Spin dynamics and magnetic structure of frustrated three-dimensional antiferromagnet Li$_2$CuW$_2$O$_8$ probed by $^7$Li NMR

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The static and dynamic properties of Cu$^{2+}$ spins (spin-1/2) in the frustrated three-dimensional antiferromagnet Li$_2$CuW$_2$O$_8$ were investigated by means of $^7$Li Nuclear Magnetic Resonance (NMR) experiments on the polycrystalline sample. The magnetic long-range ordering at $T_N \approx 3.9$ K was detected from the drastic line broadening and a peak in spin-lattice relaxation rate ($1/T_1$). The NMR spectrum above $T_N$ broadens systematically, and its full width at half maximum (FWHM) tracks the static spin susceptibility. From the analysis of FWHM vs. static susceptibility, the coupling between Li nuclei and Cu$^{2+}$ ions was found to be purely dipolar in nature. Magnitude of the maximum exchange coupling constant was calculated to be $J_{\text{max}}/k_B \approx 13$ K, which is in reasonable agreement with our leading exchange coupling ($J/k_B = 14$ K) along the chain direction estimated from the band structure calculations. NMR spectra below $T_N$ broaden abruptly and transforms into a double-horn pattern reflecting the commensurate nature of the spin structure in the ordered state. Below $T_N$, $1/T_1$ follows a $T^5$ behaviour, indicating that the relaxation is mainly governed by three-magnon process. The frustrating nature of the compound is also found from the persistence of magnetic correlations at high temperatures, well above $T_N$.

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I. INTRODUCTION

Geometrically frustrated spin-1/2 triangular systems have attracted considerable attention due to numerous quantum phenomena that they exhibit at low temperatures. The combination of geometric frustration, low spin value, and reduced dimensionality significantly enhances quantum fluctuations which can lead to the formation of exotic ground states. The most striking example is the formation of a quantum spin liquid (QSL), which is a strongly correlated disordered ground state. Anderson suggested that the spin-1/2 Heisenberg triangular antiferromagnets have a resonating-valence-bond (RVB) ground state, one kind of the QSL. Indeed, several triangular antiferromagnets, such as the spin-1 compound NiGa$_2$S$_4$ and spin-1/2 organic materials like $k$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and EtMe$_3$Sb[Pd(dmit)$_2$], do not show long-range magnetic order (LRO) and are even established as QSL candidates. On the other hand, the majority of triangular antiferromagnets entail subtle deviations from the ideal regime that may reduce the frustration and stabilize the LRO. In fact, even the idealized case of the quantum Heisenberg model on the triangular lattice features LRO with the 120$^\circ$ spin structure and thus lacks the spin-liquid phase. Most of the spin-$1/2$ triangular antiferromagnets are magnetically ordered at low temperatures. They may also show plateaux at 1/3 of the saturation magnetization, where the system evolves from a 120$^\circ$ magnetic ordering phase to an up – up – down (uud) phase in a finite field, as in spin-1/2 compounds Cs$_2$CuBr$_4$ and Ba$_3$CoSb$_2$O$_9$.

Li$_2$CuW$_2$O$_8$ crystallizes in a triclinic structure with space group $P\overline{1}$ (Ref. 12) and features a unique spin lattice, which is strongly frustrated along all three crystallographic directions. The interaction topology in the $ab$ plane resembles a triangular lattice, whereas interplane couplings are oblique and likewise frustrated. There is one Cu site, two equivalent W sites, and two equivalent Li sites in the unit cell. The Cu$_8$ octahedra that can also be viewed as CuO$_4$ planar units are connected through WO$_6$ octahedra. The Li atoms are located close to each of the Cu$^{2+}$ triangular layer. Figure 1 shows the triangular layer formed by Cu$^{2+}$ ions and the collinear arrangement of spins inferred from the neutron diffraction experiments. The Li atom is coupled to two neighbouring Cu$^{2+}$ spins (either up – up or down – down) of the same plane.

Recently, we reported magnetic susceptibility $\chi(T)$, heat capacity $C_p(T)$, and neutron diffraction on Li$_2$CuW$_2$O$_8$. Clear signatures of the magnetic three-dimensionality and strong frustration were inferred from these measurements and rationalized microscopically using band-structure calculations. $\chi(T)$ and $C_p(T)$ exhibit broad maxima at around 8.5 K and 6 K, respectively, associated with the short-range order and then a kink ($\chi$) or a $\lambda$-type anomaly ($C_p$) at $T_N \approx 3.9$ K associated with the magnetic long-range ordering (LRO). Neutron diffraction experiments reveal collinear magnetic order below 3.9 K with the propagation vector $(0,\frac{1}{2},0)$ and the ordered moment of 0.65(4) $\mu_B$, which is reminiscent of a 2D antiferromagnet even though Li$_2$CuW$_2$O$_8$ is clearly 3D. Remarkably, the collinear order is not anticipated on the classical level, where an incommensurate spiral structure would have lower energy. Therefore, a strong stabilization of the collinear order by quantum fluctuations has been envisaged.
Li$_2$CuW$_2$O$_8$ is isostructural to its Co and Ni analogues. Both Li$_2$NiW$_2$O$_8$ and Li$_2$CoW$_2$O$_8$ compounds undergo two successive magnetic transitions at low temperatures without having any short-range order above $T_N$.\cite{14,15} Many of the triangular-lattice compounds exhibit two phase transitions at low temperatures too.\cite{16} The presence of only one magnetic transition and the robust collinear order in Li$_2$CuW$_2$O$_8$ are clearly unusual and require detailed investigation.

In this paper, we report $^7$Li NMR measurements on Li$_2$CuW$_2$O$_8$. Compared to the previous study where only bulk measurements were performed,\cite{13} we use NMR, which is a powerful local tool for studying magnetic interactions and magnetic order in frustrated spin systems. For example, the reduction in the ordered magnetic moment (0.65 $\mu_B$) below its classical value of 1 $\mu_B$ has been ascribed to strong quantum fluctuations, but alternatively it could be understood as a coexistence of ordered and disordered phases below $T_N$. Our NMR study rules out this possibility and corroborates the formation of the collinear order throughout the sample. We also demonstrate the persistence of strong spin correlations well above $T_N$, which is a hallmark of strongly frustrated magnets, and analyze spin dynamics of Li$_2$CuW$_2$O$_8$.

II. EXPERIMENTAL

Polycrystalline sample of Li$_2$CuW$_2$O$_8$ was prepared by the conventional solid-state reaction technique using Li$_2$CO$_3$ (Aldrich, 99.999%) CuO (Aldrich, 99.999%) and WO$_3$ (Aldrich, 99.999%) as starting materials. The stoichiometric mixtures were ground and fired at 650°C for 24 hours to allow decarbonation and then at 700°C for 48 hours with one intermediate grinding. Phase purity of the sample was checked using powder x-ray diffraction (XRD) experiment (PANalytical, Empyrean) with Cu K$_\alpha$ ($\lambda = 1.54060$ Å) radiation.

Nuclear magnetic resonance (NMR) experiments were carried out using pulsed NMR technique on the $^7$Li nucleus with the nuclear spin $I = 3/2$ and gyromagnetic ratio $\gamma_N/2\pi = 16.546$ MHz/T. The NMR spectra were obtained either by Fourier transform of the NMR echo signal at a fixed field of $H = 1.5109$ T or by sweeping the magnetic field at a corresponding fixed frequency of 24.79 MHz. $^7$Li spin-lattice relaxation rate $1/T_1$ was measured using a conventional saturation pulse sequence. Electronic structure and electric field gradient on the Li site were calculated in the FPLO code\cite{17} using the same procedure as in Ref. 13.

III. RESULTS

A. Crystallography

Le Bail fit of the powder XRD data was performed using the FullProf software package based on the triclinic structure with the space group $P1$ to determine the lattice parameters.\cite{18} The initial parameters were taken from Ref. 12. Figure 2 shows the room-temperature powder XRD pattern of Li$_2$CuW$_2$O$_8$ along with the calculated pattern. The obtained best fit parameters listed in the caption of Table I are in close agreement with the literature data.

B. $^7$Li NMR spectra

For the quadrupolar $^7$Li ($I = 3/2$) nucleus, one expects two satellite lines along with the central line corresponding to three allowed transitions. As shown in

![FIG. 1. The triangular layer formed by Cu$^{2+}$ ions, columnar arrangement of spins, and the couplings of Li atoms to the magnetic spins are shown.](image)

![FIG. 2. X-ray powder diffraction pattern (open circles) at room temperature for Li$_2$CuW$_2$O$_8$. The solid red line represents the calculated pattern using Le Bail fit, with the vertical bars showing the expected Bragg peaks, and the lower solid blue line representing the difference between the observed and calculated intensities.](image)
TABLE I. Crystallographic data for Li$_2$CuW$_2$O$_8$ at room temperature (Triclinic structure with the space group $P\bar{1}$). Refined lattice parameters are $a = 4.9627(2)$ Å, $b = 5.4925(2)$ Å, $c = 5.8836(2)$ Å, $\alpha = 70.717(1)^{\circ}$, $\beta = 85.987(1)^{\circ}$, and $\gamma = 66.046(2)^{\circ}$, compared to the reported values $a = 4.9689(1)$ Å, $b = 5.4969(1)$ Å, $c = 5.8883(1)$ Å, $\alpha = 70.72(1)^{\circ}$, $\beta = 85.99(1)^{\circ}$, and $\gamma = 66.04(1)^{\circ}$. Our best fit yields $\chi^2 = 1.98$. Listed are the Wyckoff symbols and the fractional atomic coordinates $(x, y, z)$ for each atom type.$^{12}$

| Atom | Wyckoff position | $x$  | $y$  | $z$  |
|------|------------------|------|------|------|
| W    | 2i               | 0.2732(6) | 0.9619(6) | 0.3385(5) |
| Cu   | 1e               | 0.5000  | 0.5000 | 0.0000 |
| O1   | 2i               | -0.1521(5) | 0.2218(4) | 0.3494(4) |
| O2   | 2i               | 0.2377(5) | 0.7505(5) | 0.1810(5) |
| O3   | 2i               | 0.6640(5) | 0.7878(5) | 0.4381(4) |
| O4   | 2i               | 0.2779(5) | 0.2686(5) | 0.0890(4) |
| Li   | 2i               | -0.057(2) | 0.573(2) | 0.236(2) |

Fig 3, we observed only a narrow single spectral line without any satellites, which is likely due to the low quadrupolar frequency or distribution of intensity of the satellites over a broad frequency range. This type of single spectral line is commonly observed $^7$Li NMR on low-dimensional oxides.$^{19,20}$ Indeed, we calculated electric field gradient on the Li site and obtained a rather low value of $V_{zz} = 8.89 \times 10^{19}$ V/m$^2$ that yields the quadrupolar frequency of 40 kHz, which is comparable to the linewidth.

No shift in the central peak position was observed over the whole measured temperature range, above $T_N$. The NMR shift $K$ is directly proportional to the spin susceptibility ($\chi_{\text{spin}}$) and can be written as $K = \frac{A}{N_A} \chi_{\text{spin}}$, where the proportionality constant $A$ is the transferred hyperfine coupling between the $^7$Li nucleus and neighboring Cu$^{2+}$ spins, and $N_A$ is the Avogadro’s number. Thus our experimental observation of the temperature-independent line shift reflects a weak transferred hyperfine coupling of the $^7$Li nuclei with the Cu$^{2+}$ spins.

The spectra were found to broaden progressively upon lowering the temperature. Below about 75 K (see Fig. 3), the line shape becomes anisotropic. Figure 4 shows the full width at half maximum (FWHM) or $\Delta\nu$ of the $^7$Li NMR spectra as a function of temperature, above $T_N$. $\Delta\nu$ is increasing with decreasing temperature and then shows a broad maximum at around 10 K similar to the $\chi(T)$ data.$^{11}$ For a comparison, in the same Fig. 4, $\chi(T)$ is also plotted in the right y-axis. The shape and width of the NMR spectra are a measure of two main interactions: (i) the dipolar interaction between the nuclei and (ii) the dipolar hyperfine interaction of the $^7$Li nuclei with the neighboring Cu$^{2+}$ magnetic ions. So, one can write $\Delta\nu$ above $T_N$ as

$$\Delta\nu = \Delta\nu_0 + (\Delta\nu)_{\text{nib}},$$

where $\Delta\nu_0$ is the the contribution from the dipolar interaction between the nuclei, which is temperature- and field-independent. The second term $(\Delta\nu)_{\text{nib}}$ is the inhomogeneous linewidth due to the dipolar hyperfine interaction between the $^7$Li nuclei and magnetic Cu$^{2+}$ ions. It is proportional to the bulk magnetic susceptibility ($\chi$) and can be written as

$$\frac{(\Delta\nu)_{\text{nib}}}{\nu_L} = A_x \chi \approx \frac{\mu}{r^3 H},$$

where $\nu_L = \frac{2K}{\pi}H$ denotes the $^7$Li Larmor frequency for an applied external magnetic field $H$, $A_x$ is the average dipolar interaction between the $^7$Li nuclei and magnetic Cu$^{2+}$ ions.
lar coupling constant between the Li nucleus and magnetic Cu\(^{2+}\) ions, and \(r\) is the average distance between them.

Putting Eq. (2) in Eq. (1) we can write

\[
\Delta \nu = \Delta \nu_0 + \frac{\gamma_N}{2\pi} A_n H \chi.
\]

In the inset of Fig. 4, \(\Delta \nu\) is plotted as a function of \(\chi\) with temperature as an implicit parameter. \(\Delta \nu\) vs. \(\chi\) follows a linear behavior and is fitted by Eq. (3) in the temperature range \(9 \text{ K} \leq T \leq 175 \text{ K}\). The parameters obtained from the fit are \(\Delta \nu_0 \approx 18.4 \text{ KHz}\) and \(A_n \approx 7.83 \times 10^{-22} \text{ cm}^{-3}\). This value of \(A_n\) is similar to the values reported for several other compounds\(^2\) and is of the right order of magnitude with the expected dipolar interaction of Li nuclei with Cu\(^{2+}\) ions at a mean distance of 2.93 Å apart. Thus we conclude that the hyperfine interaction of the Li nucleus with Cu\(^{2+}\) moments is largely of dipolar origin.

C. \(^7\)Li spin-lattice relaxation rate \(1/T_1\)

The recovery of the longitudinal magnetization after a saturation pulse was fitted well by a single exponential function

\[
1 - \frac{M(t)}{M_0} = A e^{-t/T_1},
\]

where \(M(t)\) is the nuclear magnetization at a time \(t\) after the saturation pulse and \(M_0\) is the equilibrium value of the magnetization. The temperature dependence of \(1/T_1\) extracted from the fitting is shown in Fig. 5(a). At high temperatures \((T \geq 20 \text{ K})\), \(1/T_1\) is almost temperature-independent (in the paramagnetic regime), which is often observed in a system with localized moments when the temperature is higher than the exchange energy between the spins.\(^{23}\) With decreasing temperatures, \(1/T_1\) decreases almost linearly for \(T < 20 \text{ K}\) where the compound starts approaching the short-range-ordered regime \((T \approx 10 \text{ K})\). With further decrease in temperature, a weak but discernable anomaly was observed at \(T_N \approx 3.6 \text{ K}\) due to the critical slowing down of fluctuating moments while approaching the long-range magnetic ordering, nearly consistent with the thermodynamic\(^{13}\) measurements \((T_N \approx 3.9 \text{ K})\).\(^{24}\) Below \(T_N\), \(1/T_1\) decreases rapidly towards zero as a result of the disappearance of the critical fluctuations in the ordered state.

We also measured \(1/T_1\) at \(T = 8 \text{ K}\) for different applied fields in order to check the effect of spin diffusion. It is known that in Heisenberg magnets, spin correlation function exhibits a diffusive effect due to the contribution of long wavelength or small wave vector \((q \sim 0)\).\(^{25}\) In one-dimensional (1D) spin systems, spin diffusion shows a field dependence of \(1/T_1 \propto 1/\sqrt{H}\) type. Similar type of field dependence is reported in Heisenberg spin-chain compounds \((\text{CH}_3)\text{HNMnCl}_3, \text{AgVP}_2\text{S}_6, \text{CuCl}_2\text{2NC}_{5}\text{H}_{5}\), and \(\text{Sr}_2\text{CuO}_4\).\(^{26-30}\) On the other hand, in two-dimensional (2D) systems, spin diffusion results in a \(\log(1/H)\) dependence of \(1/T_1\), which has been experimentally observed in the quasi-2D Heisenberg magnet \(\text{Zn}_2\text{VO(PO}_4)_2\).\(^{31,32}\) As presented in the inset of Fig. 5(a), the \(1/T_1\) for \(\text{Li}_2\text{CuW}_2\text{O}_8\) at \(T = 8 \text{ K}\) is almost independent of the applied field confirming the absence of diffusive dynamics.

D. \(^7\)Li NMR spectra below \(T_N\)

Field-sweep \(^7\)Li NMR spectra of \(\text{Li}_2\text{CuW}_2\text{O}_8\) below \(T_N\) are shown in Fig. 6. As discussed before, the NMR line above \(T_N\) broadens systematically with decreasing temperature. While approaching \(T_N\), it broadens abruptly and then transforms into a nearly rectangular pattern well below \(T_N\). The broadening of the spectra below \(T_N\) indicates that the Li site is experiencing the static internal field in the ordered state through the hyperfine coupling between the \(^7\)Li nuclei and the ordered Cu\(^{2+}\) moments. At low temperatures, the rectangular spectra develop two horns on either side of its edges. The spec-
The internal field $H_{\text{int}}$ below $T_N$, which is proportional to the Cu$^{2+}$ sublattice magnetization, was determined by taking half of the FWHM of the spectral lines. The temperature dependence of $H_{\text{int}}$ is shown in Fig. 7. In order to extract the critical exponent ($\beta$) of the order parameter (sublattice magnetization), $H_{\text{int}}(T)$ was fitted by the power law

$$H_{\text{int}}(T) = H_0 \left( 1 - \frac{T}{T_N} \right)^{\beta}.$$  

(5)

It is noticed that $H_{\text{int}}$ decreases sharply on approaching $T_N$. To get a reliable estimation of the critical exponent $\beta$, one needs more data points close to $T_N$. Therefore, we have measured spectra in small temperature steps of 0.05 K just below $T_N$ (i.e. in the critical region). Our fit by Eq. (5) in the temperature range from 2.7 K to 3.51 K (see Fig. 7) yields $\beta = 0.31(4)$ with $H_0 = 0.05(3)$ T and $T_N = 3.52(5)$ K. In order to magnify the fit in the critical region, $H_{\text{int}}$ is plotted against the reduced temperature $\tau = \frac{T-T_N}{T_N}$ in the inset of Fig. 7. The solid line is the fit by $0.05 \times \tau^{0.31}$ where $T_N$ is fixed to the value 3.515 K. At low temperatures the $H_{\text{int}}$ value approaches saturation but much faster than the mean field prediction (see the deviation between solid spheres and solid line in Fig. 7). The value of $\beta$ represents the universality class of the spin systems. The $\beta$ values expected for different universality classes (or, dimensionalities) are tabulated in Ref. 33. Our obtained value of $\beta \simeq 0.31(4)$ is nearly close to any of the 3D spin models (Heisenberg, Ising or XY).

IV. DISCUSSION

The broadening of the spectra below $T_N$ suggests that a net field exists at the Li-site due to the nearest neighbor (nn) Cu$^{2+}$ spins. As demonstrated in Fig. 1, Li atoms are located slightly off the plane (at an angle $\sim 32^0$) but equidistant from two neighboring spins and each Li is coupled to two neighboring spins having the same direction (either both up or both down). In such a scenario, one expects a strong internal field since the hyperfine fields due to the two up- or down- spins will be added up at the Li site. This is possible only if Li is coupled strongly to the Cu$^{2+}$ ions. As shown in Fig. 7, the internal field at 1.8 K is about 0.037 T, which is relatively weak given the fact that Li is coupled to two spins having the same direction and, thus producing same direction of the local field at the Li site. This weak internal field is comparable to the value reported in $^{31}$P NMR for Zn$_2$VO(PO$_4$)$_2$, where P is strongly coupled to one up- and one down- spins, so that the resulting internal field is only due to the difference in the hyperfine couplings along different $^{31}$P–V$^{4+}$ pathways. Such a comparison proves that even though Li is coupled to two spins having the same direction, the diminutively small transferred hyperfine coupling results in only a weak static field. The weak hyperfine coupling is also confirmed by both temperature-independent line shift at high temperatures ($T > T_N$). Our spectral width analysis indeed suggests that the coupling between Li and Cu atoms is dipolar in nature, and the overlap of the s-orbital wave function of Li with the 3d wave function of Cu$^{2+}$ is almost negligible.

For a powder sample in the magnetically ordered state,
the direction of the internal field $H_{\text{int}}$ is distributed randomly in all directions. When the external field ($H$) is applied, the effective field $H_{\text{eff}}$ at a nuclear site is $H_{\text{int}} + H$. In a ferromagnetic sample, $H_{\text{eff}}$ is usually parallel to $H$ and has a unique value, $H_{\text{int}} + H$ or $|H_{\text{int}} - H|$ in its magnitude, if $H_{\text{int}}$ is unique. This is because the ferromagnetic moments are rotated easily to the direction of $H$ in a relatively weak field. On the other hand, in case of an antiferromagnet, the moments hardly change their directions in the external field in usual NMR experiments. The direction of $H_{\text{int}}$ has the random distribution even under external fields. Thus, $H_{\text{eff}}$ has a distribution in its direction and its magnitude varies from $|H_{\text{int}} - H|$ to $H_{\text{int}} + H$. In such a case one expects a typical rectangular powder spectra in the commensurate AFM ordered state which has been experimentally observed in compounds like CuV$_2$O$_6$, BaCo$_2$V$_3$O$_8$, and BiMn$_2$PO$_6$.

Our $^7$Li NMR spectra however exhibit two peaks on the top of a rectangular background. Such a spectrum with two horns has often been observed in NMR experiments on powder samples. For instance, powder NMR spectra of YMn$_2$ show a double horn pattern in the ordered state where Mn moments are coupled antiferromagnetically and collinearly. Recently, the powder spectra of Zn$_2$VO(PO$_4$)$_2$ in the commensurate AFM ordered state showed similar pattern with two horns on top of a rectangular background. According to Yamada et al., the shape of the spectra is also sensitive to instrumental features. When the axis of the sample coil of the NMR probe head, which is usually set perpendicular to the external field $H$, is not perpendicular to the distributed directions of $H_{\text{eff}}$'s then the intensity of NMR signal from the nuclei under investigation is reduced. In this case, the spectrum is curved around the middle having two peaks on either sides. Thus the double horn pattern in Fig. 6 is reminiscent of a commensurate AFM order and is consistent with the neutron diffraction results.

Generally, one can express $\frac{1}{T_1 T}$ in terms of dynamic susceptibility $\chi(\vec{q}, \omega)$ as:

$$\frac{1}{T_1 T} = \frac{2\gamma^2 k_B}{N^2 A} \sum_{\vec{q}} |A(\vec{q})|^2 \chi''(\vec{q}, \omega_0) \omega_0,$$

where the sum is over the wave vectors $\vec{q}$ within the first Brillouin zone, $A(\vec{q})$ is the form factor of the hyperfine interactions as a function of $\vec{q}$, and $\chi''(\vec{q}, \omega_0)$ is the imaginary part of the dynamic susceptibility at the nuclear Larmor frequency $\omega_0$. For $q = 0$ and $\omega_0 = 0$, the real component of $\chi''(\vec{q}, \omega_0)$ corresponds to the uniform static susceptibility $\chi$. Therefore, one would expect $1/\chi T_1 T$ to be temperature-independent in the paramagnetic regime. As shown in Fig. 5(b), $1/\chi T_1 T$ is almost temperature-independent above 30 K as expected. For $T \leq 30$ K, it increases slowly and shows a sharp increase below 10 K. This increase in $1/\chi T_1 T$ implies the dominance of $\chi''(\vec{q}, \omega_0)$ over $\chi(0, 0)$, which is due to the growth of spin fluctuations with $q \neq 0$, even at temperatures much higher than $T_N$. So, we can infer that strong antiferromagnetic spin fluctuations persist in a wide temperature range above $T_N$. This indicates the frustrated nature of the Li$_2$CuW$_2$O$_8$ in agreement with thermodynamic measurements.

Since the dipolar coupling between Li and Cu atoms is known, it is possible to calculate the leading exchange coupling between Cu$^{2+}$ ions from the high temperature value of $1/T_1$. At high temperatures, $1/T_1$ is constant and can be expressed as:

$$\left( \frac{1}{T_1} \right)_{T \to \infty} \propto \frac{(\gamma_N g \mu_B)^2 \sqrt{2 \pi \chi'' S(S+1)}}{3 \omega_{ex}} (\frac{A_z}{z'})^2,$$

where $\omega_{ex} = (|J_{\text{max}}| k_B / \hbar) \sqrt{2 z' S(S+1)/3}$ is the Heisenberg exchange frequency, $z$ is the number of nearest-neighbor spins of each Cu$^{2+}$ ion, and $z'$ is the number of nearest-neighbor Cu$^{2+}$ spins for a given Li site. The value of $A_z \simeq 7.83 \times 10^{22} \text{ cm}^{-3}$ corresponds to 1.1 kOe/$\mu_B$. Using the relevant parameters, $A_z \approx 11.1$ kOe/$\mu_B$, $\gamma_N = 103.962 \times 10^6 \text{ rad s}^{-1} \text{T}^{-1}$, $z = 2$, $z' = 2$, $g = 2.17$ [obtained from the $\chi(T)$ analysis in Ref. 13], $S = \frac{1}{2}$, and the high-temperature (45 K) relaxation rate of $\left( \frac{1}{T_1} \right)_{T \to \infty} \approx 113.37 \text{ s}^{-1}$ for the Li site, the magnitude of the maximum exchange coupling constant is calculated to be $J_{\text{max}}/k_B \simeq 13$ K, which is in reasonable agreement with our leading exchange coupling ($J/k_B = 14$ K) along the chain direction estimated from the band structure calculations.

As discussed before, $1/T_1$ decreases slowly for $T < 20$ K in contrast to the increase expected due to the growth of antiferromagnetic correlations. Similar kind of $T$-dependence has been observed in several antiferromagnets and the decrease in $1/T_1$ above $T_N$ is explained by the partial filtering of antiferromagnetic fluctuations from the neighboring spins. In those compounds, the probed nucleus is coupled to $nn$ spins having opposite directions. In contrast, the Li nuclei in Li$_2$CuW$_2$O$_8$ are coupled to two $nn$ spins having the
same direction. In this case, the filtering of antiferromagnetic fluctuations should not happen. Similar behaviour has been observed in frustrated breathing pyrochlore lattice compound LiInCr$_2$O$_8$, where the decrease in $1/T_1$ is explained by the opening of a spin gap above $T_N$.\[43\] In LiInCr$_2$O$_8$, $\chi(T)$ also shows an activated behaviour at low temperatures.\[44\] However, in this compound $\chi(T)$ does not show any exponential decrease, thus ruling out the possibility of a spin gap at low temperatures. For spin-1/2 Heisenberg AFM spin chains, it has been predicted theoretically that the contribution of the staggered component ($q = \pm \pi/a$) to the spin-lattice relaxation rate behaves as $1/T_1 \sim T^0$ while the contribution of the uniform component ($q = 0$) scales as $1/T_1 \sim T$.\[45\] The contributions of staggered and uniform components normally dominate in the low-temperature ($T < T_N$) and high-temperature ($T \sim J$) regimes, respectively.\[46\] Our experimentally observed linear behavior of $1/T_1$ with temperature over the 5.5 $K < T < 16$ $K$ range in Fig. 5(a) is possibly due to 1D physics. Indeed, we found moderate 1D anisotropy of the 3D spin lattice in Li$_4$CuW$_2$O$_8$ with the leading interaction running along the $b$-direction.\[13\] However, the purely 1D model is by far insufficient to describe the physics of the compound even in the $T \sim J$ temperature range.\[13\]

At the 3D ordering temperature, the correlation length is expected to diverge, and $1/T_1$ in a narrow temperature range just above $T_N$ (i.e., in the critical regime) should be described by the power law, $1/T_1 \propto \tau^{-\gamma}$, where $\gamma$ is the critical exponent. The value of $\gamma$ represents universal property of the spin system depending upon its dimensionality, the symmetry of the spin lattice, and the type of interactions. To analyze this critical behavior, $1/T_1$ is plotted against the reduced temperature $\tau$ in Fig. 8. The data just above $T_N$ ($\tau \leq 0.5$) were fitted by the power law with a fixed $T_N \approx 3.6$ $K$ yielding $\gamma \approx 0.10$. For a 3D Heisenberg antiferromagnet, a mean-field theory predicts $\gamma = \frac{1}{2}$ and a dynamic scaling theory gives $\gamma = \frac{1}{7}$.\[47,48\] Our experimental value of $\gamma \sim 0.10$ is far below these theoretically predicted values. This effect requires further investigation and may be intertwined with the strong frustration in 3D that affects spin dynamics above $T_N$.

In the magnetically ordered state ($T < T_N$), the strong temperature dependence of $1/T_1$ is a clear signature of the relaxation due to scattering of magnons by the nuclear spins.\[49\] For $T \gg \Delta/k_B$, $1/T_1$ follows either a $T^3$ behavior or a $T^5$ behavior due to a two-magnon Raman process or a three-magnon process, respectively, where $\Delta$ is the energy gap in the spin-wave spectrum.\[37,50\] On the other hand, for $T \ll \Delta/k_B$, it follows an activated behavior $1/T_1 \propto T^2 e^{-\Delta/k_B T}$. As shown in Fig. 5(b), $1/T_1$ for Li$_4$CuW$_2$O$_8$ below $T_N$ follows a $T^5$ behaviour rather than a $T^3$ behaviour which ascertains that the relaxation is mainly governed by three-magnon process similar to that reported for spin-

\[\frac{1}{2}\] square-lattice compound Zn$_2$VO(PO$_4$)$_2$ (Ref. 32) and the decorated Shastry-Sutherland lattice in the spin-

\[\frac{1}{2}\] compound CdCu$_2$(BO$_3$)$_2$ (Ref. 48).

V. CONCLUSIONS

We have investigated static and dynamic properties of the frustrated 3D quantum antiferromagnet Li$_4$CuW$_2$O$_8$ via $^7$Li NMR measurements. This compound undergoes a long-range antiferromagnetic ordering around $T_N \approx 3.9$ $K$. NMR spectra below $T_N$ confirm the commensurate nature of the magnetic order. The double-horn NMR spectral shape below $T_N$ is attributed to the non-perpendicularity between the axis of the NMR coil and the resonance field. Spin-lattice relaxation rate $1/T_1$ below $T_N$ follows the $T^5$ behavior suggesting that the relaxation is governed by the three-magnon process. Analysis of $1/\chi T_1$ suggests the frustrated nature of the compound. Below 20 $K$, $1/T_1$ decreases linearly akin to 1D systems. The critical exponent $\beta$ obtained from the sub-lattice magnetization below $T_N$ is consistent with any of the 3D spin models.

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\[\textsuperscript{1}\textsuperscript{L. Balents, Nature 464, 199 (2010).}

\[\textsuperscript{2}\textsuperscript{P. Anderson, Mat. Res. Bull. 8, 153 (1973).}

\[\textsuperscript{3}\textsuperscript{S. Nakatsuji, Y. Nambu, H. Tonomura, O. Sakai, S. Jonas, C. Broholm, H. Tsunetsugu, Y. Qiu, and Y. Maeno, Science 309, 1697 (2005).}

\[\textsuperscript{4}\textsuperscript{M. Yamashita, N. Nakata, Y. Senshu, M. Nagata, H. M. Yamamoto, R. Kato, T. Shibauruchi, and Y. Matsuda, Science 328, 1246 (2010).}

\[\textsuperscript{5}\textsuperscript{Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Phys. Rev. Lett. 91, 107001 (2003).}

\[\textsuperscript{6}\textsuperscript{B. Bernu, P. Lecheminant, C. Lhuillier, and L. Pierre, Phys. Rev. B 50, 10048 (1994).}

\[\textsuperscript{7}\textsuperscript{A. Chernyshev and M. Zhitomirsky, Phys. Rev. B 79, 144416 (2009).}

\[\textsuperscript{8}\textsuperscript{A. V. Chubakov and D. I. Golosov, J. Phys.: Condens. Matter 3, 69 (1991).}

\[\textsuperscript{9}\textsuperscript{T. Ono, H. Tanaka, H. Aruga Katori, F. Ishikawa, H. Mitamura, and T. Goto, Phys. Rev. B 67, 104431 (2003).}

\[\textsuperscript{10}\textsuperscript{N. A. Fortune, S. T. Hannahs, Y. Yoshida, T. E. Sherline, T. Ono, H. Tanaka, and Y. Takano, Phys. Rev. Lett. 102, 257201 (2009).}
