

# Interplay of quantum paraelectricity and quantum magnetism in $\text{Li}_2\text{ZrCuO}_4$

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We report  $^7\text{Li}$  nuclear magnetic- (NMR),  $\text{Cu}^{2+}$  electron spin resonance (ESR) and complex dielectric constant  $\epsilon = \epsilon' + i\epsilon''$  studies of the frustrated quantum spin-1/2 chain cuprate  $\gamma\text{-Li}_2\text{ZrCuO}_4$ . Mobile and immobile  $\text{Li}^+$  ions are located in this system at regularly occupied  $\text{Li}_{\text{II}}$  sites and half-occupied  $\text{Li}_{\text{I}}$  sites, respectively. The  $\text{Li}_{\text{I}}$  ions form a frustrated sublattice of tunnelling pseudospin-1/2 centers or quantum Ising-like reorienting electric dipoles which is intercalated between the planes of spin-1/2  $\text{CuO}_2$  chains. The  $^7\text{Li}$ -NMR data give clear indications for a glass-like ordering of the mobile  $\text{Li}_{\text{I}}$  sublattice at  $T_g \sim 80 - 100$  K which is further confirmed by frequency-dependent anomalies of  $\epsilon'$  and  $\epsilon''$  around  $T_g$ . Related to the ordering of the electric dipoles, the  $\text{Cu}^{2+}$  ESR results give evidence for the emergence of nonequivalent spin sites in the  $\text{CuO}_2$  chains at  $T < T_g$ . Such a remarkable interplay between electrical and spin degrees of freedom suggests  $\text{Li}_2\text{ZrCuO}_4$  as a new intrinsic magnetoelectric composite where a frustrated one dimensional (1D) quantum Heisenberg magnetic sublattice meets a frustrated 3D quantum Ising electric sublattice.

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Search for new functional materials providing magnetic phase control using an electric field or vice versa stimulated a great interest to multiferroic materials with coupled magnetic and electrical order parameters. Only very few materials of this kind have been found and in most cases this coupling was not strong enough for possible technological applications [1]. In quest of enhanced cross-coupling effects attention has been recently attracted to spin-1/2 chain compounds  $\text{LiVCuO}_4$  [2] and  $\text{LiCu}_2\text{O}_2$  [3], where ferroelectricity was found to occur simultaneously with a spiral magnetic order. Further efforts are focussed on *extrinsic* composite media that combine, e.g., a material with a large piezoelectric constant and a material with a large magnetostriction and on *intrinsic* magnetoelectric (ME) composites, i.e. single-phase systems where a magnetic sublattice meets an electrically active one as in the most extensively studied multiferroic  $\text{BiFeO}_3$  [1].

Here we report that the quantum spin-1/2 chain cuprate  $\text{Li}_2\text{ZrCuO}_4$  provides a peculiar new type of *intrinsic* ME composites where the quantum magnetism of  $\text{CuO}_2$  chains meets the quantum behavior of an electrically active sublattice of tunnelling  $\text{Li}^+$  ions. Just recently this frustrated quantum spin system with the magnetic ordering temperature  $T_N \approx 6$  K was shown to exhibit unusual magnetic properties due to the proximity to a quantum critical point [5]. Though showing indications for an incommensurate helical spin structure at  $T < T_N$  no ferroelectricity associated with the spin order has been however detected hitherto [4]. In contrast, our  $^7\text{Li}$  nuclear magnetic- (NMR),  $\text{Cu}^{2+}$  electron spin resonance (ESR) and dielectric constant measurements reveal that a coupling between active electrical and magnetic

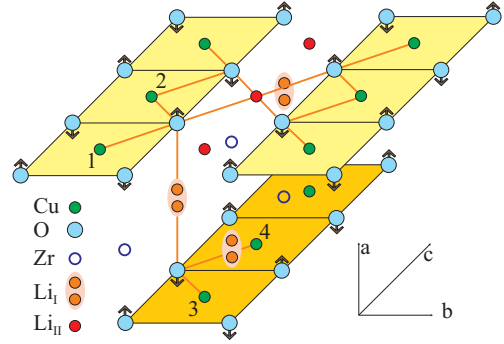


FIG. 1: (Color online). Fragment of slightly idealized  $\gamma\text{-Li}_2\text{ZrCuO}_4$  structure with the supertransferred  $\text{Cu-O-}^7\text{Li}_{\text{I,II}}$  bonds. Arrows show schematically the oxygen ion displacements in the real structure.

degrees of freedom occurs already in the paramagnetic regime far above  $T_N$ . We argue that this peculiar effect is due to the interaction of interpenetrating magnetic and electrical sublattices formed specifically in  $\text{Li}_2\text{ZrCuO}_4$ .

The orthorhombic crystal structure of  $\gamma\text{-Li}_2\text{ZrCuO}_4$  [6] is composed of chains formed by edge-shared  $\text{CuO}_4$  plaquettes running along the  $c$ -axis (Fig. 1). Owing to an almost  $90^\circ$   $\text{Cu-O-Cu}$  bonding geometry the quantum  $S=1/2$  spins of  $\text{Cu}^{2+}$  ions are coupled along the chain by the nearest neighbor (NN) ferromagnetic and the next-NN (NNN) antiferromagnetic exchange interaction causing a spin frustration [5]. The  $\text{CuO}_2$  chains in  $\text{Li}_2\text{ZrCuO}_4$  form planes similar to, e.g.,  $\text{LiCu}_2\text{O}_2$ . However, the interplane distance of  $4.7 \text{ \AA}$  markedly exceeds that of other quasi-2D cuprates. At variance with many

other Li-containing cuprates the Li ions in  $\text{Li}_2\text{ZrCuO}_4$  occupy two different types of positions:  $4b$  ( $\text{Li}_{\text{II}}$ ) with the 100% occupancy and  $8l$  ( $\text{Li}_{\text{I}}$ ) with an occupancy of 50% (Fig. 1). An unusually high thermal vibration parameter suggests a splitting of the  $\text{Li}_{\text{I}}$  position[6], i.e. the  $\text{Li}_{\text{I}}$  ion can hop between two contiguous  $8l$  positions. Such a situation can be modeled by an anharmonic double-well potential, that is the  $\text{Li}_{\text{I}}$  ion can be approximated by a two-level system (TLS) described in terms of tunnelling pseudospin  $s=1/2$  centers with a quantum reorienting electric dipole directed along the  $a$ -axis:  $d_a = |e|ds_z$ . Here  $d$  is the extension of the  $\text{Li}_{\text{I}}$  split position along the  $a$ -axis. Thus, the  $\text{Li}_{\text{I}}$  subsystem can be described as a 3D pseudo-tetragonal pseudospin-1/2 lattice though actually we deal with nearly square  $\text{Li}_{\text{I}}$  lattices sandwiched between the adjacent planes of  $\text{CuO}_2$  chains (Fig. 1).

The effective TLS-Hamiltonian for the  $\text{Li}_{\text{I}}$  subsystem using the pseudo-spin notation can be written as follows:

$$\hat{H}_{\text{Li}} = \sum_{i<j} I_{ij}^{\parallel} \hat{s}_{iz} \hat{s}_{jz} + \hbar\Omega \sum_i \hat{s}_{ix} + \sum_{i<j} I_{ij}^{\perp} \hat{s}_{ix} \hat{s}_{jx}, \quad (1)$$

where the first term describes the NN  $\text{Li}_{\text{I}}$  - $\text{Li}_{\text{I}}$  interaction, the second one does the  $\text{Li}_{\text{I}}$  tunnelling between contiguous  $8l$  positions with the frequency  $\Omega$ , while the third one does the correlated exchange tunnelling for NN and more distant  $\text{Li}_{\text{I}}$  sites. The Hamiltonian (1) describes the well known pseudospin-1/2 transversal field Ising model frequently used in the theory of (anti)ferroelectrics and quantum glasses. The phase ordering depends essentially on the relation between  $\hbar\Omega$  and effective NN coupling energy  $I_{nn}^{\parallel}$ , however, it is an inter-plane frustration and/or the coupling to the spin system that governs the  $\text{Li}_{\text{I}}$  dipole ordering. Turning to a magnetoelectric coupling between the  $\text{Cu}^{2+}$  planes and the  $\text{Li}_{\text{I}}$  pseudospin-1/2 sublattice one should first note that the  $\text{Li}_{\text{I}}$  ion hopping between two contiguous  $8l$  positions modulates the  $2p$  orbital occupation at nearest oxygen ions and their displacement. The latter in turn modulates locally the  $\text{Cu}^{2+}$  crystal field, the in-plane  $t^{\parallel}$  and inter-plane  $t^{\perp}$  transfer integrals within a single-band Hubbard-type model which describes the electron (hole) transfer between the  $\text{CuO}_4$  plaquettes of the magnetic subsystem. These correlated electronic models can be mapped afterwards on a Heisenberg model for the Cu spins hence resulting in a modulation of the corresponding exchange integrals. Focussing on one of the  $\text{Li}_{\text{I}}$  pseudospin sites (Fig. 1), both for the  $\text{Cu}^{2+}$  crystal field  $V_{cf}$  and the in-plane  $\text{Cu}^{2+}$ - $\text{Cu}^{2+}$  charge transfer we deal with an anticorrelation effect leading to a local nonequivalence of upper and lower  $\text{CuO}_2$  chains:  $\Delta V_{cf}(1) = -\Delta V_{cf}(4) \propto s_z$ ;  $\Delta V_{cf}(2) = -\Delta V_{cf}(3) \propto s_z$ . The interaction term of the two subsystems reads

$$\Delta H_{tr}^{\parallel} = \Delta t^{\parallel} (\hat{a}_1^{\dagger} \hat{a}_2 - \hat{a}_3^{\dagger} \hat{a}_4) s_z + h.c., \quad (2)$$

where  $\hat{a}_i^{\dagger}$  and  $\hat{a}_j$  are electronic annihilation and creation operators and  $t^{\parallel}$  denotes the NN-transfer integral in the

chain direction. The modulation of the inter-plane  $\text{Cu}^{2+}$ - $\text{Cu}^{2+}$  electron transfer reads as follows

$$\Delta H_{tr}^{\perp} = \Delta t^{\perp} \left( \sum_{i=1,2;j=3,4} \hat{a}_i^{\dagger} \hat{a}_j \right) \hat{s}_x + h.c.. \quad (3)$$

The  $\text{Li}_{\text{I}}$  sublattice might provide an essential coupling between the spin planes and explain the relatively high temperature of the 3D magnetic ordering despite a large interplane distance. In fact, the magnetic  $\text{Cu}^{2+}$  sublattice does produce an effective electric field which acts on the  $\text{Li}_{\text{I}}$  dipoles. Thus,  $\text{Li}_2\text{ZrCuO}_4$  provides a unique model system to study a synergetic interplay of the quantum magnetic and the quantum electric subsystems forming a natural laminar composite structure.

To verify the above conjectures we have carried out  $^7\text{Li}$  NMR,  $\text{Cu}^{2+}$  ESR, and dielectric measurements on oriented polycrystals of  $\text{Li}_2\text{CuZrO}_4$  (for the synthesis, see Ref. 6). Owing to a small anisotropy of the  $g$ -factor (see below) it was possible to align powder particles mixed with epoxy resin in a strong magnetic field. After hardening of the resin a sample with a magnetic "easy" axis parallel to the  $a$ -axis has been obtained.

We start with the  $^7\text{Li}$  NMR measurements that proved to be very useful before to study both the magnetic ordering in cuprates [4, 8, 9] and the Li ion mobility (see, e.g., Ref. 7). The  $^7\text{Li}$  ( $I=3/2$ ) NMR spectra of  $\text{Li}_2\text{ZrCuO}_4$  samples were measured by a Tecmag pulse spectrometer in two orientations:  $\mathbf{H} \parallel \mathbf{a}$  and  $\mathbf{H} \perp \mathbf{a}$  by sweeping the magnetic field at a fixed frequency  $\omega_N = 38$  MHz. The signal was obtained by integrating the spin-echo envelope. The longitudinal  $T_1^{-1}$  and transversal  $T_2^{-1}$  relaxation rates were measured at the peak of the signal using the stimulated echo sequence and  $\pi/2 - \pi$  sequence, respectively. The quadrupole splitting, typical for  $^7\text{Li}$  nuclei in different cuprates [8, 9] and estimated to be of the order of 0.05 MHz, is unresolved in the spectrum which shape can be described by a single Gaussian line profile. In the paramagnetic state at high temperatures ( $T \geq 150 \text{ K} \gg T_N$ ) the  $^7\text{Li}$  NMR response of  $\text{Li}_2\text{ZrCuO}_4$  (Fig. 2) seemingly presents a single line. However, a careful analysis of the lineshape and  $T_2^{-1}$  rates shows that we deal with an unresolved superposition of two lines with a full width of 0.01 T, which may be ascribed to the response of the two lithium species, i.e. of the immobile  $\text{Li}_{\text{II}}$  and the mobile  $\text{Li}_{\text{I}}$  ions, respectively. For  $\mathbf{H} \perp \mathbf{a}$  lowering the temperature below  $T \sim 100 \text{ K}$  allows for a clear separation of the NMR spectrum in two well resolved lines with a strong and unusual  $T$ -dependent frequency redshift and inhomogeneous broadening of the low field (left) line (Fig. 2) that can be associated with the NMR response of the mobile  $\text{Li}_{\text{I}}$  ions. For  $\mathbf{H} \parallel \mathbf{a}$  the signals from the different Li sites merge and only at temperatures  $T > T_g \sim 100 \text{ K}$  one can separate two contributions due to the narrowing of one of them, apparently of  $\text{Li}_{\text{I}}$ . A characteristic temperature  $T_g \sim 100 \text{ K}$  can be associated with the onset of the quenching of the  $\text{Li}_{\text{I}}$  hopping

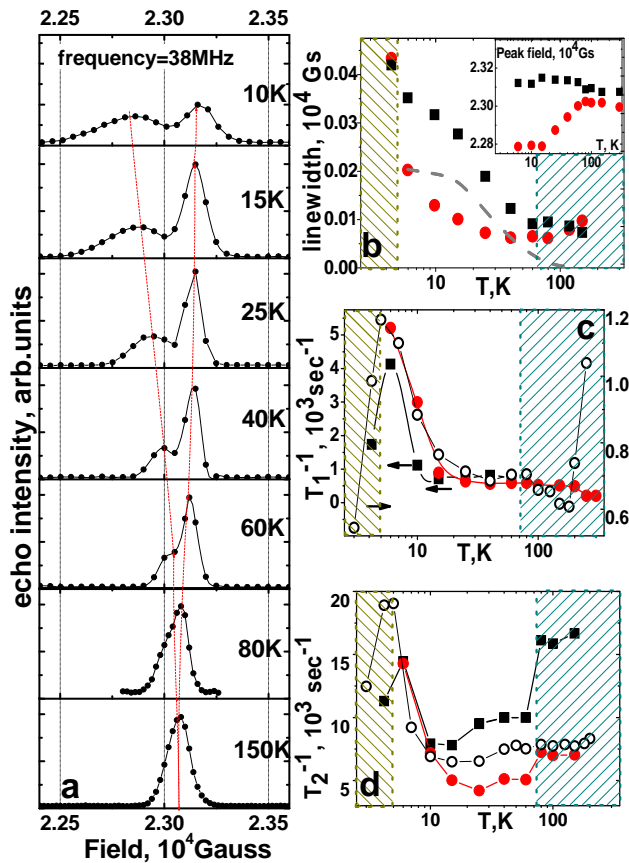


FIG. 2: (Color online). (a) - Selected  ${}^7\text{Li}$  NMR spectra of the oriented  $\text{Li}_2\text{ZrCuO}_4$  sample at  $\omega_N = 38.0$  MHz for  $\mathbf{H} \parallel \mathbf{a}$ ; (b) -  $T$ -dependence of the NMR linewidth for low- and high-field NMR lines. Dashed curve denotes an inhomogeneous broadening due to a glass-like ordering of  $\text{Li}_\text{I}$  ions. Inset shows the behavior of resonance fields; (c) and (d) -  $T$ -dependences of the spin-lattice  $T_1^{-1}$  and spin-spin relaxation rates  $T_2^{-1}$ , respectively. In (b), (c) and (d) open circles denote data for  $\mathbf{H} \parallel \mathbf{a}$ , filled squares and circles are data for low- and high-field lines for  $\mathbf{H} \perp \mathbf{a}$ , respectively.

between two equivalent positions, i.e. with the offset of the motional narrowing. It means that at  $T > T_g$  the  $\text{Li}_\text{I}$  pseudospin system reveals most likely a classical high-temperature paraelectric behavior. One should note that the  $T$ -dependence of the  ${}^7\text{Li}$  NMR linewidth for immobile  $\text{Li}_\text{II}$  ions (high-field right line) shows up a rather conventional low- $T$  rise due to the critical spin fluctuations developing with approach to  $T_N$ . Assuming roughly the same spin fluctuation contribution to both NMR signals one can single out the additional contribution to the inhomogeneous broadening of the left line (dashed line in Fig. 2b) whose  $T$ -dependence turns out to be typical for systems with mobile Li ions (see, e.g., Ref. 7). Note that the NMR motional narrowing takes place when the rate of fluctuations of the local magnetic fields and/or electric field gradient is of the order of the rigid lattice linewidth whereby the onset temperature for the motional narrow-

ing is usually correlated with the glass transition temperature  $T_g$  which thus in our case is of the order of 100 K.

The low- $T$  behavior of  $T_2^{-1}$  (Fig. 2d) with characteristic values of about  $10^4 \text{ s}^{-1}$  and a pronounced peak near  $T_N$  for both  ${}^7\text{Li}$  species and both field directions is typical for spin ordering cuprates [9]. The spin-lattice relaxation (SLR) rates  $T_1^{-1}$  for both Li species reveal a very similar temperature behavior with a nearly the same constant value of  $\sim 750 \text{ sec}^{-1}$  down to a low temperature  $T \sim 10$  K where both start to increase with a peak at  $T \sim 6$  K for the  ${}^7\text{Li}_\text{I}$  line and a divergence for the  ${}^7\text{Li}_\text{II}$  line in the case of  $\mathbf{H} \perp \mathbf{a}$ . The same behavior can be observed for the  $\mathbf{H} \parallel \mathbf{a}$  orientation where we deal with a hardly resolved contribution from both  ${}^7\text{Li}_\text{II}$  and  ${}^7\text{Li}_\text{I}$  nuclei.

A typical mobility induced SLR rate for  ${}^7\text{Li}$  NMR in a wide number of nonmagnetic solids is due to the quadrupole mechanism which is usually small as compared to a strong SLR due to a magnetic mechanism. In  $\text{Li}_2\text{ZrCuO}_4$  where strong magnetic fluctuations take place in the anisotropic lattice the decrease of relaxation rates below 100 K reflects the ceasing of the motion that was averaging local magnetic fields created by fluctuations of Cu magnetic moments. The anisotropic character of this motion becomes apparent in the different relaxation behavior in different field orientations. One can see in Fig. 2c,d that the increase of the rates is observed in the  $T_1$  for  $\mathbf{H} \parallel \mathbf{a}$  and in the  $T_2$  for  $\mathbf{H} \perp \mathbf{a}$  which are both caused by magnetic fluctuations perpendicular to the  $a$ -direction. To summarize this part, all  ${}^7\text{Li}$  NMR data clearly indicate a freezing of the  $\text{Li}_\text{I}$  paraelectric sublattice below  $T_g \sim 100$  K.

A direct evidence of a glass-like structural ordering of this sublattice can be provided by measurements of the complex dielectric constant  $\varepsilon = \varepsilon' + i\varepsilon''$  that have been performed with pressed pellets of  $\text{Li}_2\text{ZrCuO}_4$ . The behavior of the real part  $\varepsilon'$  above 300 K (Fig. 3) evidences most likely a contribution of  $\text{Li}_\text{I}$  to ionic conductivity. However, the most remarkable change of  $\varepsilon'$

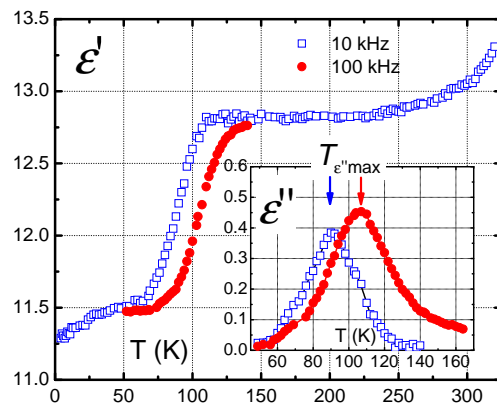


FIG. 3: (Color online). Temperature dependence of the real ( $\varepsilon'$ ) and imaginary ( $\varepsilon''$ ) parts of the dielectric constant for a pressed sample of  $\gamma\text{-Li}_2\text{CuZrO}_4$  at 10 and 100 kHz.

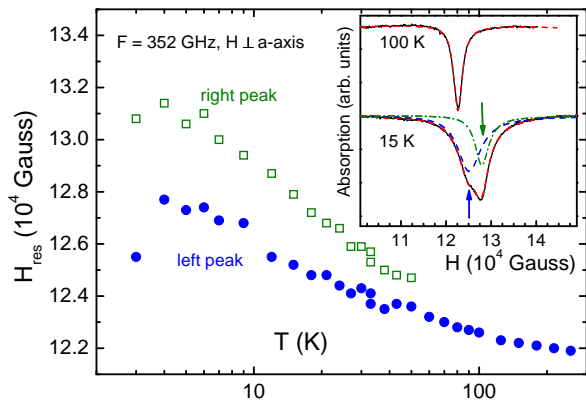


FIG. 4: (Color online). Inset: HF-ESR spectra at 352 GHz for  $\mathbf{H} \perp \mathbf{a}$  at 100 K and 15 K, black solid lines. Dash lines (red online) are fits indistinguishable from the experiment. Decomposition of the spectrum at 15 K in two lines is shown by dash (blue online) and dash-dot (green online) curves. Main panel:  $T$ -dependence of the resonance field of the peak(s).

occurs in the  $T$ -range 50-150 K. A significant reduction of  $\epsilon'$  clearly indicates a freezing of the paraelectric subsystem in  $\text{Li}_2\text{ZrCuO}_4$ . Frequency dependence of the step in  $\epsilon'(T)$  concomitant with the shift of the peak temperature  $T_{\epsilon''_{\text{max}}}$  of the imaginary part  $\epsilon''(T)$  to higher  $T$  with increasing frequency (Fig. 3, inset) is typical for a glass-like transition (see, e.g., Ref. 10). As it was anticipated from the  $^7\text{Li}$  NMR study, this transition is spread over a wide  $T$ -range whereby  $T_{\epsilon''_{\text{max}}}$  is close to the characteristic temperature  $T_g$  identified in the NMR data.

How can the magnetic  $\text{Cu}^{2+}$  subsystem respond to this effect? First of all one may anticipate a change of the crystal field and of the effective  $g$ -factors for  $\text{Cu}^{2+}$  ions which can be detected by the ESR technique. We have carried out high field ESR (HF-ESR) experiments in the sub-THz frequency domain in a broad temperature range with a home-made spectrometer (for details, see Ref. 11). In the high- $T$  regime above  $T_g \sim 100$  K the ESR spectrum comprising a single Lorentzian absorption line has been found (Fig. 4, inset). The resonance field of the line corresponds to  $g$ -factors amounting to  $g_{\parallel} = 2.19$  and  $g_{\perp} = 2.02$  for  $\mathbf{H} \parallel \mathbf{a}$  and  $\mathbf{H} \perp \mathbf{a}$ , respectively. Such a typical anisotropy of the  $g$ -factor enables to unambiguously identify the ESR response with the  $\text{Cu}^{2+}$  ions in a distorted square planar ligand coordination [12]. A remarkable evolution of the ESR spectrum has been observed upon cooling the sample below  $\sim 100$  K where the spectrum begins to split in two lines. The shape of the spectrum can be perfectly fitted with two Lorentzians of similar intensity (Fig. 4, inset). The representative temperature dependences of the resonance fields at a frequency of 352 GHz obtained from the fit are shown in Fig. 4. The two lines in the HF-ESR spectrum whose separation increases with decreasing  $T$  can be straightforwardly assigned to the occurrence of two nonequivalent Cu sites with slightly dif-

ferent  $g$ -factors. Since the  $g$ -factor is very sensitive to the symmetry and the strength of the ligand electrical field potential  $V_{cf}$ , the splitting of the spectrum gives evidence that the mobile  $\text{Li}_I$  ions freeze in the lattice on a particular pattern yielding two distinct local crystal field potentials  $V_{cf} \pm \Delta V_{cf}$  at the  $\text{Cu}^{2+}$  sites. The shift of both lines to higher fields indicates the onset of the low frequency spin correlations which develop in the low-dimensional spin systems far above  $T_N$ . Owing to a much shorter timescale of the ESR experiment they are detected at higher  $T$  compared to the NMR relaxation data (Fig. 2c,d). One should note that an additional decrease of  $\epsilon'$  below  $\sim 30$  K may be also related to the development of quantum magnetism in  $\text{CuO}_2$  chains that affects the glass-like ordered  $\text{Li}_I$  subsystem.

In conclusion, we have performed  $^7\text{Li}$  NMR,  $\text{Cu}^{2+}$  ESR, and dielectric measurements of the quantum spin-1/2 incommensurate chain cuprate  $\text{Li}_2\text{ZrCuO}_4$  where a unique interplay of mobile and immobile Li ions, both coupled with a single spin system, takes place. We conjecture that the mobile Li ions form a sublattice of quantum reorienting electric dipoles. The examination of the  $T$ -dependences of the  $^7\text{Li}$  NMR lineshape and the nuclear relaxation rates enables us to conclude that at  $T_g \sim 100$  K a glass-like structural ordering of this sublattice sets in. A direct proof of that is obtained in dielectric measurements which reveal a typical frequency-dependent behavior of the dielectric constant at these temperatures. A remarkable impact of the freezing of the paraelectric subsystem on the spin system is evidenced by the observation of a splitting of the  $\text{Cu}^{2+}$  ESR signal as a result of the developing of a local  $\text{Cu}^{2+}$  site nonequivalence. The obtained data put forward  $\text{Li}_2\text{ZrCuO}_4$  as a unique type of the intrinsic magnetoelectric composite material that shows a remarkable interplay of interpenetrating quantum paraelectric and paramagnetic sublattices.

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