NMR study of the high-field magnetic phase of LiCuVO₄

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We report on NMR studies of the quasi–1D antiferromagnetic S = 1/2 chain cuprate LiCuVO₄, focusing on the high-field spin–modulated phase observed recently in applied magnetic fields H > H_c2 (µ_0H_c2 ≈ 7.5 T). The NMR spectra of ^7Li and ^53V around the transition from the ordered to the paramagnetic state were measured. It is shown that the spin–modulated magnetic structure forms with ferromagnetic interactions between spins of neighboring chains within the ab–plane at low temperatures 0.6 K < T < T_N. The best fit provides evidence that the mutual orientation between spins of neighboring ab–planes is random. For elevated temperatures T_N < T ≲ 15 K, short–range magnetic order occurs at least on the characteristic time scale of the NMR experiment.

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I. INTRODUCTION

The problem of nontrivial ordering in frustrated quantum–spin chains is considered theoretically as a challenging issue.¹⁻⁴ Recently, the quasi–one–dimensional (1D) antiferromagnetic S = 1/2 chain cuprate LiCuVO₄ gained interest as a real material in this context with a low magnetic ordering temperature T_N due to weak inter–chain interactions.¹⁻⁴ In this particular compound, magnetic frustration due to the intra–chain nearest neighbor (NN) ferromagnetic and the next–nearest neighbor (NNN) antiferromagnetic exchange interactions yields an incommensurate helix structure of the magnetic Cu^{2+} moments. Additionally, the magnetic structure at T_N is accompanied by ferroelectric order with spontaneous polarization at the same temperature.⁵⁻⁷

LiCuVO₄ crystallizes in an inverse spinel structure AB₂O₄ with an orthorhombic distortion induced by a cooperative Jahn–Teller effect of the Cu^{2+} ions. The elementary cell contains four magnetic ions Cu^{2+}(S = 1/2) with the coordinates (0,0,0), (1/2,0,1/2), (1/2,0,1/2), and (1/2,1/2,1/2) (see Fig. 1). From elastic neutron–diffraction experiments it was established that in the low temperature phase for T < T_N and zero applied magnetic field H = 0 an incommensurate planar spiral spin structure forms which has the propagation wave vector k_{ic} directed along the Cu^{2+} chains (k_{ic} || b, see Fig. 1). We parametrized the helix of this spin structure with magnetic moments μ of the Cu^{2+} ions utilizing the coordinates x, y, and z along the a, b, and c directions, respectively (Ref. 10):

\[
\mu(x, y, z) = \mu_{Cu} \cdot l_1(-1)^{2z/c} \cdot \cos(k_{ic} \cdot y + \phi) + \mu_{Cu} \cdot l_2(-1)^{2z/c} \cdot \sin(k_{ic} \cdot y + \phi),
\]

where l₁ and l₂ are orthogonal unit vectors within the ab–plane. At zero applied magnetic field H = 0, the absolute value of the propagation wave vector is k_{ic} = (1 − 0.532) · 2π/b and the ordered Cu moment amounts to μ_Cu = 0.31µ_B (Refs. 9,11). The angle φ in Eq. 1 denotes an arbitrary phase shift.

Inelastic neutron–scattering experiments confirmed that the magnetically ordered structure of LiCuVO₄ is quasi–1D with dominating exchange interactions J_1,2 within the chains. It was shown that the incommensurate structure is due to strong intra–chain NN ferromagnetic and NNN antiferromagnetic exchange interactions with J_1 = −18 K and J_2 = 49 K, respectively (see Fig. 1). Note that this hierarchy of interactions causes strong magnetic frustration. A three dimensional magnetic order results from ferromagnetic exchange in–
teractions $J_a \approx -4.3$ K between magnetic moments of neighboring chains within an ab-plane (red arrows in Fig. 1), and about five times weaker interactions between magnetic moments of different ab–planes. By application of a static magnetic field $H$, a number of consecutive magnetic phase transitions was observed with increasing field.\textsuperscript{10,11,12} The saturation fields were determined to be $\mu_0 H_s \approx 40$ T and 50 T for the orientations $H \parallel c$ and $H \parallel a$, respectively. In the low–field range ($\mu_0 H < 12$ T) the magnetically ordered structures were studied by means of ESR and NMR techniques.\textsuperscript{10} On increasing the field $\mu_0 H > 0$, the first phase transition takes place at $\mu_0 H_{c1} \approx 2.5$ T with the direction of $H$ applied within the ab-plane. It can be explained as a spin–flop reorientation of the spiral spin plane of the magnetic structure where the spin plane is oriented perpendicularly to the applied magnetic field according to $H \parallel (l_1 \times l_2)$. The transition field $\mu_0 H_{c1}$ is determined by the value of the anisotropic exchange and by the anisotropy of the magnetic susceptibility.

A more interesting and unexpected phase transition is observed at higher fields $\mu_0 H_{c2} \approx 7.5$ T. The observation of this magnetic transition for all three directions $H \parallel a, b, c$ reveals an exchange nature of this transition. The NMR spectra observed at $H > H_{c2}$ can only be explained by the assumption that a spin–modulated structure is realized, where the ordered component of the spin structure is oriented parallel to the applied magnetic field $H \parallel l_1$ and $l_2 = 0$. An indirect confirmation of this sequence of magnetic phase transitions suggested in Ref. \textsuperscript{10} was obtained by experimental investigation of the dielectric properties of LiCuVO\textsubscript{4}.\textsuperscript{2} A closer inspection of the high–field phase for $H > H_{c2}$ will be given in this work by means of NMR spectroscopy and different scenarios are discussed for the collinear magnetic structure which is realized for $H > H_{c2}$.

## II. NMR EXPERIMENT

The single crystal under investigation is the identical crystal used in Refs. \textsuperscript{8} and \textsuperscript{10}. The NMR experiments were performed with a phase coherent, homemade spectrometer at radio frequencies within the range $45.1 < \nu < 165$ MHz (for details see Ref. \textsuperscript{10}). The effective local magnetic field acting on nuclei of a nonmagnetic ion is determined by long–range dipolar fields from the surrounding magnetic ions and by so called 'contact' hyperfine fields from NN magnetic ions. The positions of Li\textsuperscript{1+} and V\textsuperscript{5+} ions surrounded by the copper ions are shown in figure 1. The Li\textsuperscript{1+} ions are located between the ab–plane of Cu ions and the V\textsuperscript{5+} ions are very close to one single ab–plane of Cu ions. Therefore, the \textsuperscript{7}Li NMR spectra are sensitive to the mutual orientation between Cu spins of adjacent ab–planes. In case of the \textsuperscript{51}V NMR in LiCuVO\textsubscript{4}, this mutual orientation between the Cu spins of adjacent ab–planes does not affect the spectral shape, because the effective local magnetic field at the V sites is dominated by contact hyperfine fields from the four Cu\textsuperscript{+2} moments of the nearest ab–plane.

Figure 2 shows the \textsuperscript{51}V NMR spectra at different frequencies, i.e. different applied magnetic fields, for all
three directions $\mathbf{H} \parallel \mathbf{a, b, c}$. All spectra with resonance fields $H < H_{c2}$ exhibit one single line, irrespective of the orientation of the applied magnetic field. For fields $H > H_{c2}$, the NMR spectra have the characteristic double–horn shape which is a fingerprint of modulated magnetic structures. The arrows in Fig. 2 indicate the anisotropy of the transition fields $H_{c2}$ obtained in Refs. 8, 10 and 12. For $\mathbf{H} \parallel \mathbf{b}$, the value for $H_{c2}$ is obtained from NMR data: at magnetic fields $\mu_0 H \approx 6.7$ T, the $^{51}$V NMR spectral line already transforms to the double–horn pattern which is specific for the high–field magnetic phase (see the middle frame in Fig. 2). From the $^7$Li NMR spectral shape for $\mathbf{H} \parallel \mathbf{b}$ it was concluded that $\mu_0 H_{c2} > 6.05$ T (cf. Ref. 10). Therefore, we find the value of $H_{c2}$ for the orientation $\mathbf{H} \parallel \mathbf{b}$ within the range $6.05 < \mu_0 H_{c2} < 6.7$ T. This uncertainty is depicted in the middle frame of Fig. 2 by the hatched area. The single line of the $^{51}$V NMR spectra which is obtained for all three orientations for $H_{c1} < H < H_{c2}$ shows that the spin rotating axis of the helical magnetic structure is parallel to the applied field $\mathbf{H} \parallel (\mathbf{l}_1 \times \mathbf{l}_2)$ confirming the observations made in reference 10.

Figure 3 shows the temperature dependences of the NMR spectra of $^7$Li and $^{51}$V at irradiation frequencies of 165 MHz and 110 MHz, respectively. These frequencies were chosen in order to obtain NMR spectra of both nuclei at the same applied magnetic field $\mu_0 H = 10$ T, exceeding the transition field $H_{c2}$. The $^7$Li spectra for all temperatures exhibit a single line whereas the $^{51}$V spectra in the low–temperature range reveal the double–horn pattern. For temperatures $T < 1.3$ K, the NMR spectral shapes occur to be temperature independent. As it was shown in Ref. 10 such spectral shapes of both nuclei can only be realized for a collinear spin–modulated structure with $\mathbf{H} \parallel \mathbf{l}_1$ and $\mathbf{l}_2 = 0$. Figure 4 gives the temperature dependences of the NMR line width of $^7$Li and $^{51}$V obtained from Gaussian fits of the data presented in figure 3. In case of the $^{51}$V spectra, such fitting to Gaussian lines was only possible for temperatures $T > 2.1$ K, because the spectral shape for $T < 2.1$ K changes to a broad plateau–like pattern. It is important to note that there is an abrupt 10 % step–like decrease of the $^7$Li line width $\Delta H(T)$ at around 2 K for the field orientation $\mathbf{H} \parallel \mathbf{a}$. Thus, the temperature $T_N \approx 2.1$ K identifies the transition temperature into the magnetically ordered phase in agreement with the phase diagram established in Refs. 8 and 12. At elevated temperatures $T_N < T < 15$ K, the line widths $\Delta H(T)$ for both nuclei decrease with increasing temperature. A temperature independent, isotropic line width $\Delta H$ which is characteristic for paramagnetic behavior is only established for $T > 15$ K, far above $T_N$.

III. DISCUSSION AND CONCLUSION

In order to further investigate this high–field phase $H > H_{c2}$ we will consider two types of magnetic structures which assure such modulated spin components directed along $H$, i.e. a planar spiral spin structure with $\mathbf{H} \perp \mathbf{n}$ (where $\mathbf{n} = \mathbf{l}_1 \times \mathbf{l}_2$) and a collinear structure with $\mathbf{H} \parallel \mathbf{l}_1$, respectively.

Moreover, we take into account the hierarchy of the magnetic exchange interactions in LiCuVO$_4$. As the exchange interactions within the $ab$–plane greatly exceed the inter–plane interactions, we will test on one hand the case with long–range magnetic order in $c$–direction (3D in the following), and on the other hand the case of a long–range order within the $ab$–planes but an arbitrary mutual orientation of spins along the $c$–direction, i.e. between different $ab$–planes (2D).

Figure 5 presents the experimental $^7$Li NMR spectra at $T = 0.6$ K (symbols) and the simulated spectra (solid lines) according to the suggested spin structures mentioned above. The simulations result from calculations of the Cu$^{2+}$ dipolar fields at the probing $^7$Li nuclear site (cf. Ref. 10). The left (right) column of Fig. 5 shows the simulated $^7$Li NMR spectra for the planar spiral spin structure (collinear spin–modulated structure), respectively. The 3D long–range magnetic order is taken into account by a constant phase $\phi(x, z)$ in Eq. 1 whereas in case of the 2D long–range magnetic order the phase $\phi$ is only constant with respect to $x$ but arbitrary with respect to the $z$–coordinate $|\phi(x, z) = \text{random}(z)|$. The best agreement between experiment and simulations is obtained for the spin–modulated 2D magnetic structure, i.e. with a random phase relation between spins along the $c$–axis (cf. lower right frame in Fig. 5).

The incommensurate propagation wave vector $k_{ic}$ at high applied magnetic fields is experimentally unknown, but the simulations revealed that a variation of $k_{ic}$ does not change the shape of the calculated NMR spectra. Thus, at low temperatures and high magnetic fields $H > H_{c2}$ long–range magnetic order in the $ab$–plane
without inter–plane coupling along the c–direction is realized in LiCuVO₄. This proposed magnetic structure is consistent with the ⁵¹V NMR spectra; the effective magnetic fields on these nuclei are dominated by contact fields of the four neighboring Cu ions of the nearest ab–plane (see Fig. 4). Therefore, these spectra are not sensitive to magnetic disorder in c–direction. This explains the double–horn shape of the ⁵¹V NMR spectra for H > H₂ at very low temperatures T = 0.6 K. In addition, the lack of a spiral spin structure proposed for H > H₂ accounts for the paraelectric behavior according to reference 8.

At elevated temperatures T ≥ 2 K, the shape of the ⁵¹V NMR spectra transforms from the double–horn shape to a single line pattern which can be fitted by Gaussian lines. In the lower frame of Fig. 4, the temperature dependence of the line width ∆H of these Gaussian lines is plotted. It is important to note that broad Gaussian lines can be observed up to approximately 15 K indicating short–range magnetic ordering at the time scale of the NMR experiment, far above the ordering temperature Tₙ ≈ 2 K. A lower bound of the time scale is given by the time for spin–echo formation which was achieved in our experiments with pulse separation times τ₅₅ = 35 μs. From the spin–lattice relaxation time T₁ of our measurements we estimate an extension of the time scale even to milliseconds.

Most probably this transformation of the ⁵¹V NMR spectral shape (see right column in Fig. 4) indicates the loss of ferromagnetic interactions along the a–direction towards higher temperatures. In order to corroborate this assumption we simulated the ⁵¹V NMR spectra at 1.3 and 3 K for this scenario. The simulated spectra are included in Fig. 3 (right column, green solid lines): the simulation at 1.3 K is based on the spin–modulated 2D magnetic structure with random phase relation φ along the c–direction mentioned above for the ⁷Li NMR spectra. For the simulation at 3 K, the release of ferromagnetic interactions between neighboring chains in the a–direction towards higher temperatures is taken into account by randomizing the phase relation φ along the a–direction as well [φ(x, z) = random(x, z) in Eq. 1].

In conclusion, the magnetic structure of the high–field magnetic phase of the quasi–1D antiferromagnet LiCuVO₄ was studied by NMR experiments. We determined that the spin–modulated magnetic structure (H || l₁) with long–range magnetic order within the ab–plane and a random phase relation between the spins of neighboring ab–planes is realized in LiCuVO₄ at H > H₂ and low temperatures T < Tₙ. The observed NMR spectra can be satisfactorily described by the following structure:

$$\mu(x, y, z) = \mu_Cu \cdot l \cdot \cos[k_{ic} \cdot y + \phi(z)],$$

where l is the unit vector parallel to the applied magnetic field H and the phase φ(z) between adjacent spins in c–direction is random. Within the temperature range Tₙ < T ≤ 15 K, the NMR spectra can be described if we assume that the phase relation φ between neighboring spin chains in the ab–plane is random too. The particular phases for both structures below and above Tₙ for H > H₂ are time independent at least on the characteristic time scale of the NMR experiment of microseconds.

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1 A.V. Chubukov, Phys. Rev. B 44, 4693 (1991).
2 A.K. Kolezhuk, Phys. Rev. B 62, R6057, (2000).
3 A.K. Kolezhuk and T. Vekua, Phys. Rev. B 72, 094424 (2005).
4 D.V. Dmitriev and V.Yu. Krivnov, Phys. Rev. B 77, 024401 (2008).
5 J. Sudan, A. Lüscher, and A.M. Läuchli, Phys. Rev. B 80, 140402(R) (2009).
6 F. Heidrich–Meisner, I.P. McCulloch, and A.K. Kolezhuk, Phys. Rev. B 80, 144417 (2009).
7 Y. Naito et al., J. Phys. Soc. Jpn. 76, 023708 (2007).
8 F. Schrettle et al., Phys. Rev. B 77, 144101 (2008).
9 B.J. Gibson et al., Physica B 350, e253 (2004).

10 N. Büttgen et al., Phys. Rev. B 76, 014440 (2007).
11 M. Enderle et al., Europhys. Lett. 70, 237 (2005).
12 M.G. Banks et al., J. Phys.: Condens. Matter 19, 145227 (2007).
13 R. Smith et al., Physica B 378-380, 1060 (2006).