Nuclear Magnetic Resonance Signature of the Spin-Nematic Phase in LiCuVO₄ at High Magnetic Fields

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We report a ⁵¹V nuclear magnetic resonance investigation of the frustrated spin-1/2 chain compound LiCuVO₄, performed in pulsed magnetic fields and focused on high-field phases up to 56 T. For the crystal orientations $H∥c$ and $H∥b$, we find a narrow field region just below the magnetic saturation where the local magnetization remains uniform and homogenous, while its value is field dependent. This behavior is the first microscopic signature of the spin-nematic state, breaking spin-rotation symmetry without generating any transverse dipolar order, and is consistent with theoretical predictions for the LiCuVO₄ compound.

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The search for new states of quantum matter is one of the most active research fields in condensed-matter physics. In this respect, frustrated magnetic systems attract a lot of interest as they accommodate various unconventional quantum states, having no direct classical analogues, ordered and disordered, induced by the competing interactions [1]. One particularly interesting state is the spin-nematic phase, in which the quantum magnet behaves like a liquid crystal. Taking an external magnetic field $H$ as the reference direction, a spin-nematic phase is defined as a state without any transverse dipolar (i.e., vector-type) order, $(-1)^i(\hat{S}_i^+ + ı\hat{S}_i^x + \hat{S}_i^z + ı\hat{S}_i^y + ıH.c.) = 0$, but possessing instead a transverse quadrupolar (tensor-type) order, $(-1)^i(\hat{S}_i^+\hat{S}_{i+1}^- + \text{H.c.}) ≠ 0$.

The quadrupolar order parameter develops on the bonds between neighboring spins and can be described as a condensate of two-magnon pairs. It breaks the spin-rotational symmetry about the magnetic field, but only partially, as $\pi$ rotations transform the order parameter into itself. The also broken translational symmetry of the order parameter is invisible in the dipolar channel. There is also an analogy between the spin-nematic phase and the superconducting state; the nematic phase can be considered as a “bosonic” superconductor formed as a result of two-magnon condensation [1,2].

The concept of a spin-nematic state was developed by Andreev and Grishchuk more than 30 years ago [3], which incited an intense search for a realization in real materials. However, a definite experimental proof for the existence of such a phase has not been provided yet. Several magnetic insulators have been proposed as possible candidates, including the two-dimensional magnet NiGa₂S₄ (spin-1 system) [4–6] and thin films of ³He [7–9].

In the past 10 years a large number of theoretical studies have supported the formation of the spin-nematic phase in frustrated zigzag 1D (chain) systems [10–14]. Among these, orthorhombic LiCuVO₄ is one of the most promising candidates [15,16]. It consists of spin-1/2 Cu²⁺ chains along the orthorhombic $b$ axis with a dominant nearest-neighbor ferromagnetic interaction $J_1 = -1.6$ meV, a frustrated next-nearest-neighbor antiferromagnetic interaction $J_2 = 3.8$ meV, and an interchain coupling $J = -0.4$ meV [17,18]. At zero magnetic field an incommensurate planar spiral structure is realized below $T_N = 2.3$ K, having the moments lying in the $ab$ plane [19,20]. Above 10 T, an incommensurate, collinear spin-density wave (SDW) phase is stabilized [21–24]. Neutron-diffraction experiments show that it consists of bound magnon pairs with $S_z = 2$ that form a periodic structure [25,26]. The temperature dependence of the nuclear magnetic resonance (NMR) spin-relaxation rate in that phase reveals an energy gap developing in the transverse spin-excitation spectrum below the magnetic ordering temperature $T_N$, corresponding to the binding energy of the bound magnon pairs [24].

The theoretical prediction for the existence of a long-range ordered spin-nematic phase in LiCuVO₄ at high fields, stabilized by the presence of a sizable interchain coupling, was made by Zhitomirsky and Tsunetsugu [15]. Below the saturation field, the conditions for the appearance of a spin-nematic state are fulfilled: gapped magnon excitations and an attractive interaction between them due to the ferromagnetic exchange interaction $J_1$. Under these circumstances, the energy of the two-magnon bound state lies below the energy of the single-magnon state, thereby stabilizing the spin-nematic phase.
Although LiCuVO₄ has been extensively studied, the existence of the spin-nematic phase is still under debate. A principal experimental obstacle is the very high saturation fields $H_{sat}$ around 45 T for $H_c$ and 52 T for $H_b$ and $H_a$. Therefore, experimental studies require the highest available dc fields or even pulsed magnetic fields. Following the first prediction for the existence of the spin-nematic state in LiCuVO₄ [15], pulsed-field magnetization measurements [16] indicated a phase occurring 4–5 T below the saturation field $H_{sat} = 45$ T (52 T) for $H_c$, $H_b$, and $H_a$, which was attributed to a spin-nematic state. However, dc-field NMR studies up to 45 T, on a sample from the same batch, question the spin-nematic state by the magnetization data [27]. Whether the elimination of defects could stabilize the spin-nematic state by the magnetization data [27].

FIG. 1. (a) Simultaneous NMR time record of the $^{63}$Cu-metal FID and $^{51}$V spin echo of LiCuVO₄ for $H_c$ at $\mu_0H = 42.91$ T and a resonance frequency of 487.2 MHz. The two $^{63}$Cu FID signals are preceded by the strong transients from radio-frequency pulses saturating the receiver. (b) Fourier transforms of the NMR time record, separately applied to zone 1 and zone 2 to provide the NMR spectra of $^{63}$Cu and $^{51}$V, used for field reference and the determination of the local field in LiCuVO₄, respectively.

Motivated by this challenging open question, we performed NMR experiments on a high-quality LiCuVO₄ single crystal in pulsed magnetic fields up to 56 T, providing access to the saturation fields not only for $H_c$ but also for the perpendicular $H_b$ orientation. Our measurements of the NMR line position and width allow for a very precise determination of the field dependence of the local distribution of the magnetization near $H_{sat}$. The spin-nematic state is a homogeneous, field-dependent, longitudinal spin state without any transverse dipolar order, thus corresponding to a field-dependent NMR line position without any change of its width with respect to the saturated phase. Our NMR results in LiCuVO₄, together with the bulk magnetization measurements [28,29], perfectly match these predictions; they thus provide the first microscopic experimental evidence for the existence of a spin-nematic phase.

NMR measurements were performed at $T = 1.3$ K on a $2.5 \times 2 \times 0.3$ mm³ LiCuVO₄ single crystal. The studied sample was taken from the same batch that was used for the neutron-scattering experiments [26]. As in the previous high-field study [27], the $^{51}$V (nuclear spin $I = 7/2$) nuclei at the nonmagnetic sites were used as a probe of the local magnetic properties of the Cu$^{2+}$ moments. The method and the experimental setup for the NMR measurements in pulsed magnetic field have been discussed elsewhere [30–32]. Transient pulsed magnetic fields up to 56 T with 70 ms rise time, generated by a new homogeneous pulsed-field magnet [31], were applied parallel to the $c$ and $b$ axes of the crystal. At the desired value of the pulsed external field $H$, the NMR signal was recorded during a short time slot, with echo-pulse sequences consisting of two 0.5 µs excitation pulses separated by 20 µs. The very short duration of the NMR pulses ensures a spectral excitation bandwidth of 1.2 MHz, which is sufficient to record the entire $^{51}$V spectrum by a single data acquisition.

Unlike in usual experiments, NMR in pulsed-field magnets requires a calibration of the instantaneous value of the (time-dependent) external field $H$ within the time slot of the NMR experiment. Therefore, an internal NMR reference signal has to be simultaneously recorded. Here, we use the $^{63}$Cu NMR signal from copper-metal powder placed in the same radio-frequency NMR coil together with the sample. Because of the close proximity of the gyromagnetic ratios for the $^{51}$V ($\frac{I+1}{2} = 11.199$ MHz/T) and $^{63}$Cu ($\frac{I-\frac{1}{2}}{2} = 11.285$ MHz/T) nuclei, each single NMR acquisition contains both signals [Fig. 1(a)]: the spin-echo signal of $^{51}$V and the free-induction decay (FID) signal of the $^{63}$Cu metal. Fourier transforms of the corresponding time zones provide the $^{63}$Cu and $^{51}$V NMR spectra shown in Fig. 1(b). The frequency of the $^{51}$V NMR line position $\nu(\nu)$ in LiCuVO₄ is related to the total local magnetic field $\mu_0H(H) = \nu(\nu)/\mu_0H$, $H$ is obtained from $^{63}$Cu spectral line position, $\mu_0H = \nu(\nu)/\mu_0H(1 + K)$, $^{63}$K = 0.238% being the Knight shift of metallic copper. The large signal-to-noise ratio of the $^{51}$V and $^{63}$Cu signals and the small linewidth of the $^{63}$Cu NMR line (60 kHz) confer to these pulsed-field measurements of $H_{sat}$ a very high precision, equivalent to what is detected in conventional constant-field NMR magnets.
To the collapse of the SDW.

The width of the line and its asymmetry are decreasing due to the transient magnetic field. The overall behavior of the NMR spectra is similar for both orientations, where we distinguish three regions showing different behavior.

(i) At high fields the spectra are field independent and consist of narrow and symmetric lines. Such behavior is observed above 43.55 T for \( H\parallel c \) and above 50.55 T for \( H\parallel b \). This is characteristic for a saturated homogeneous magnetic phase.

(ii) Below 42.41 T for \( H\parallel c \) and 48.95 T for \( H\parallel b \) there appears a strong line broadening; both linewidth and line position are field dependent, which is consistent with the previously identified SDW state [22–24]. This phase is characterized by a modulated spin polarization, where the moments are collinear with the external field. With increasing magnetic field, the width of the line and its asymmetry are decreasing due to the collapse of the SDW.

(iii) In the field ranges between 42.41 and 43.55 T for \( H\parallel c \) and between 48.95 and 50.55 T for \( H\parallel b \), the line positions change with \( H \) as in the SDW phase, but their widths remain unchanged relative to those of the saturated phase. This behavior is new and has not been observed in previous NMR studies [27]. It clearly corresponds to the formation of a homogeneous magnetic state as expected for a spin-nematic state.

In general, spins (\( S \)) bear both a longitudinal \( M_z = g_z \mu_B \langle S_z \rangle \) and a transverse component of the magnetization \( A_z = g_z \mu_B \langle S \rangle \), where \( g_z \) and \( g_z \) are the corresponding components of the \( g \) tensor. Therefore, both longitudinal \( \langle S_z \rangle \) and transversal \( \langle S \rangle \) components of the spin define the spread of the local-field distribution. From Eq. (1), we first determine the saturated spin values for \( H > H_{sat} \), \( \langle S \rangle = \langle H_{sat} \rangle / (4A_{zz}g_z\mu_B) \). Using the observed saturation fields \( \langle H_{sat,c} \rangle = 0.605 \text{T} \) and \( \langle H_{sat,b} \rangle = 0.725 \text{T} \), the \( A_{zz} \) values (\( A_{zz} = 0.129 \text{T}/\mu_B \)) determined independently in the paramagnetic state [24], and \( g_z \) (\( g_z = 2.313 \) and \( g_z = 2.095 \)) from Ref. [33], we find \( \langle S \rangle = 0.505 \) and \( \langle S \rangle = 0.521 \) for \( H\parallel c \) and \( H\parallel b \), respectively. These values are close to 0.5 expected for the saturation value of a copper spin.

We then plot in Fig. 3 the field dependence of the local spin polarization \( S_z \) normalized by \( S_{sat} \) and the spread of the local-field distribution \( \Delta H_{int} \). These data summarize the...
magnetic fields. They characterize a spin-nematic state, which is not observed here. Therefore, our results clearly show that the underlying state is homogeneous and thus eliminates inhomogeneous transverse magnetic order, and, thereby, increase would thus generate a distribution or splitting of local fields for $H \parallel c$, with clear kinks at the saturation field and at the transition to the SDW phase, while $S_z(H)$ shows a more smooth field dependence for $H \parallel b$. This is probably related to an anisotropy effect: LiCuVO$_4$ has an easy-plane anisotropy ($ab$ plane), preserving all symmetry properties only in the $H \parallel c$ direction. Indeed, from the ESR data [33], the anisotropy has been attributed to the anisotropy of the exchange coupling $J$, estimated to be nearly axially symmetric, with the $J_{cc}$ value reduced by $\approx 6\%$. Within a purely 1D model without frustration, a transverse anisotropy of $J$ induces even at zero temperature a small finite depolarization at the critical field $H_c$, well described by the mean-field approximation [34]. We find

$$\langle S^z \rangle = \arccos(\delta)/\sqrt{1 - \delta^2},$$

where $\delta \approx |J_{xx} - J_{yy}|/\|J_{xx} + J_{yy} + J_{zz}\|$. Applied to LiCuVO$_4$, the depolarization would be zero for $H \parallel c$ and 1.3% for $H \parallel b$, meaning that it may somewhat influence the magnetization only for this latter orientation. While this is consistent with our NMR data, a complete theoretical description that includes both frustration and anisotropy remains to be done.

In summary, using $^{51}$V NMR, we microscopically characterized the high-field properties of LiCuVO$_4$ for two crystal orientations, $H \parallel c$ and $H \parallel b$. Just below the full saturation, the $^{51}$V NMR spectra evidence a field range where the homogeneous local magnetization is increasing with field. We argue that such behavior corresponds to the predicted spin-nematic phase, a state partially breaking spin-rotation symmetry around the magnetic-field axis without generating any transverse dipolar magnetic order. The experimentally observed field dependences of $S_z$ and their difference for $H \parallel c$ and $H \parallel b$, probably reflecting the behavior of the NMR spectra and allow us to obtain more quantitative information, in particular, for the intermediate, nematic phase, where $S_z$ changes with field while $\Delta H_{\text{int}}$ remains constant, keeping the same value as in the saturated phase. The total change of the spin polarization is there about 4%, within a field range of 1.2 T for $H \parallel c$ and 1.6 T for $H \parallel b$. As $\Delta H_{\text{int}}$ is sensitive to both $\langle S^z \rangle$ and $\langle S^z \parallel \rangle$ spin components, the absence of the line broadening in this field range excludes inhomogeneous transverse magnetic order, such as a conical state, and rules out any formation of inhomogeneous magnetization (distribution of magnetic moments). The coupling to $\langle S^z \parallel \rangle$ is very strong in LiCuVO$_4$, $A_{\parallel} = 0.12$ T/$\mu_B$ [24], and a transverse order would thus generate a distribution or splitting of local fields and, thereby, increase $\Delta H_{\text{int}}$ relative to the saturated phase, which is not observed here. Therefore, our results clearly show that the underlying state is homogeneous and thus preserves translation symmetry. Since these properties are characteristic for a spin-nematic state, they provide an experimental proof for its existence in LiCuVO$_4$ at high magnetic fields.

Our results fundamentally differ from previous NMR work of Büttgen et al. [27]. First, below saturation they observe an inconsistency between the bulk magnetization and the NMR data. They conclude that the majority of the sample is already in the saturated phase as monitored by NMR even though the magnetization still exhibits a linear slope due to the presence of defects. This is in contrast to our result, where the bulk magnetization measured on the same sample batch approximately coincides with the local magnetization measured by NMR, and also shows the signature of the nematic phase [28]. Second, they attribute a possible spin-nematic phase to a narrow field range between 40.5 and 41.4 T, where the (local) magnetization exhibits a very steep slope and the NMR spectra present a continuous change of $\Delta H_{\text{int}}$ as a function of $H$, which signifies a developing inhomogeneous nonuniform magnetization that should be absent in a spin-nematic phase. Our results, however, fulfill both criteria for a spin-nematic state: a linear local $M_x(H)$ dependence and a constant $\Delta H_{\text{int}}$. The two different NMR observations might be related to different defect concentrations in the two samples, and further experimental studies appear to be necessary to clarify this point. In addition, we consistently observe the same NMR signature of the spin-nematic phase for two crystal orientations.

A careful examination of Fig. 3 reveals that there is a subtle difference in the field dependence of $S_z(H)$ in the spin-nematic phase for the two crystal orientations: $S_z$ changes linearly for $H \parallel c$, while for $H \parallel b$. This is probably related to an anisotropy effect: LiCuVO$_4$ has an easy-plane anisotropy ($ab$ plane), preserving all symmetry properties only in the $H \parallel c$ direction. Indeed, from the ESR data [33], the anisotropy has been attributed to the anisotropy of the exchange coupling $J$, estimated to be nearly axially symmetric, with the $J_{cc}$ value reduced by $\approx 6\%$. Within a purely 1D model without frustration, a transverse anisotropy of $J$ induces even at zero temperature a small finite depolarization at the critical field $H_c$, well described by the mean-field approximation [34]. We find

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easy-plane anisotropy in LiCuVO$_4$, provide a qualitative and quantitative basis for further theoretical investigation of this material, and should help in distinguishing different models for the spin-nematic phase.

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