Dynamics of Bound Magnon Pairs in the Quasi-One-Dimensional Frustrated Magnet LiCuVO₄

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We report on the dynamics of the spin-1/2 quasi-one-dimensional frustrated magnet LiCuVO₄ measured by nuclear spin relaxation in high magnetic fields 10–34 T, in which the ground state has spin-density-wave order. The spin fluctuations in the paramagnetic phase exhibit striking anisotropy with respect to the magnetic field. The transverse excitation spectrum probed by $^{71}$V nuclei has an excitation gap, which increases with field. On the other hand, the gapless longitudinal fluctuations sensed by $^7$Li nuclei grow with lowering temperature, but tend to be suppressed with increasing field. Such anisotropic spin dynamics and its field dependence agree with the theoretical predictions and are ascribed to the formation of bound magnon pairs, a remarkable consequence of the frustration between ferromagnetic nearest neighbor and antiferromagnetic next-nearest-neighbor interactions.

I. INTRODUCTION

Frustrated spin systems with competing interactions provide an active playground to explore exotic quantum states such as various types of spin liquids, valence bond solids, or spin nematic. A typical example is the spin-1/2 quasi-one-dimensional frustrated Heisenberg magnets with competing ferromagnetic nearest neighbor interaction $J_1$ and antiferromagnetic next-nearest neighbor interaction $J_2$ of LiCuVO₄. Properties of such $J_1$–$J_2$ chains in magnetic fields have been extensively studied theoretically, leading to the prediction for novel spin nematic and spin density wave (SDW) phases.

A distinct feature of $J_1$–$J_2$ chains is that the lowest energy excitation in the fully polarized state just above the saturation is not a single magnon but a bound magnon pair, which is stable for a wide range of $\alpha \equiv J_1/J_2 \geq 2$. The bound magnon pairs undergo a Bose-Einstein condensation when the field is reduced below saturation, resulting in a spin nematic order that breaks the spin rotation symmetry but preserves the time reversal symmetry. When the field is further reduced, magnon pairs with their increased density exhibit spatial order. This leads to a SDW state, where the longitudinal magnetization has a spatial modulation. At very low fields, however, magnon pairing is not a valid concept and a classical helical spin order is expected to appear.

These different phases of $J_1$–$J_2$ chains in magnetic fields are expected to show distinct spin dynamics. When the bound magnon pairs are formed, an energy gap will appear in the transverse spin excitations (perpendicular to the external field) because such excitations cost energy to unbind the magnon pairs. The longitudinal spin correlation, on the other hand, has a quasi-long-range order for a purely one-dimensional system with a power-law decay. The crossover from SDW to nematic phases is accompanied by a change of the power law exponent, making the SDW (nematic) correlation less (more) dominant at higher fields. Since nematic correlation cannot be measured directly, it is very important to examine the spin dynamics in a wide range of fields to test these theoretical predictions. The nuclear relaxation rate is one of the best probes for this purpose as proposed by Sato et al. (2011).

Several cuprates are known to be experimental realizations of $J_1$–$J_2$ chains, among which LiCuVO₄ is the most studied material (19). The crystal structure contains edge-sharing CuO₄ plaquettes forming spin-1/2 frustrated chains along the $b$ axis. An incommensurate helical order was observed below $T_N = 2.1$ K at zero or low fields (20), while a longitudinal SDW order appears above 7 T (21). The magnetization curve exhibits anomalous linear field variation in a narrow range of fields 41–45 T for $H \parallel c$ immediately below saturation, which was thought to be a signature of the spin nematic phase. The origin of this linear variation is still under discussion. High-field NMR experiments performed by Büttgen et al. have revealed that this is not a bulk property but is likely to be caused by defects (5). On the other hand, recent NMR experiments have indicated that the linear variation is present as a bulk property between 42.41 and 43.55 T (19). The reason why the detected magnetization is so different is not clear but likely due to different defect concentrations.

Although recent studies on LiCuVO₄ have developed a better understanding on its static properties, spin dynamics in magnetic fields remains poorly investigated. A drastic suppression of transverse spin fluctuations has been revealed by the NMR experiments upon increasing the field across the helical to SDW boundary, supporting the presence of an energy gap (20). In this paper, we report on systematic measurements of nuclear relaxation rate $1/T_1$ of $^7$Li and $^{51}$V nuclei in LiCuVO₄ in the paramagnetic state in a wide range of field values 10–34 T, where the ground state has an SDW order. By carefully choosing nuclei and field directions, we were able to detect the transverse and longitudinal spin fluctuations separately. Our results agree with the theoretical predictions for the
$J_1-J_2$ chains, thereby providing microscopic understanding of the anomalous spin dynamics of bound magnon pairs.

II. EXPERIMENTS

The nuclear spin-lattice relaxation rate ($1/T_1$) was measured for $^{7}\text{Li}$ and $^{51}\text{V}$ nuclei on a single crystal of the size $1.0 \times 1.2 \times 0.5 \text{mm}^3$, grown by a flux method. A superconducting magnet was used to obtain magnetic fields up to 16 T, in which either the $a$- or $c$ axis of the crystal was oriented along the field within 0.3 deg. Higher fields up to 34 T were obtained by a 20 MW resistive magnet at LNCMI Grenoble, where the accuracy of the crystal orientation was within 2 deg. The ordering temperature $T_N$ was determined from the temperature dependence of the $^{51}\text{V}$ NMR line width to check the sample quality (see Appendix A for the details). The inversion recovery method was used to determine $1/T_1$. The recovery curve can be fit to an exponential function in the paramagnetic phase. In the ordered phase, however, a stretched exponential function had to be used due to inhomogeneous relaxation.

III. RESULTS AND DISCUSSIONS

The temperature dependencies of $1/T_1$ at $^{7}\text{Li}$ and $^{51}\text{V}$ nuclei ($1/T_1$ and $1/\tau_{\text{rel}}$) for various magnetic fields along the $a$ and $c$ directions are shown in Fig. 2. They exhibit remarkable variation depending on the nuclei and the direction of magnetic field. To understand such behavior, we consider the general expression for $1/T_1$,

$$
\frac{1}{T_1} = \frac{1}{N} \sum_{\mathbf{q}} \{ \Gamma_{\xi}^\perp(\mathbf{q}) S_{\perp}(\mathbf{q}, \omega) + \Gamma_{\xi}^\parallel(\mathbf{q}) S_{\parallel}(\mathbf{q}, \omega) \},
$$

where $N$ is the number of magnetic ions, $\xi = a$, $b$ or $c$ denotes the field direction, and $S_{\perp}(\mathbf{q}, \omega)$ ($S_{\parallel}(\mathbf{q}, \omega)$) is the wave-vector-dependent dynamical spin-correlation function perpendicular (parallel) to the magnetic field at the NMR frequency $\omega$. The coefficients $\Gamma_{\xi}^\perp(\mathbf{q})$ and $\Gamma_{\xi}^\parallel(\mathbf{q})$ are defined as,

$$
\Gamma_{\xi}^\perp(\mathbf{q}) = \frac{\gamma_N}{2} \left( g_{\xi \alpha}^2 |A(\mathbf{q})_{\alpha \alpha}|^2 + g_{\xi \beta}^2 |A(\mathbf{q})_{\alpha \beta}|^2 \right) + g_{\xi \gamma}^2 |A(\mathbf{q})_{\alpha \gamma}|^2 + g_{\xi \delta}^2 |A(\mathbf{q})_{\alpha \delta}|^2,
$$

$$
\Gamma_{\xi}^\parallel(\mathbf{q}) = \frac{\gamma_N}{2} \left( g_{\xi \alpha}^2 |A(\mathbf{q})_{\alpha \alpha}|^2 + g_{\xi \beta}^2 |A(\mathbf{q})_{\alpha \beta}|^2 \right) + g_{\xi \gamma}^2 |A(\mathbf{q})_{\alpha \gamma}|^2 + g_{\xi \delta}^2 |A(\mathbf{q})_{\alpha \delta}|^2,
$$

where $\gamma_N$, $g_{\xi \mu}$, and $A(\mathbf{q})_{\mu \nu}$ are a gyromagnetic ratio, a $\mu \nu$ component of a $\xi$ tensor, and a Fourier sum of a hyperfine coupling constant, $A(\mathbf{q})_{\mu \nu} = \sum_i A(r_i)_{\mu \nu} e^{i \mathbf{q} \cdot \mathbf{r}_i}$, respectively. The sum is taken over all Cu sites within 60-Å distance from the nuclei.

In the following discussion, we present analyses using data at relatively low temperatures close to $T_N$. At such a low temperature, it is reasonable to assume that the dominant fluctuations are associated with the ordering wave vector $Q_0$, $S(\mathbf{q}, \omega) \simeq N \delta(\mathbf{q} - Q_0) \langle S(\mathbf{q}, \omega) \rangle$, where $\langle \cdots \rangle$ indicates the average over $\mathbf{q}$. Then, $\Gamma_{\xi}(\mathbf{q})$ in Eq. (1) can be replaced by the value at $Q_0$, leading to the relation

$$
\frac{1}{T_1} \simeq \Gamma_{\xi}^\perp(Q_0) \langle S_{\perp}(\mathbf{q}, \omega) \rangle + \Gamma_{\xi}^\parallel(Q_0) \langle S_{\parallel}(\mathbf{q}, \omega) \rangle,
$$

which is applicable in a limited temperature range close to $T_N$. Owing to Eq. (2), $\langle S(\mathbf{q}, \omega) \rangle$ can be roughly estimated from $1/T_1$ and $\Gamma_{\xi}(Q_0)$. The field dependence of $\Gamma_{\xi}(Q_0)$ is shown in Fig. 1. It is calculated by replacing $\mathbf{q}$ in Eq. (2) by $Q_0$, which is related to the magnetization $\langle S_z \rangle$ as $Q_0 = 2\pi(1,1/2 - \langle S_z \rangle,0)$ in the SDW phase.

Let us first discuss the results for $^{51}\text{V}$ nuclei with $H \parallel a$ (Fig. 2(c)). As shown in Fig. 1(c), $\Gamma_{\xi}^\parallel(Q_0) = 0$ holds independently on the magnetic field. The longitudinal fluctuations are canceled out due to a local symmetry of a V nuclei; magnetic moments along the $a$ direction cannot induce the internal field along the $b$ and $c$ directions since a V nucleus is located in the middle of two ferromagnetically coupled chains. Thus, only the transverse fluctuations should contribute to $1/\tau_{\text{rel}}$ independently on the magnetic field as

$$
\langle S_{\perp}(\mathbf{q}, \omega) \rangle = \frac{1}{m \Gamma_{\alpha}^\perp} \frac{1}{51 \Gamma_{\alpha}^\parallel}.
$$

A remarkable feature is that $1/T_1$ decreases steeply with decreasing temperature in the paramagnetic phase, indicating an energy gap in the transverse spin excitations.
This result is in sharp contrast to the behavior at a lower field (4 T) reported in Ref. 29, where the ground state has a helical spin order and 1\(^{51}\)V NMR shows the field dependence of \(\Delta\) for \(\parallel\) fields as suggested by neutron-scattering experiments. Instead, at higher fields, 1\(^{51}\)V shows no anomaly at the transition into the SDW state as described later. For both \(\parallel\) and \(\perp\) spins, the NMR spectrum shows a helical spin order and 1\(^{51}\)V, indicating critical divergence of quantum fluctuations enhanced by frustration. In addition, analyses of magnetic susceptibility give different results: Koo et al. concluded that negative Weiss temperature of \(\theta_W = -(J_1 + J_2)/2\) strongly indicates \(|\alpha| < 0.4\) (\(J_2 = 44\) K)\(^{26}\), while Sirker indicated \(\alpha = -2.0\) (\(J_2 = 91\) K)\(^{26}\) from DMRG calculations\(^{26}\). The analyses may be sensitive to a fitting range and free parameters such as a temperature independent term \(\chi_0\). Furthermore, density functional theory calculations also give both results of \(|\alpha| < 0.4\)\(^{26}\) and \(|\alpha| > 0.4\)\(^{26}\). In the present paper, the field dependence of \(\Delta\) supports \(|\alpha| < 1\).

Let us now turn to the temperature and field dependence of the longitudinal spin-correlation function \(\langle S_\omega(q,\omega)\rangle\). This is best represented by 1\(^{1}/T_1\) at Li nuclei with the field along the \(c\) direction (1\(^{1}/T_1\)) since this is the only case that satisfies the condition \(\Gamma^\parallel \gg \Gamma^\perp\) (see Fig. 1(b)). As shown in Fig. 2(b), \(1\^{1}/T_1\) exhibits a pronounced peak near \(T_N\), indicating critical divergence of the low-frequency component of gapless longitudinal spin fluctuations associated with the SDW order. This is in sharp contrast to the gapped behavior of the transverse fluctuations.

Theories have indeed predicted such anisotropic spin fluctuations for the \(J_1-J_2\) chains, qualitatively consistent with our results. However, longitudinal spin excitations in purely one-dimensional models are described by a
Tomonaga–Luttinger (TL) liquid, leading to a power-law divergence of $1/T_1$ toward $T = T_N$ [29,33], in contrast to the experimentally observed peak near $T_N$ driven by three dimensional ordering. Thus the results of 1D theories cannot be used directly to fit our data.

Instead, we take a phenomenological approach to extract $\langle S_\parallel(q,\omega) \rangle$ from the $1/T_1$ data. Since $\gamma T_1^\parallel > \gamma T_1^\perp$ and $\langle S_\parallel(q,\omega) \rangle \gg \langle S_\perp(q,\omega) \rangle$ near $T_N$, we neglect the first term in Eq. (3) and determine $\langle S_\parallel(q,\omega) \rangle$ by

$$\langle S_\parallel(q,\omega) \rangle = \frac{1}{\gamma T_1^\parallel} \langle \gamma T_1^\perp \rangle.$$  

(6)

The top panel of Fig. 3(c) shows the field dependence of $\langle S_\parallel(q,\omega) \rangle$ at the peak temperature of $1/T_1^\parallel$ (denoted as $\langle S_\parallel \rangle_{\text{max}}$). With increasing field, $\langle S_\parallel \rangle_{\text{max}}$ first increases, then exhibits a maximum at $H \sim 0.4H_{\text{sat}}$ (16 T), and decreases above $0.4H_{\text{sat}}$. Since the peak temperature of $1/T_1^\parallel$ is slightly shifted from $T_N$, we also show $\langle S_\perp(q,\omega) \rangle$ at $T_N$ (denoted as $\langle S_\perp \rangle(T_N)$). The field dependence of $\langle S_\parallel \rangle(T_N)$ is qualitatively similar to that of $\langle S_\parallel \rangle_{\text{max}}$ but the maximum shifts to a higher field. Note that $T_N$ also shows similar behavior (the middle panel of Fig. 3(c)), supporting that the fluctuations observed by NMR are indeed related to the three dimensional ordering.

The temperature dependence of $1/T_1$ is fitted to a power law,

$$\frac{1}{T_1^c} = \gamma A \left( \frac{T - T^*}{T^*} \right)^{-\nu_c},$$  

(7)

using a fitting parameter $\gamma A$ and a phenomenological parameter $T^*$ instead of $T_N$ to improve the fit. The difference between $T^*$ and $T_N$ is smaller than 0.2 K and the fit is good except very near the peak as shown by the green line in Fig. 2(b). The exponent $\nu_c$ provides a measure of the strength of critical fluctuations. As displayed in the lower panel of Fig. 3(c), $\nu_c$ shows a similar field dependence as $\langle S_\parallel(q,\omega) \rangle$ and $T_N$.

The non-monotonic field dependence with a broad peak commonly observed for all the plots in Fig. 3(c) indicates that, approaching from the high field side, the longitudinal SDW correlation gets enhanced with decreasing field down to $H/H_{\text{sat}} \sim 0.4-0.6$, then reduced towards the phase boundary with the helical state. The former behavior is indeed consistent with the theoretical prediction for the one dimensional $J_1$-$J_2$ chains described as a TL liquid of bound magnon pairs. The longitudinal spin correlation $\langle S_\parallel(x) \rangle$ and the nematic correlation $N(x)$ both show long range algebraic decay, $\langle S_\parallel(x) \rangle \sim x^{-\eta}$ and $N(x) \sim x^{-1/\eta}$. At high fields near the saturation, the nematic correlation is dominant ($\eta > 1$) due to the gain in kinetic energy of dilute bound magnon pairs. With decreasing the field, $\eta$ gets smaller, making the SDW correlation dominant ($\eta < 1$) due to interaction among magnon pairs with their increased density. The SDW fluctuations contribute to $1/T_1$ as $\langle S_\parallel(q,\omega) \rangle \sim T^{\eta-2}$. Which is enhanced at lower fields with smaller $\eta$, consistent with the experimental observation.

What is not predicted by the 1D theories is the reduction of SDW correlation with further decreasing the field and approaching the boundary with the helical phase. This can be explained by considering the interchain coupling. According to the analysis of the spin-wave dispersion [29], the most dominant interchain interaction is ferromagnetic and connects a spin on one chain to two spins on the neighboring chain in the $ab$ plane separated by $a$, whereas the nearest neighbor distance along a chain is $b/2$ (see Fig. 4). Since the SDW order occurs at
However, both contributions in different temperature ranges. Since shown in Fig. 2(d) exhibits characteristic behavior of the SDW phase in a spatially anisotropic spin-1/2 triangular lattice antiferromagnet of the nuclei ($^{75}$Li or $^{51}$V) and the field directions, with the aid of thorough knowledge of the hyperfine coupling tensors, enabled us to analyze the transverse and longitudinal spin dynamics separately. Their contrasting temperature and field dependencies are consistent with the theoretical predictions for the frustrated $J_1$–$J_2$ chains. This demonstrates that further exploration of clean defect-free materials with $J_1$–$J_2$ chains remains a promising route to discover an elusive spin nematic phase.

IV. SUMMARY

In conclusion, we have examined field dependence of spin dynamics in the frustrated $J_1$–$J_2$ chain spin system LiCuVO$_4$ by NMR experiments. Appropriate choice of the nuclei ($^{75}$Li or $^{51}$V) and the field directions, with the aid of thorough knowledge of the hyperfine coupling tensors, enabled us to analyze the transverse and longitudinal spin dynamics separately. Their contrasting temperature and field dependencies are consistent with the theoretical predictions for the frustrated $J_1$–$J_2$ chains. This demonstrates that further exploration of clean defect-free materials with $J_1$–$J_2$ chains remains a promising route to discover an elusive spin nematic phase.

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Appendix A: Determination of the transition temperature

The transition temperature $T_N$ is determined from the variation of the $^{51}$V NMR spectra. Figure 6(a) shows typical $^{51}$V field swept NMR spectra measured at the NMR frequency of 337.79 MHz. The NMR line shape
FIG. 6. (a) $^{51}$V field-sweep NMR spectra measured near 30 T. (b) Temperature dependence of $M^2_2$/$M_4$ at various fields for $H \parallel c$. Solid circles indicate the points of the steepest slope.

changes from a single peak pattern at high temperatures to a double-horn pattern at the lowest temperature, indicating occurrence of an SDW order. However, the line shape changes rather gradually over a finite range of temperature likely due to disorder. Therefore, it is difficult to determine $T_N$ simply from visual inspection and an unbiased systematic method is required. We calculated the second and fourth moments, $M_2$ and $M_4$, defined as

$$M_2 \equiv \int dH (M_1 - H)^2 I(H)$$

$$M_4 \equiv \int dH (M_1 - H)^4 I(H),$$

where $I(H)$ is the normalized NMR spectrum ($\int dHI(H) = 1$) and $M_1$ is the first moment

$$M_1 \equiv \int dHHI(H).$$

The ratio $M^2_2$/$M_4$ is plotted against temperature in Fig. 6(b) for various field values. This ratio is much smaller than 1 for a singly peaked symmetric line, for example, $M^2_2$/$M_4 = 1/3$ for a Gaussian, but approaches 1 if the spectrum consists of two well-separated lines. Therefore, we expect a rapid increase of this ratio at the onset of an incommensurate spin order. Such behavior is indeed observed in the experimental plots of Fig. 6(b). We determined $T_N$ from the point of steepest slope. The field dependence of $T_N$ thus determined is shown in the middle panel of Fig. 2(c). This procedure gives $T_N$ which is 0–1 K smaller (depending on the magnetic field) than that in the previous study. The discrepancy is partly due to difference in the methods to determine $T_N$; temperature dependencies of integrated NMR intensity are used to determine $T_N$ in the previous study. We have confirmed that application of our procedure to the previous results reduces the differences of $T_N$ to less than 0.3 K. The residual difference may be due to a sample-dependence related to disorder such as Li-deficiencies.

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To improve the estimation of $\Gamma$, the range of the sum is expanded for $^{51}$V nuclei compared to Ref 29.

We confirmed that the magnetization of our sample ($H \parallel c$) is almost consistent with that presented in Ref. 34 below 35 T [K. Nawa, A. Matsuo, K. Kindo, M. Takigawa, and K. Yoshimura (unpublished)]. Thus, the magnetization curve of our sample is used to estimate $\Gamma_c$, and that ($H \parallel a$) in Ref. 34 is used to estimate $\Gamma_a$.

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