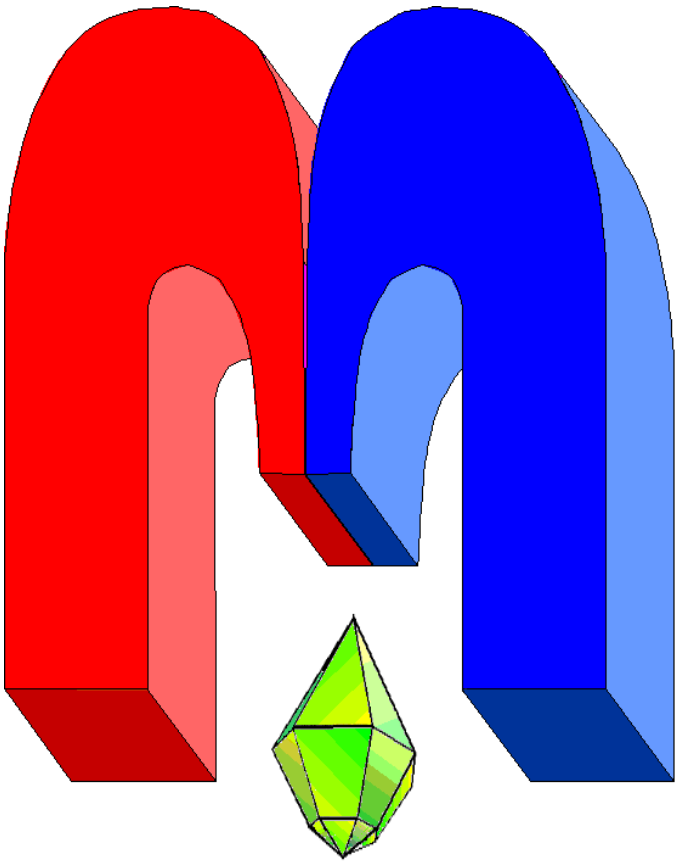
ISSN 2072-5981
doi: 10.26907/mrsej



Magnetic Resonance in Solids

Electronic Journal

Volume 25
Issue 2
Article No 23202
1-9 pages
2023
doi: **10.26907/mrsej-23202**

http://mrsej.kpfu.ru
http://mrsej.ksu.ru

Established and published by Kazan University*
Endorsed by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press (#015140), August 2, 1996
First Issue appeared on July 25, 1997

"***Magnetic Resonance in Solids. Electronic Journal***" (**MRS*ej***) is a peer-reviewed, all electronic journal, publishing articles which meet the highest standards of scientific quality in the field of basic research of a magnetic resonance in solids and related phenomena.

Indexed and abstracted by
Web of Science (*ESCI*, Clarivate Analytics, from 2015), *Scopus* (Elsevier, from 2012), *RusIndexSC* (*eLibrary*, from 2006), *Google Scholar*, *DOAJ*, *ROAD*, *CyberLeninka* (from 2006), *SCImago Journal & Country Rank*, etc.

* Address: "Magnetic Resonance in Solids. Electronic Journal", Kazan Federal University; Kremlevskaya str., 18; Kazan 420008, Russia

† In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Ordered state of the intrinstic two-component magnetoelectric material Li_2CuZrO_4 according to ^{7}Li NMR data

E.L. Vavilova*

Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS, 420029 Kazan, Russia

E-mail: jenia.vavilova@gmail.com

(received November 11, 2022; revised July 6, 2023; accepted July 19, 2023; published July 24, 2023)

The magnetic system of the Li_2CuZrO_4 compound is characterized by the formation of helical spin structures in CuO_2 chains due to strong frustrations of the exchange interaction. The double position of lithium ions determines the existence of the dielectric glass state at $T < 70$ K. In this work, using the NMR technique, we found the activation energy of the dipole glass system $E_a = 101$ K and determined the type of helicoidal copper spin structure as a "screw". It was demonstrated how the high-temperature interaction of strongly correlated spin and dielectric subsystems in this compound paradoxically prevents the appearance of multiferroic behavior in the ordered phase.

PACS: 76.60.-k, 75.10.Jm, 75.47.Lx, 75.85.+t, 67.57.Lm, 67.30.er

Keywords: low-dimensional magnetism, frustration, spin chains, nuclear magnetic resonance, magnetization, magnetoelectric interactions.

1. Introduction

Despite extensive experimental and theoretical efforts over the past decades, spin ordering in frustrated quasi-1D $S = 1/2$ quantum spin chains is still the subject of widespread activity. Most of the research has focused on various cuprates with CuO_4 plaquettes sharing corners or edges. Edge-sharing plaquettes form CuO_2 chains with a Cu-O-Cu bond angle of almost 90°, causing some decrease in exchange interactions between nearest neighbors (NN) and next nearest neighbors (NNN) of a similar magnitude, which leads to frustration effects. Rich phase diagrams with various commensurate and incommensurate phases have been predicted and shown to contain non-trivial phenomena like spin and charge ordering, dimerization or superconductivity in frustrated compounds. Variants of the physical realization of weakly interacting quantum chains $S = 1/2$ with ferromagnetic (FM) NN exchange and stronger antiferromagnetic (AFM) NNN exchange have been discovered in cuprates ($LiCu_2O_2$, $NaCu_2O_2$, $LiCuVO_4$, $LiCuSbO_6$ [1–5] in two last decade. These cuprates have Cu-O-Cu bond angles close to 90° and have helical ground states with relatively short quasi-periodicity and the sharp rotation angles. The key characteristic of the magnetic subsystem of a frustrated spin chain is chirality vector $\mathbf{k}$, which is determined by the vector product of spins at neighbors lattice sites $\mathbf{S}_i \times \mathbf{S}_j$. The helical twisting of the chain spins can induce the so-called spin-controlled ferroelectricity through the inversed Dzyaloshinskii-Moriya interaction; therefore, multiferroic behavior in the ordered phase should be expected for such systems. At the same time, due to the very weak interaction between the chains in quasi 1D magnets, the magnetic order in them is strongly suppressed and occurs at temperatures that are significantly lower than the value of the exchange interaction in the chains. In this case, the local regions with one-dimensional helical structures can exist in a wide temperature range above the ordering temperature. The gradual destruction of the long-range spin order of the helix at finite temperatures allows the helical correlations of finite length to survive for a sufficiently long time, which characterize the so-called vector-chiral phase, in which there is also a close interplay of magnetic and electrical properties [6].

The lithium-containing frustrated quantum spin system Li_2CuZrO_4 exhibits an interesting combination of magnetic and dielectric properties. Band structure calculations, as well as studies of the exact diagonalization of the extended Hubbard model for large clusters show [7] that Li_2CuZrO_4 can be considered as a quasi-one-dimensional chain compound with ferromagnetic NN and antiferromagnetic NNN exchange in the close vicinity of the quantum critical point. Copper ions surrounded by oxygen ligands form distorted CuO_4 plaquettes in Li_2CuZrO_4 which forms CuO_2 chains with sheared edges and a Cu-O-Cu bond angle of 94.13° (see Figure 1). These chains, together with Li_{II} atoms, form layers in the *bc*- plane. Due to weaker interchain

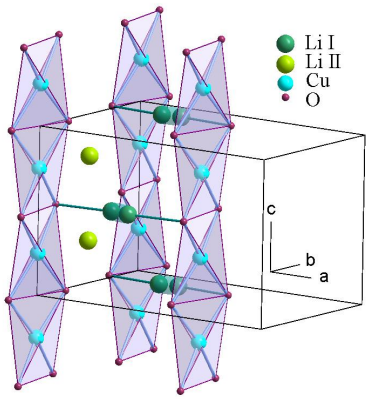


Figure 1. Fragment of the crystal structure of γ-Li_2CuZrO_4 . Medium-sized blue spheres indicate copper ions, large dark green spheres indicate the split position of Li_I ions, light green spheres indicate lithium Li_{II} ions, and small burgundy spheres indicate oxygen ions. Lilac highlights copper-oxygen chains formed by deformed CuO_4 plaquettes.

exchanges, the system passes into a three-dimensional ordered state at a temperature of about 7 K. Unlike many lithium-containing cuprates, lithium ions in γ-Li_2CuZrO_4 occupy two different types of positions: 4b (Li_{II}) with an occupancy of about 100% and 8l Li_I with 50% occupancy. This means that there are two crystallographically equivalent positions for the localization of Li_I ions with the possibility of hopping or quantum tunneling between split 8l positions. Thus, in the case of Li_2CuZrO_4 a unique opportunity arises to study the behavior of restrictedly mobile lithium ions in contact with the system of copper spins and the influence of such a structure on its potential multiferroic behavior.

In our previous works [8, 9] using experimental and theoretical studies of NMR spectra, electron paramagnetic resonance, and the dielectric response data of oriented powder samples γ-Li_2CuZrO_4 it was shown that lithium ions in the half-filled Li_I position perform hopping motions between paired sites. As the temperature decreases, this motion slows down and an effective electric dipole is formed when the ion is localized in one of the asymmetric positions. The sublattice of Li_I electric dipoles is glassy-like ordered at $T_g \approx 70$ K, which leads to the non-equivalence of spin centers in CuO_2 chains. Such an interaction between the electric and spin degrees of freedom can strongly affect the properties of the helical spin state in Li_2CuZrO_4 in the proximity of the quantum ferromagnetic critical point. In this context, it becomes interesting to study the effect of a magnetic field on the nucleation of a chiral phase above the Néel temperature in presence of an electric dipoles formed by of Li_I ions over doubled positions during the transition to the glassy state.

As noted above, most known spin-chain compounds in which spin-helical structures are expected to appear belong to a wide class of sodium- and lithium-containing cuprates, where

lithium/sodium ions are either ordinary components of the crystal matrix ($LiCu_2O_2$, Li_2CuO_2, $NaCu_2O_2$, $LiCuVO_4$, $Li_3Cu_2SbO_6$, $LiCuSbO_6$), or (substituents) impurities ($La_2Cu_{1-x}Li_xO_4$). In all cases, NMR on alkali metal nuclei are an effective tool for studying phase transitions and other transformations of the spin structure [1, 5, 10–12]. It should be noted that metal-oxide systems containing lithium or sodium have recently attracted big attention as materials for batteries, as well as a subject of the fundamental studies of various aspects of the diffusion of light ions in solids. NMR turned out to be a unique local method for direct observation and study of lithium mobility in different substances including the concentrated magnets (see, for example [13–15]). That is why we choose NMR as the main experimental method in this work. This article presents the results of studying the ^{7}Li NMR spectra in Li_2CuZrO_4 depending on the magnetic field and sample orientation. The temperature behavior of the line width and shift above the ordering temperature, as well as the transformation of the spectra at low temperatures under application of different external magnetic field values, are studied.

2. Experimental details

The samples were fabricated and their structure was characterized at the Institute of Solid State Physics and Materials Science, Dresden, similarly to the procedure described in [16]. The field dependences of static magnetization at low temperature were obtained using a Quantum Design SQUID magnetometer. NMR measurements were done on ^{7}Li nuclei in fields up to 8.15 T in a wide temperature range. The ^{7}Li nucleus has a spin $S = 3/2$ and has a quadrupole moment $^7Q = -0.04$ barn. The experiments were carried out using a broadband pulsed NMR spectrometer Redstone manufactured by Tecmag. The spectra of nuclear magnetic resonance, due to their strong inhomogeneous broadening, could not be obtained by the Fourier transformation of the spin echo at the Larmor frequency. To get the correct spectra for the step-by-step sweeping of the external magnetic field, the integration of the intensity of the power signal of echo at each point of the field was used. Since the signal amplitude was not calibrated at different temperatures, the obtained spectra were normalized to the amplitude maximum for convenience of presentation.

3. Results and discussion

In a zero external magnetic field, Li_2CuZrO_4 passes into the antiferromagnetic state at a temperature $T_N \approx 6.5$ K [16]. From the temperature dependence of the heat capacity of a powder sample in various external magnetic fields presented in [16], one can construct the field dependence of the Néel temperature (Figure 2), which is well described by the empirical formula

$$T_N \sim (1 - B/B_0)^2, \tag{1}$$

where B_0 is the field where antiferromagnetic order is completely suppressed. From the approximation, the suppression field B_0 can be estimated as 16 T. Since the g-factor is anisotropic [8], a quasi-crystal was prepared from the powder by the method described in [8]. By orienting the powders at room temperature in a strong magnetic field and fixing them with epoxy resin, we obtained a sample with a magnetic "easy" axis parallel to the a-axis (the other two crystallite axes are located arbitrarily in a plane perpendicular to the a-axis). On such a quasicrystal, the field dependence of the magnetization was measured at a temperature of 2.5 K, which is definitely below T_N. It is not possible to estimate a magnetic moment per formula unit due to the presence of epoxy resin in the composition of the sample, but the shape of the curve indicates that at 7 T the magnetization is still far from saturation. A kink of the curve that is typical for

a spin-flop transition is observed in a field $B_1 \approx 3.5$ T directed along the easy a-axis (Figure 2).

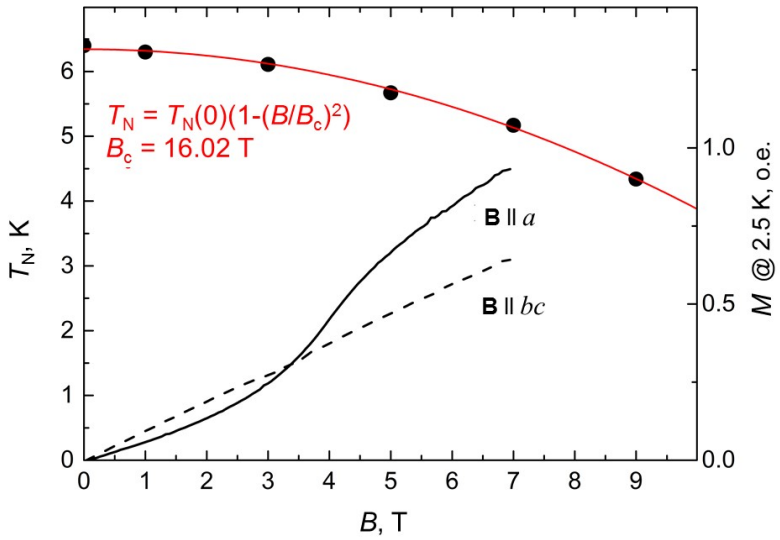


Figure 2. Magnetic field dependence of the Néel temperature (left axis) and magnetization (right axis) measured at 2.5 K in two field orientations. The field dependence of the Néel temperature is approximated by formula (1).

The temperature transformation of the NMR spectra obtained above the ordering temperature in both external field orientations in fields below and above B_1 is shown in Figure 3. Both in low fields and at 8.15 T the signals from Li_I (low-field line) and Li_{II} (high-field line) nuclei in the planar field orientation below ≈ 100 K while temperature decreases. This deviation is caused by two reasons: the opposite sign of related hyperfine tensor component and the gradual suppression of the hopping motion of the Li_I ion between doubled structural positions [8]. The inhomogeneous broadening of both components is caused by the difference of the time-averaged internal field registered by different nucleus. The origin of these dynamic internal field is the spin fluctuations of magnetic copper ions. Slowing down of fluctuations produces the similar temperature dependence of the inhomogeneous width of both components, since caused by the same mechanism. This allows us to extract the additional broadening w' of the low-field line associated with the freezing of the ion motion at the Li_I split site. Using formula [17]

$$w'(T) = w_R[1 + (w_R/(B-1)\exp(E_A/k_BT)]^{-1} + D, \quad (2)$$

where w_R is the contribution to the linewidth from the dipole-dipole interaction, B and D are temperature-independent parameters, we can estimate the activation energy of hopping $E_A = 101 \pm 2.3$ K (see inset in the right panel of figure 4). The assumption of additivity of different contributions to the linewidth is not completely correct, but when the inhomogeneous broadening is caused by a variation in the average field values at the nuclei positions, it makes it possible to estimate quite well the order of magnitude of the activation energy. Freezing of Li_I ions in an unsymmetrical position causes an additional shift of its NMR signal in this temperature range. Except for this motion contribution, both the shift K and the line broadening w are caused mainly by the interaction with the copper spin system. In a purely paramagnetic region, one should expect that the local fields at the lithium position will be proportional to the time-averaged value of z-component of copper spin and, accordingly, proportional to the external field. As it can be seen in figure 4, the shift and linewidth behave similarly for both

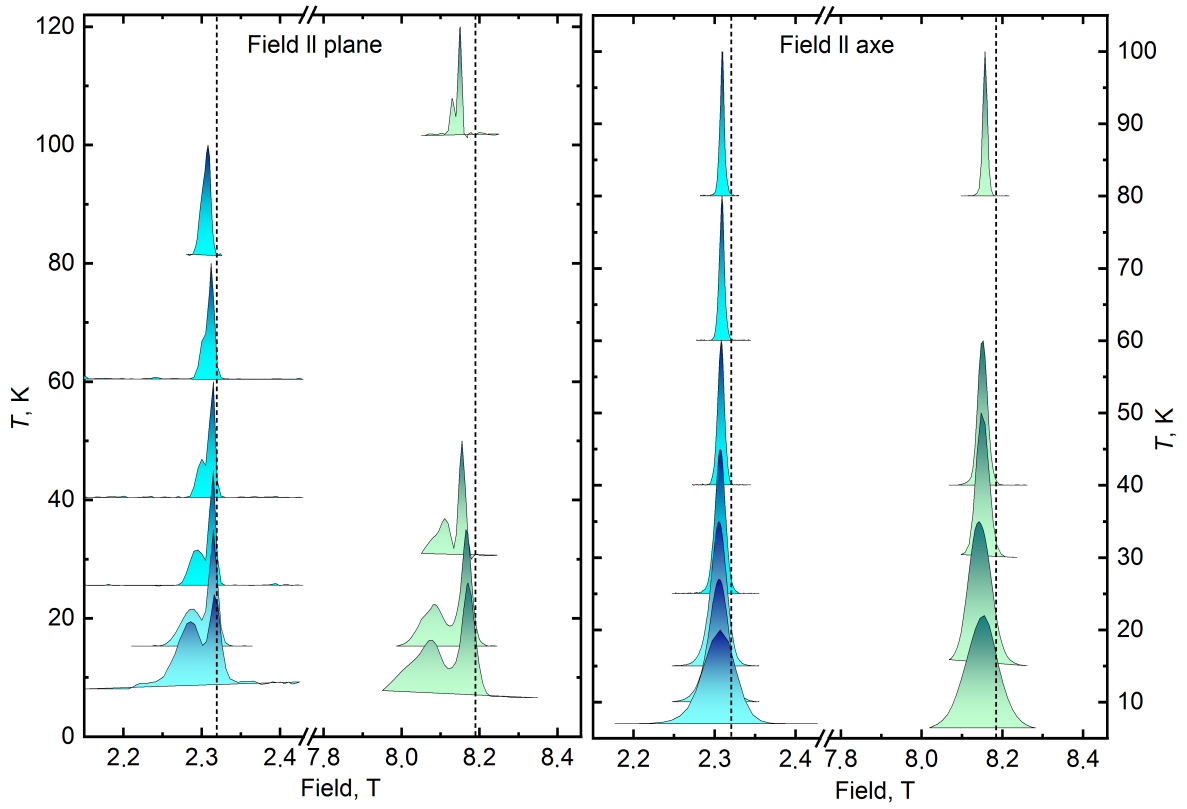


Figure 3. ^{7}Li NMR spectra obtained at different orientations of the quasi-crystal above the Néel temperature in fields above (blue color) and below (green color) the spin-flop transition.

field values, but they grow with field by factors of 2.36 and 2.83 correspondingly with the field, while the field changes by a factor of 3.54. This difference indicates that the system is not in a purely paramagnetic but strongly correlated at temperatures much higher than T_N. It can be confirmed by the ESR data [18], demonstrating the deviation of the effective g-factor from the high-temperature value, accompanied by an increase in the linewidth at temperatures below 100 K (having a much shorter measurement time scale, ESR is sensitive to the slowdown of spin dynamics at higher temperatures than NMR) . Recently the existence of a dynamic chiral-vector phase above the ordering temperature was discovered in similar compound $LiCuVO_4$ formed from spin chains with a strongly frustrated combination of NN and NNN exchanges. This phase is characterized by the existence of not only one-dimensional helical structures with a very large correlation length (up to the appearance of a long-range order), but also the development of ferroelectricity in external magnetic fields [19]. Apparently, the development of similar structures can also be expected in Li_2CuZrO_4 .

The magnetic transition occurring in the ordered phase in a field of about 3.5 T is reflected in the NMR spectra (figure 5). Spin flop transition is observed in $\mathbf{B}_{ext} \perp bc$ plane therefore the helicoid contains the spins perpendicular to the chain plane in zero field. So, the spin structure is either a cycloid ($\mathbf{k} \parallel b$) or a "screw" ($\mathbf{k} \parallel c$) [20]. As shown in [21], a magnetic structure at metamagnetic transition (for example, induced by a field) can transform somewhat differently in presence of helical correlations than in collinear antiferromagnets. In a field range between the transition field and the saturation field, the cycloid or "screw" transforms into inharmonic configuration (see the description and Fig. 6 in [22]), where not only the first, but also the second degree of the sine or cosine of spin-field angle appears in magnetization function. Another

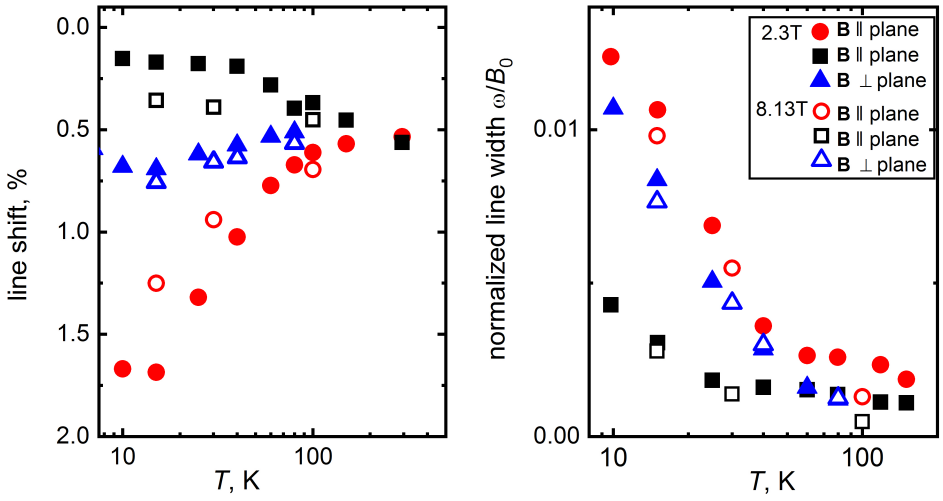


Figure 4. Temperature dependence of the line shift (a) and line width (b) of the ^{7}Li NMR spectrum in different orientations of the quasi-crystal at $B > B_{sf}$ (right axes of both panels) and $B < B_{sf}$ (left axes of both panels) . The black squares and red circles mark the parameters of the two lines of the spectrum at $\mathbf{B}_{ext} \perp a$, the blue triangles are the parameters of the $\mathbf{B}_{ext} \parallel a$ spectrum. Inset of the right panel: temperature dependence of the additional contribution to the width of the high-field component of the spectrum at $\mathbf{B}_{ext} \perp a$. The dashed line is an approximation according to equation (2).

scenario considers the rotation of the chirality vector, which is oriented along the field above the metamagnetic transition with the subsequent gradual alignment of the helix spins along the field. The field applied along the chirality vector generates a spiral-conical phase, which is effectively leads to the additional spin magnetization proportional to the field along the field. And finally, the field in the third orientation entails a slight increase in the spin magnetization in its direction, which is not proportional to the external field. Dipolar model gives estimations of the Li_{II} nuclear hyperfine tensor values $A_{aa} = 0.31\,\mathrm{kOe}/\mu_B$, $A_{bb} = 0.10\,\mathrm{kOe}/\mu_B$ and $A_{cc} = -0.23\,\mathrm{kOe}/\mu_B$, while the off-diagonal components are close to zero. The Li_I tensor components can be estimated as $A_{aa} = 0.4\,\mathrm{kOe}/\mu_B$, $A_{bb} = 0.45\,\mathrm{kOe}/\mu_B$ and $A_{cc} = -0.17\,\mathrm{kOe}/\mu_B$, with $A_{ab} = A_{ba} = 1.07\,\mathrm{kOe}/\mu_B$. A small number of experimental points does not allow us to refine the obtained values, but the estimation allows to conclude that

(i) The A_{aa} components are comparable with experimentally observed values, the rest of the numbers are much smaller than the experimental values, that indicates a significant contribution of the contact hyperfine field from the nearest copper ions.

(ii) The signs of calculated tensor components look reasonable. Also, considering the ordered state, we must make an assumption about the mutual orientation of the spin helices. We will adhere to a model that assumes a phase difference equal to π between adjacent spirals in a plane and equal to $\pi/2$ between spirals in neighboring planes. This configuration removes the frustration of interchain interactions and promotes magnetic order.

As shown in [9], the low-field spectrum at $\mathbf{B} \parallel a$ consists of a broad signal from Li_I and a two-horn signal from Li_{II} due to field modulation created by nearby copper spin helices. The field transformation of the NMR spectrum at $\mathbf{B} \parallel a$ is easily understandable within **k**-vector rotation scenario: the specific "two-horn" contribution of the signal from Li_{II} , caused by the sinusoidal modulation of the copper spin component along the a- axis, transforms into a single peak with

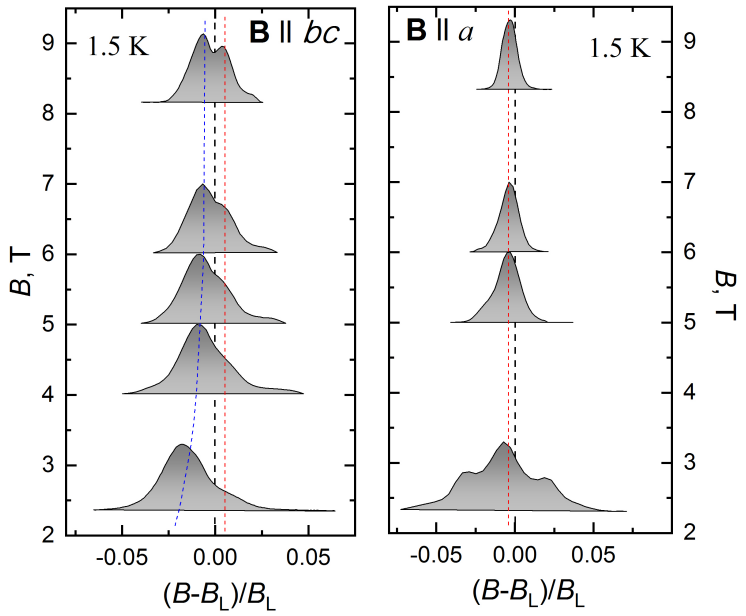


Figure 5. ^{7}Li NMR spectra obtained at 1.5 K at $\mathbf{B}_{\text{ext}} \perp a$ (a) and $\mathbf{B}_{\text{ext}} \parallel a$ (b) in different fields. For best representation, the relative shift of the line from the Larmor field $B_{\text{L}} =^7 \gamma\omega_{\text{L}}$. is shown on X-axis. Red dash line shows field-independent relative shift, blue line shows field-dependent relative shift.

absolute shift proportional to the external field. The transformation of the Li_{I} signal is more complicated, since it has nonzero matrix elements A_{ba}, but for the above mutual orientation of spins in the neighboring helices, the calculated splitting caused by spatial modulation of the in-plane spin components does not exceed 0.015 T, which is less than the total linewidth. Thus, above the transition, we get a Gauss-like spectrum with field-independent relative shift. A more complex scenario [22] does not match the experimental results, since should lead to a doubling of the intensity of one of the split Li_{II} line shoulders. The situation looks somewhat more complicated for the perpendicular orientation of the field, where the sample consists of all possible in-plane orientations of the powder particles. Nevertheless, it is possible to make qualitative estimations for two extreme cases: a "screw" ($\mathbf{k} \parallel$ chain i.e. c-axis) and a cycloid ($\mathbf{k} \perp$ chain i.e. b-axis) in a low external field. The spin flop in this orientation is not observed in the magnetization data, so the transformation of the spin system occurs continuously. When the field is parallel to the **k**-vector, the helix gradually transforms into a conical phase and the contribution from the projection of spins parallel to the field increases proportionally to the field. When the field is perpendicular to **k**-vector, the increase in the spin magnetization parallel to the field occurs in a more complex manner. The spiral pattern is retained to a certain extent, and one can expect the non-field-proportional increasing contribution of field-canted spins. Taking into account that for both positions of lithium $A_{bb} > 0$, and $A_{cc} < 0$, it can be expected that in the case of a "screw" the field-proportional signal component will have an absolute shift to larger fields, and the non-proportional component to smaller ones. For the "cycloid" the situation is opposite. The experimental spectrum contains a high-field component with a field-independent relative shift and a low-field component with a field-dependent relative shift. This means that most likely spin structure realized in Li_2CuZrO_4 is a "screw". Such a spin structure excludes the inversed Dzyaloshinskii-Moriya interaction, since the chirality vector is parallel to the helix propagation vector. Therefore, multiferroic behavior in the compound is not expected to be observed.

4. Summary

The results of studying the properties of the Li_2CuZrO_4 quasi-crystal depending on the magnetic field can be summarized as follows. The anisotropy of the field behavior of the magnetization at low temperatures shows that the chirality vector of the helical ordering in the AFM phase is aligned in the chain plane. The transformation of the NMR spectra with an increase in the magnetic field supported by calculation of the dipole fields at the lithium positions gives reason to conclude that the most probable spin structure is the "screw". Dynamic correlations of the copper spin system are observed much higher than the ordering temperature and can be a moderator of a certain type of glassy freezing of Li_I electric dipoles at $T_g = 70\,\mathrm{K}$. This dielectric subsystem is characterized by an activation energy $E_a = 101\,\mathrm{K}$ and, in turn, modulates the crystal field at the copper positions through oxygen ligands. This results in the formation of a "screw" rather than a "cycloid" helix. Thus, Li_2CuZrO_4 is an paradoxical example of the system where the interaction of strongly correlated dielectric and magnetic subsystems at temperatures above ordering does not promote but prevents multiferroic behavior in the ordered phase.

Acknowledgments

The work was supported by the budget financing of Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS

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