conclude that there is no magnetic ordering of the electronic spins down to $T = 20$ mK ($\sim J/10^4$) for $x = 1$, as in the Zn counterpart.

The spin dynamics are revealed by experiments under longitudinal fields. From 10 to 100 G ($> 10H_{\mu-OH}$), the static relaxation of nuclear origin is progressively decoupled as expected (Fig.2). Above 100 G, $P_{\text{nucl}}(t) = 1$ and a single stretched exponential fit of $P(t)$ yields the relaxation rate $\lambda = 1/T_1^\mu$ of electronic origin. $\lambda = 1/T_1^\mu$ is linked to the spin-spin time correlation function by $1/T_1^\mu \sim \int_0^{\infty} \langle S(t)S(0) \rangle \cos(\gamma_H L E \mu) dt$, $H_{LE}$ is the longitudinal applied magnetic field. Starting from a high-$T$ value $\sim 0.005 \mu s^{-1}$, $\lambda$ increases upon cooling below 1 K and saturates at lower temperature at a value which differs from sample to sample (Fig.3). This increase of $\lambda$ indicates a dynamical slowing down. We notice that the shape of the relaxation at low $T$ slightly changes between Mg ($\beta = 0.9$) and Zn compounds ($\beta = 1.1$). The origin could be related to a presently unclear difference between the spin-spin time correlation in the two materials.

We now argue that the muon is dominantly coupled to the interlayer Cu$^{2+}$ moments from the following experimental observations: (i) The low-$T$ muon shift $K^\mu$ was shown to track the intersite defect susceptibility [18]. This is in fair agreement with recent $^3$D NMR study [15] but contrasts with NMR results on $^{17}$O which is strongly coupled to the planes. (ii) From Fig.3 (b) and the inspection of Table I $\lambda$ is found to increase linearly with $n$, the concentration of intersite defects, but is anticorrelated with the level of in plane defects, $p$. Since the distance between Zn sites is $d = 6.12$ Å, the linearity in $n$ can be easily explained by an “all or nothing” model: some muons ($n$) sit next to an interlayer Cu$^{2+}$ defect with a relaxation rate $\lambda_1$ whereas the others ($1-n$) stay...
FIG. 2: Upper panel: Polarization in zero field (ZF, black circles) and under longitudinal applied fields (LF) from 10 to 2500 G. The black line is a fit (see text). Bottom panel: The relaxation is faster at low temperatures and when \( n \) increases. Lines are stretched exponential fits.

far from a defect with a relaxation rate \( \lambda_2 \rightarrow 0 \). Under the valid condition \( \lambda_{1,2} t \ll 1 \), we get a total polarization \( P(t) = n \exp(-\lambda_1 t) + (1-n) \exp(-\lambda_2 t) \sim \exp(-n \lambda_1 t) \), which explains the linear \( n \)-dependence of \( \lambda \). (iii) From the scaling of \( K^{\mu} \) versus \( \lambda^{\text{bulk}} \), one can extract the coupling constant \( A_{\mu} = 0.05 T/\mu_B \), consistent with a dipolar interaction. From \(^{17}\)O NMR \( T_1^{17} \), the contribution of the kagome planes \( \text{Cu}^{2+} \) to the muon relaxation can then be estimated using: \( 1/T_1^{17} = 1/T_1^{17} \times (\gamma_\mu A_\mu/\gamma_n A_n^{17} A_{n}^{17})^{2} \sim 3 \cdot 10^{-5} \mu s^{-1} \). This leads at high-\( T \) to a value 150 times smaller than the measured one, which calls for a different source of relaxation. (iv) Finally in the high-\( T \) Moriya paramagnetic limit \( 21 \), \( 1/T_1^{17} \) is given by \( 1/T_1^{17} = 2\gamma_\mu^2 H_{\text{int}}^2 n/\nu \) with \( \nu = \sqrt{4J^2 z S(S+1)}/3\pi \hbar^2 \) and \( H_\mu = gA_\mu \sqrt{S(S+1)/3} = 880 \) G. From the high-\( T \) constant value \( 1/T_1^{17} \sim 5 \cdot 10^{-3} \mu s^{-1} \), an average value \( n \sim 0.22 \) and a number of nearest neighbors \( z = 6 \), one obtains the coupling between an interlayer \( \text{Cu}^{2+} \) and a kagome \( \text{Cu}^{2+} \) \( J^\prime \sim 3 \) K, in rough agreement with the temperature of the magnetic ordering \( T_C = 6 \) K in the clinoatacamite \( \text{Cu}_2(\text{OH})_3\text{Cl} \) parent compound \( 21, 22 \).

In this context, the slowing down below 1 K of intersite defects can be attributed either to the strengthening of the correlations with the two nearby kagome planes or to a coupling between two intersite defects mediated by the kagome plane to which they are coupled. The temperature scale of 1 K is in line with subtle effects detected in magnetization measurements \( 14 \).

We now discuss the \( T \rightarrow 0 \) value of the relaxation rate. In order to reveal the dynamics of the correlated regime under 1 K, we probe the excitation spectrum \( S(\omega) \) in the low energy range by applying a longitudinal field \( H_{\text{LF}} = \omega/\gamma_\mu \), \( H_{\text{LF}} < 0.25 \) T. Two scenarios can be considered based on different correlation functions \( S(t) = \langle S(t)S(0) \rangle \) for the interplane spins. 

Exponential correlation function \( S(t) = e^{-\nu t} \) associated with field induced polarization of the interlayer defects. Such correlation leads to the usual lorentzian spectral density \( S(\omega) \) and

\[
\lambda_1 = \frac{2\gamma_\mu^2 H_{\text{int}}^2 \nu}{\nu^2 + \gamma_\mu^2 H_{\text{LF}}^2}
\]

where \( H_{\text{LF}} \) is the fluctuating component of the field at the muon site perpendicular to its initial polarization, \( \nu \) is the fluctuation frequency, and \( \gamma_\mu = 851.6 \) Mrad/s/T.
is the muon gyromagnetic factor. However, not only the expected $H_{LF}^2$ dependence of $\lambda$ is not convincing (Fig. 4), but a forced fit will result in an unphysical $H_{\text{fluct}} \sim 20$ G, while the lowest possible dipolar field value is 200 G which corresponds to a maximal distance of the $\mu^+$ to interiste Cu$^{2+}$. We therefore propose that the fluctuating field is reduced when the $S = \frac{1}{2}$ interlayer starts to be polarized in the external applied field $H_{LF}$. In a mean field Brillouin approach, the fluctuating moment is

$$m^{\text{fluct}} = \mu_B (1 - \tanh(\mu_B S H_{LF}/k_B (T + \theta)))$$

where $\theta$ is introduced to account for interactions. The reduced value of $H_{\text{fluct}} = m^{\text{fluct}} \mu_B / \mu_B$ can be injected in Eq. (11) and leads to only two shared fit parameters to account for the $T_1^\rho(H_{LF})$ variation for all $x$. Although the obtained fits are not perfect, this approach yields reasonable physical parameters $\nu = 100 \pm 20$ GHz and $\theta = 0.7 \pm 0.2$ K that are consistent with both magnetization measurements and the 1 K $T$-scale where the slowing down occurs.

**Power law correlation function** $S(t) = (1/t)^{1-\alpha}$

The corresponding spectral density $\tilde{S}(\omega)$ yields a power law relation $T_1^\rho \propto \omega^\alpha$. This more exotic approach is at play ($\alpha = 0.35$) in the spin liquid case of the $S = \frac{1}{2}$ antiferromagnetic chain $^{[23]}$, where a spinon continuum of excitations is well established. Such a spectral density ($\alpha = 1$) was also invoked for the spin liquid pyrochlore TbTi$_2$O$_7$ $^{[24, 25]}$. A perfect fit of our data can be found with $1/\lambda_1 = T_1^\rho(x) + A \cdot \omega^{1.63}$, which would point to an exotic relaxation channel for the intersite defect. Using the scaling of $\chi''T_1^\rho \sim (T/\omega)^\alpha \tanh(\omega/\beta T)$ from neutron experiments $^{[26]}$, this leads to $1/T_1 \sim k_B T \chi''/\omega \sim \omega^{-\alpha}$ ($\alpha = 0.66$ $^{[26]}$) by means of the fluctuation dissipation theorem, in agreement with the value reported here. This points to a common origin and following $^{[27]}$ one could invoke a distribution of couplings between intersite defects as a source of the power law. Another possibility could be that the kagome planes dynamics drives that of the intersite defects. The inconsistency between the $T$-plateau of the relaxation rate measured at low fields and the $T^{-0.7}$ dependence of $T_1^\rho$ at 7 T $^{[10]}$ would then require that the field impacts on the kagome plane dynamics.

In conclusion, the spin liquid behavior of the new kagome antiferromagnet Mg$_{x}$Cu$_{4-x}$(OH)$_6$Cl$_2$ for $x > 0.84$ is clearly established by our $\mu$SR experiments. Our data show that the measured interlayer site dynamics differs from those of the kagome plane one at 7 T. This calls for a careful inspection of probes which integrate both responses and/or the field impact on relaxation. Whether the exotic character of the $\mu^+$ relaxation might also relate to the spin liquid behavior of the kagome lattice is still a matter of speculation. The ability to refine the structure for Mg-Herbertsmithite in a reliable manner opens the possibility to control the level of defects and to discriminate between the various sources of dynamics at low $T$. Our results open routes for future investigations of the kagome spin liquid ground state in well controlled mate-

![FIG. 4: The $T_1$ dependence with external field $H_{LF}$ underlines the unconventional spin dynamics at $T = 50$ mK. The lines refer to different models (see text).](image-url)
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