NMR study of the high-field magnetic phase of $LiCuVO_4$

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We report on NMR studies of the quasi-one-dimensional antiferromagnetic $S=1/2$ chain cuprate $LiCuVO_4$, focusing on the high-field spin-modulated phase observed recently in applied magnetic fields $H>H_{c2}(\mu_0 H_{c2} \approx 7.5$ T). The NMR spectra of ^{7}Li and ^{51}V 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 $0.6\ \mathrm{K}<T<T_N$. The best fit provides evidence that the mutual orientation between spins of neighboring **ab** planes is random. For higher temperatures $T_N<T\lesssim 15$ 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 $LiCuVO_4$ gained interest as a real material in this context with a low magnetic ordering temperature T_N due to weak interchain interactions.[5,6] In this particular compound, magnetic frustration due to the intrachain 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.[7,8]

$LiCuVO_4$ crystallizes in an inverse spinel structure AB_2O_4 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), (0,1/2,0), (1/2,0,1/2), and (1/2,1/2,1/2) (see Fig. 1). From elastic neutron-diffraction experiments it was established[9] 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 $\mathbf{k_{ic}}$ directed along the Cu^{2+} chains ($\mathbf{k_{ic}}\|\mathbf{b}$, 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):

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

where $\mathbf{l_1}$ and $\mathbf{l_2}$ are orthogonal unit vectors within the **ab** plane. At zero applied magnetic field $H=0$, the absolute value of the propagation wave vector is $k_{ic} = (1-0.532)\cdot 2\pi/b$ and the ordered Cu moment amounts to $\mu_{\mathrm{Cu}}=0.31\mu_B$ (Refs. 9 and 11). The angle ϕ in Eq. (1) denotes an arbitrary phase shift.

Inelastic neutron-scattering experiments[11] confirmed that the magnetically ordered structure of $LiCuVO_4$ is quasi-1D with dominating exchange interactions $J_{1,2}$ within the chains. It was shown that the incommensurate structure is due to strong intrachain 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 interactions $J_a\approx -4.3$ 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.[10–12] The saturation fields were determined to be $\mu_0 H_s \approx 40$ T and 50 T for the orientations $\mathbf{H}\|\mathbf{c}$ and $\mathbf{H}\|\mathbf{a}$, respectively. At lower fields ($\mu_0 H<12$ T) the magnetically ordered structures were studied by means of ESR and NMR techniques.[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 $(\mathbf{l_1}\times\mathbf{l_2})\|\mathbf{H}$. 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 $\mathbf{H}\|\mathbf{a},\mathbf{b},\mathbf{c}$ 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 $\mathbf{l_1}\|\mathbf{H}$ and $\mathbf{l_2}=0$. An indirect confirmation of this sequence of magnetic phase transitions suggested in Ref. 10 was obtained by experimental investigation of the dielectric properties of $LiCuVO_4$.[8] 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 $H>H_{c2}$.

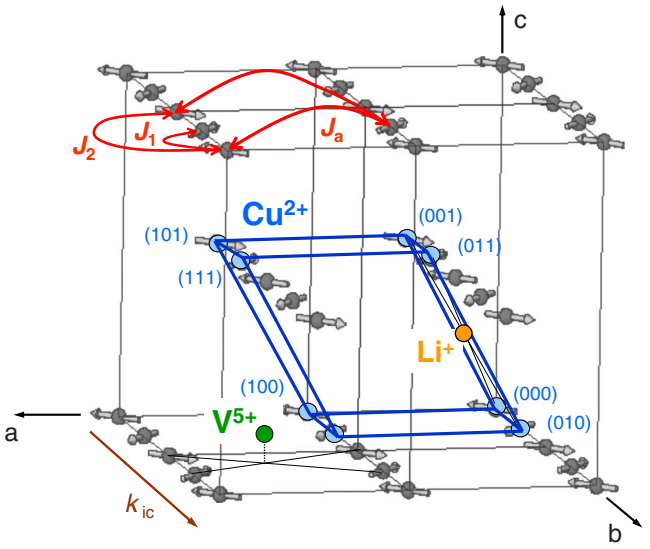

FIG. 1. (Color online) Scheme of the Cu^{2+} moments in the crystal structure of $LiCuVO_4$ (Ref. 9). Copper ions are marked by gray circles, where the arrows at each site constitute the helical spin structure at $H=0$ below T_N (Ref. 9). J_1, J_2, and J_a (red arrows) denote the main exchange integrals (Ref. 11) defining the magnetic structure of $LiCuVO_4$. Additionally, the positions of Li (orange) and V (green) ions are exemplarily depicted by one ion each. In favor of clarity, the V^{5+} ion is shifted into the foreground of the cell.

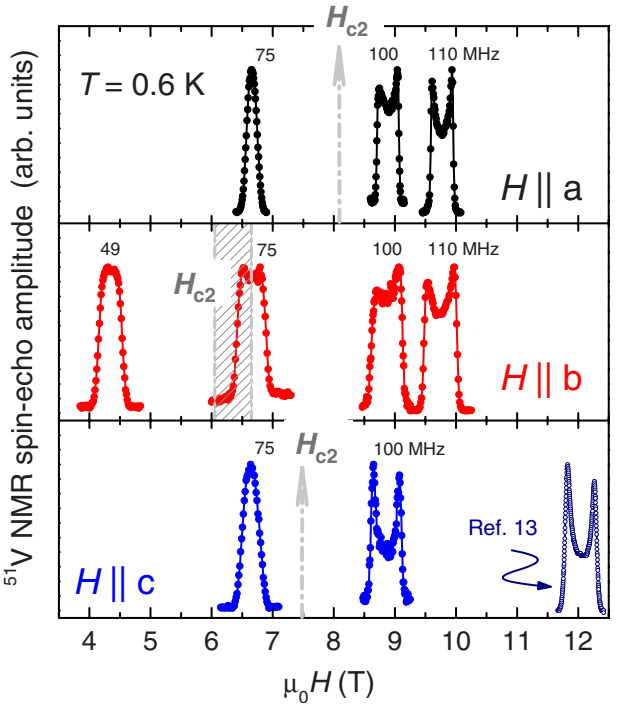

FIG. 2. (Color online) NMR spectra of ^{51}V measured at $T=0.6$ K for different frequencies, i.e., different applied magnetic fields H. The spectrum obtained in Ref. 13 at T=1.64 K is included.

II. NMR EXPERIMENT

The single crystal under investigation is the identical crystal used in Refs. 8 and 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. 10). The uncertainty of the collected spectral data points is depicted by the symbol size in the figures. 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^{1+} and V^{5+} ions surrounded by the copper ions are shown in Fig. 1. The Li^{1+} ions are located between the **ab** plane of Cu ions and the V^{5+} ions are very close to one single **ab** plane of Cu ions. Therefore, the ^{7}Li NMR spectra are sensitive to the mutual orientation between Cu spins of adjacent **ab** planes. In case of the ^{51}V NMR in $LiCuVO_4$, 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^{+2} moments of the nearest **ab** plane.

Figure 2 shows the ^{51}V NMR spectra at different frequencies, i.e., different applied magnetic fields, for all three directions $\mathbf{H}\|\mathbf{a},\mathbf{b},\mathbf{c}$. All spectra with resonance fields $H < H_{c2}$ exhibit a narrow 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 $\mathbf{H}\|\mathbf{b}$, 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 $\mathbf{H}\|\mathbf{b}$ 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 $\mathbf{H}\|\mathbf{b}$ 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 narrow 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 $(\mathbf{l_1} \times \mathbf{l_2}) \| \mathbf{H}$ confirming the observations made in reference.[10] Note that for the spin-flop phase $(H_{c1} < H < H_{c2})$ we expect a cancellation of the contact fields only. Therefore, a small but detectable splitting of the ^{51}V spectral line due to residual dipolar fields is observed in the spin-flop phase for $H\|b$ (cf. Fig. 2, for $H\|b$ at $\nu = 49$ MHz).

Figure 3 shows the temperature dependences of the NMR spectra of ^{7}Li and ^{51}V at irradiation frequencies of 165 and 110 MHz, respectively. These frequencies were chosen in order to obtain NMR spectra of both nuclei at the same applied magnetic field around $\mu_0 H = 10$ 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 $\mathbf{l_1} \| \mathbf{H}$ 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 in Fig. 3. In case

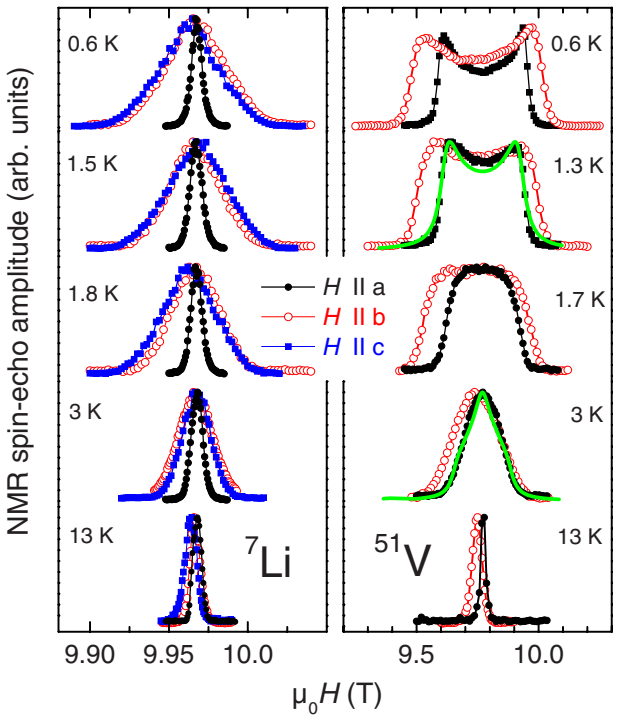

FIG. 3. (Color online) NMR spectra of ^{7}Li (165 MHz, left column) and ^{51}V (110 MHz, right column) at different temperatures for $H > H_{c2}$. Additionally, the ^{51}V spectra at $T = 1.3$ K and 3 K for $\mathbf{H} \| \mathbf{a}$ are displayed together with simulation curves (green solid lines).

of the ^{51}V spectra, such fitting to Gaussian lines was only possible for temperatures $T > 2.2$ K, because the spectral shape for $T < 2.2$ K changes to a broad plateaulike pattern. Together with specific heat measurements (not shown) on our crystal we obtain the temperature $T_N = (2.2 \pm 0.2)$ K as the transition temperature into the magnetically ordered phase in agreement with the phase diagram established in Ref. 12. It is important to note that there is an abrupt 10% steplike anomaly of the ^{7}Li line width $\Delta H(T)$ at around T_N. At higher 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 ΔH which is characteristic for paramagnetic behavior is only established for $T > 15$ K, far above T_N.

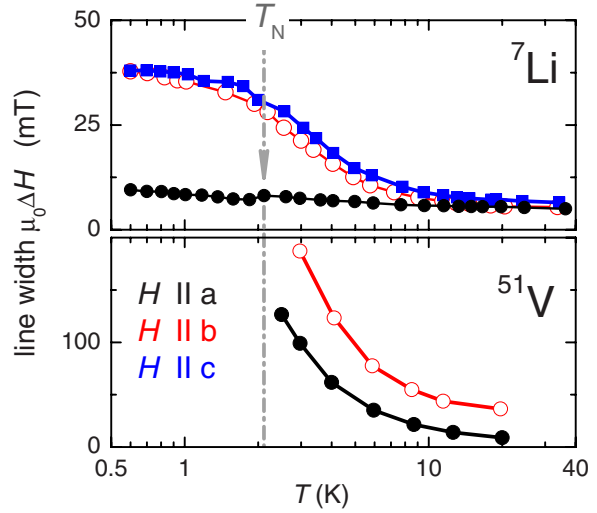

FIG. 4. (Color online) Temperature dependences of the line widths $\Delta H(T)$ obtained from Gaussian fits to the data in Fig. 3 at $H > H_{c2}$. Upper and lower frame for ^{7}Li and ^{51}V nuclei, respectively. $T_N \approx 2.2$ K is marked by an arrow (see text).

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 $\mathbf{n} \perp \mathbf{H}$ (where $\mathbf{n} = \mathbf{l}_1 \times \mathbf{l}_2$) and a collinear structure with $\mathbf{l}_1 \| \mathbf{H}$, 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 interplane interactions, we will test on one hand the case with long-range magnetic order in **c** direction [three-dimensional (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 ϕ 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 $\mathbf{k}_{ic}$ at high applied magnetic fields is experimentally unknown, but the simulations revealed that a variation in 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 interplane coupling along the c direction is realized in $LiCuVO_4$. This proposed magnetic structure is consistent with the ^{51}V 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. 1). Therefore, these spectra are not sensitive to magnetic disorder in c direction. This explains the double-horn shape of the ^{51}V NMR spectra for $H > H_{c2}$ at very low temperatures $T = 0.6$ K. In addition, the lack of a spiral spin structure proposed for $H > H_{c2}$ accounts for the paraelectric behavior according to Ref. 8.

At higher temperatures $T \gtrsim 2$ K, the shape of the ^{51}V NMR spectra transforms from the double-horn shape at low temperatures to a single line pattern which can be fitted by

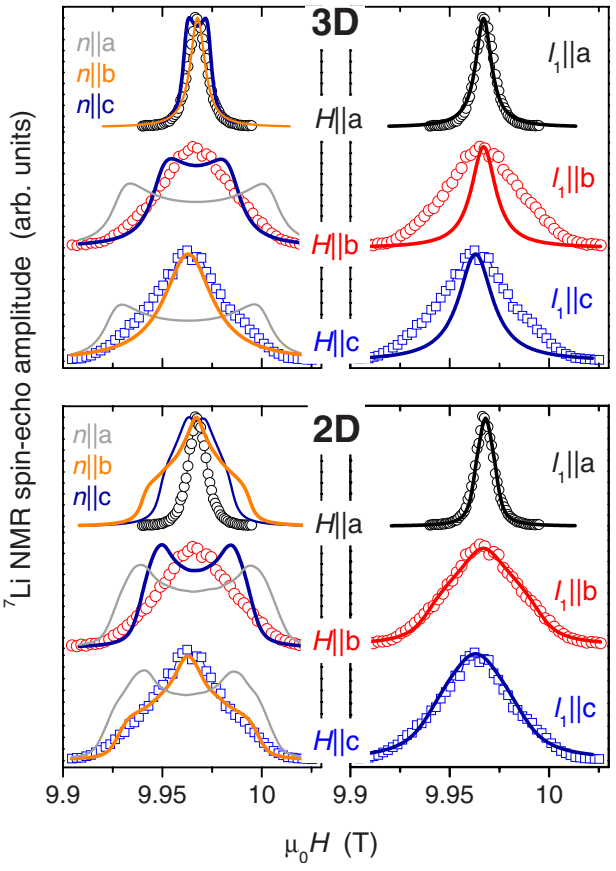

FIG. 5. (Color online) ^{7}Li NMR spectra at $T=0.6$ K and 165 MHz (symbols). The solid lines represent the simulations (see text): left (right) column shows the simulated spectra for the planar spiral structure with $\mathbf{H}\perp\mathbf{n}$ (collinear spin-modulated structure, $\mathbf{l_1}\|\mathbf{H}$ and $\mathbf{l_2}=0$), respectively.

Gaussian lines. In the lower frame of Fig. 4, the temperature dependence of the line width ΔH 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 $T_N\approx 2.2$ 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 $\tau_D=35$ μs. From the spin-lattice relaxation time T_1 of our measurements we estimate an extension of the time scale even to milliseconds.

Most probably this transformation of the ^{51}V NMR spectral shape (see right column in Fig. 3) indicates the loss of ferromagnetic interactions along the **a** direction toward higher temperatures. In order to corroborate this assumption we simulated the ^{51}V 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 ^{7}Li NMR spectra. For the simulation at 3 K, the release of ferromagnetic interactions between neighboring chains in the **a** direction toward higher temperatures is taken into account by randomizing the phase relation ϕ along the **a** direction as well [$\phi(x,z)=\text{random}(x,z)$ in Eq. (1)].

In conclusion, the magnetic structure of the high-field magnetic phase of the quasi-1D antiferromagnet $LiCuVO_4$ was studied by NMR experiments. We determined that the spin-modulated magnetic structure ($\mathbf{l_1}\|\mathbf{H}$) with long-range magnetic order within the **ab** plane and a random phase relation between the spins of neighboring **ab** planes is realized in $LiCuVO_4$ at $H>H_{c2}$ and low temperatures $T<T_N$. The observed NMR spectra can be satisfactorily described by the following structure:

$$\mu(x,y,z)=\mu_{Cu}\cdot\mathbf{l}\cdot\cos[k_{ic}\cdot y+\phi(z)], \qquad (2)$$

where $\mathbf{l}$ is the unit vector parallel to the applied magnetic field $\mathbf{H}$ and the phase $\phi(z)$ between adjacent spins in **c** direction is random. Within the temperature range $T_N<T\lesssim 15$ 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 T_N for $H>H_{c2}$ are time independent at least on the characteristic time scale of the NMR experiment of microseconds.

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