Interplay of quantum paraelectricity and quantum magnetism in Li_2ZrCuO_4

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We report ^{7}Li nuclear magnetic- (NMR), Cu^{2+} electron spin resonance (ESR) and complex dielectric constant $\epsilon = \epsilon' + i\epsilon''$ studies of the frustrated quantum spin-1/2 chain cuprate γ-Li_2ZrCuO_4. Mobile and immobile Li^+ ions are located in this system at regularly occupied Li_{II} sites and half-occupied Li_I sites, respectively. The Li_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 CuO_2 chains. The ^{7}Li-NMR data give clear indications for a glass-like ordering of the mobile Li_I sublattice at $T_g \sim 80-100$ K which is further confirmed by frequency-dependent anomalies of ϵ' and ϵ'' around T_g. Related to the ordering of the electric dipoles, the Cu^{2+} ESR results give evidence for the emergence of nonequivalent spin sites in the CuO_2 chains at $T < T_g$. Such a remarkable interplay between electrical and spin degrees of freedom suggests Li_2ZrCuO_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 $LiVCuO_4$ [2] and $LiCu_2O_2$ [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 $BiFeO_3$ [1].

Here we report that the quantum spin-1/2 chain cuprate Li_2ZrCuO_4 provides a peculiar new type of *intrinsic* ME composites where the quantum magnetism of CuO_2 chains meets the quantum behavior of an electrically active sublattice of tunnelling 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}Li nuclear magnetic- (NMR), Cu^{2+} electron spin resonance (ESR) and dielectric constant measurements reveal that a coupling between active electrical and magnetic 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 Li_2ZrCuO_4.

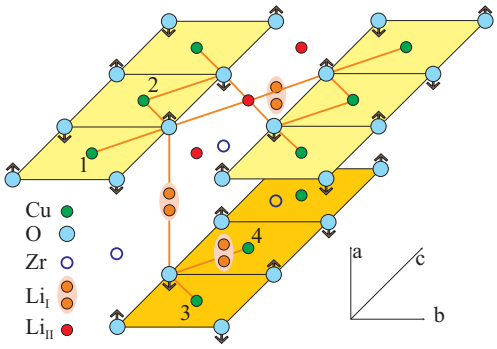

FIG. 1: (Color online). Fragment of slightly idealized γ-Li_2ZrCuO_4 structure with the supertransferred Cu-O-^{7}$Li_{I,II}$ bonds. Arrows show schematically the oxygen ion displacements in the real structure.

The orthorhombic crystal structure of γ-Li_2ZrCuO_4 [6] is composed of chains formed by edge-shared CuO_4 plaquettes running along the c-axis (Fig. 1). Owing to an almost 90° Cu-O-Cu bonding geometry the quantum S=1/2 spins of 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 CuO_2 chains in Li_2ZrCuO_4 form planes similar to, e.g., $LiCu_2O_2$. However, the interplane distance of 4.7 Å markedly exceeds that of other quasi-2D cuprates. At variance with many

other Li-containing cuprates the Li ions in Li_2ZrCuO_4 occupy two different types of positions: $4b$ (Li_{II}) with the 100 % occupancy and $8l$ (Li_I) with an occupancy of 50 % (Fig. 1). An unusually high thermal vibration parameter suggests a splitting of the Li_I position[6], i.e. the Li_I ion can hop between two contiguous $8l$ positions. Such a situation can be modeled by an anharmonic double-well potential, that is the Li_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 Li_I split position along the a-axis. Thus, the Li_I subsystem can be described as a 3D pseudo-tetragonal pseudospin-1/2 lattice though actually we deal with nearly square Li_I lattices sandwiched between the adjacent planes of CuO_2 chains (Fig. 1).

The effective TLS-Hamiltonian for the Li_I subsystem using the pseudo-spin notation can be written as follows:

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

where the first term describes the NN Li_I -Li_I interaction, the second one does the Li_I tunnelling between contiguous $8l$ positions with the frequency Ω, while the third one does the correlated exchange tunnelling for NN and more distant Li_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 Li_I dipole ordering. Turning to a magnetoelectric coupling between the Cu^{2+} planes and the Li_I pseudospin-1/2 sublattice one should first note that the Li_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 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 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 Li_I pseudospin sites (Fig. 1), both for the Cu^{2+} crystal field V_{cf} and the in-plane Cu^{2+}-Cu^{2+} charge transfer we deal with an anticorrelation effect leading to a local nonequivalence of upper and lower 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 Cu^{2+}-Cu^{2+} electron transfer reads as follows

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

The Li_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 Cu^{2+} sublattice does produce an effective electric field which acts on the Li_I dipoles. Thus, Li_2ZrCuO_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}Li NMR, Cu^{2+} ESR, and dielectric measurements on oriented polycrystals of Li_2CuZrO_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}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}Li (I=3/2) NMR spectra of Li_2ZrCuO_4 samples were measured by a Tecmag pulse spectrometer in two orientations: $\mathbf{H}\|\mathbf{a}$ and $\mathbf{H}\perp\mathbf{a}$ by sweeping the magnetic field at a fixed frequency ω_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}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 ($T \geq 150\,\mathrm{K} \gg T_N$) the ^{7}Li NMR response of Li_2ZrCuO_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 Li_{II} and the mobile Li_I ions, respectively. For $\mathbf{H}\perp\mathbf{a}$ lowering the temperature below $T\sim$100 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 Li_I ions. For $\mathbf{H}\|\mathbf{a}$ the signals from the different Li sites merge and only at temperatures $T>T_g$ ~100 K one can separate two contributions due to the narrowing of one of them, apparently of Li_I. A characteristic temperature T_g ~100 K can be associated with the onset of the quenching of the Li_I hopping

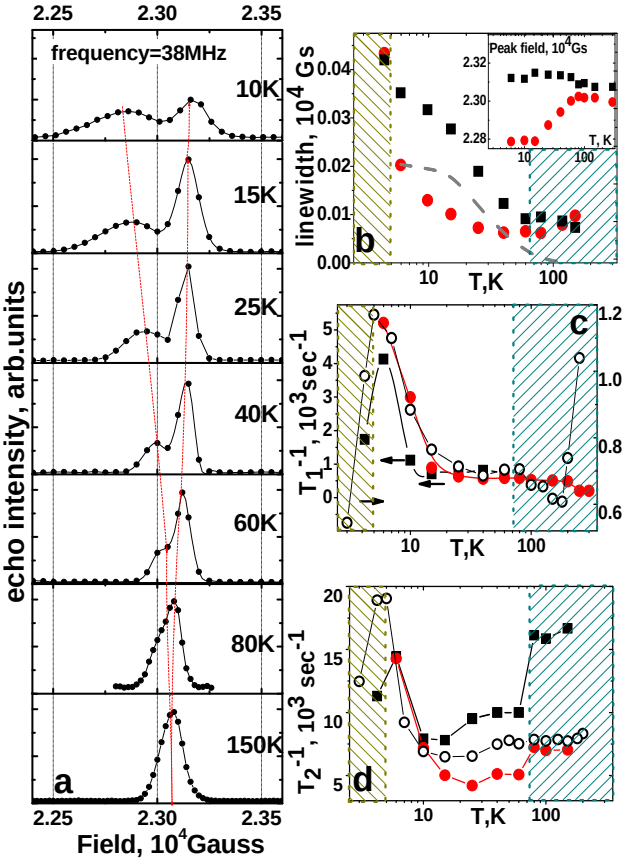

FIG. 2: (Color online). (a) - Selected ^{7}Li NMR spectra of the oriented Li_2ZrCuO_4 sample at $\omega_N = 38.0$ MHz for $\mathbf{H}\perp\mathbf{a}$; (b) - T-dependence of the NMR linewidth for low- and high-field NMR lines. Dashed curve denotes an inhomogeneous broadening due to a glass-like ordering of Li_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 $\mathbf{H}\|\mathbf{a}$, 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 Li_I pseudospin system reveals most likely a classical high-temperature paraelectric behavior. One should note that the T-dependence of the ^{7}Li NMR linewidth for immobile Li_{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 narrowing 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 $10^4\,s^{-1}$ and a pronounced peak near T_N for both ^{7}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 $\sim 750\,sec^{-1}$ down to a low temperature $T \sim 10$ K where both start to increase with a peak at $T \sim 6$ K for the ^7Li_I line and a divergence for the $^7Li_{II}$ line in the case of $\mathbf{H}\perp\mathbf{a}$. The same behavior can be observed for the $\mathbf{H}\|\mathbf{a}$ orientation where we deal with a hardly resolved contribution from both $^7Li_{II}$ and ^7Li_I nuclei.

A typical mobility induced SLR rate for ^{7}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 Li_2ZrCuO_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}Li NMR data cleary indicate a freezing of the Li_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 Li_2ZrCuO_4. The behavior of the real part ε' above 300 K (Fig. 3) evidences most likely a contribution of Li_I to ionic conductivity. However, the most remarkable change of ε'

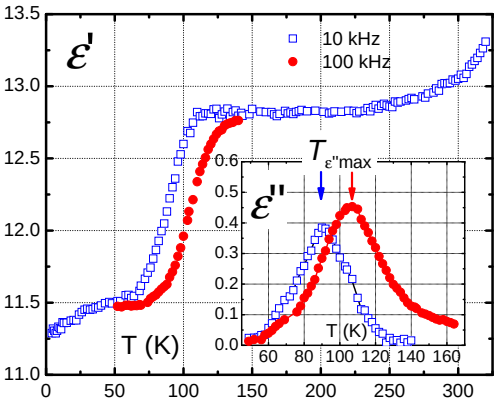

FIG. 3: (Color online). Temperature dependence of the real (ε') and imaginary (ε'') parts of the dielectric constant for a pressed sample of γ-Li_2CuZrO_4 at 10 and 100 kHz.

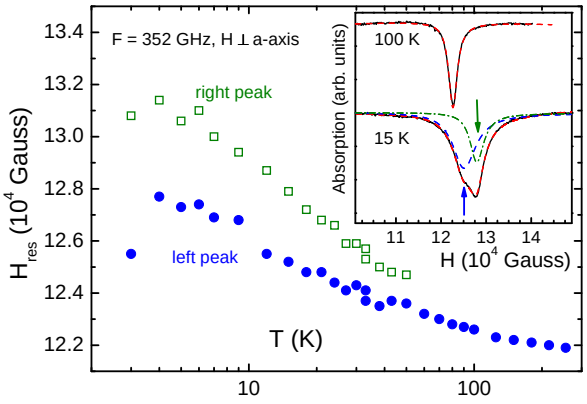

FIG. 4: (Color online). Inset: HF-ESR spectra at 352 GHz for $\mathbf{H} \perp \mathbf{a}$ at 100 K and 15 K, black solid lines. Dash lines (red online) are fits indistinguishable from the experiment. Decomposition of the spectrum at 15 K in two lines is shown by dash (blue online) and dash-dot (green 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 ε' clearly indicates a freezing of the paraelectric subsystem in Li_2ZrCuO_4. Frequency dependence of the step in $\varepsilon'(T)$ concomitant with the shift of the peak temperature $T_{\epsilon''\max}$ of the imaginary part $\varepsilon''(T)$ 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}Li NMR study, this transition is spread over a wide T-range whereby $T_{\epsilon''\max}$ is close to the characteristic temperature T_g identified in the NMR data.

How can the magnetic 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 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 $\mathbf{H} \| \mathbf{a}$ and $\mathbf{H} \perp \mathbf{a}$, respectively. Such a typical anisotropy of the g-factor enables to unambiguously identify the ESR response with the 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 ~ 100 K where the spectrum begin 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 different 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 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 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 ε' below ~ 30 K may be also related to the development of quantum magnetism in CuO_2 chains that affects the glass-like ordered Li_I subsystem.

In conclusion, we have performed ^{7}Li NMR, Cu^{2+} ESR, and dielectric measurements of the quantum spin-1/2 incommensurate chain cuprate Li_2ZrCuO_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}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 Cu^{2+} ESR signal as a result of the developing of a local Cu^{2+} site nonequivalence. The obtained data put forward Li_2ZrCuO_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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