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Frustrated magnet $\text{Li}_2\text{ZrCuO}_4$ - paramagnetism meets paraelectricity

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Abstract. By measuring ^7Li nuclear magnetic resonance, Cu^{2+} electron spin resonance and a complex dielectric constant in the frustrated spin-1/2 chain compound $\gamma\text{-Li}_2\text{ZrCuO}_4$ we find that the electric sublattice of mobile Li^+ ions orders glass-like at $T_g \sim 100$ K. This yields the emergence of non-equivalent spin sites in the spin-1/2 CuO_2 chains. We suggest that such a remarkable interplay between electrical and spin degrees of freedom may influence the properties of the spiral spin state in $\text{Li}_2\text{ZrCuO}_4$ which develops in this material at low temperatures.

1. Introduction

Search for new functional materials with cross-coupling between electrical and magnetic degrees of freedom constitutes an active research field in condensed matter physics and material science. Such coupling can be achieved, e.g., in artificial nanostructures that combine a material with a large piezoelectric constant and a material with a large magnetostriction. In this work we present an example of an *intrinsic* single-phase system where the magnetic sublattice meets the electrically active one. This is a frustrated quantum spin-1/2 chain cuprate $\text{Li}_2\text{CuZrO}_4$ with a possible spiral spin structure whose peculiar low-temperature magnetic properties have been recently discussed in terms of the proximity to a quantum critical point¹.

2. Materials and methods

The orthorhombic crystal structure of $\text{Li}_2\text{CuZrO}_4$ (space group *Cccm*) is composed of chains formed by edge-shared "flattened out" CuO_4 tetrahedra running along the *c*-axis. The CuO_2 strongly frustrated spin-1/2 chains in $\text{Li}_2\text{CuZrO}_4$ form planes similar to LiCu_2O_2 that are stacked along the *b*-axis. $\text{Li}_2\text{CuZrO}_4$ orders magnetically at ~ 6 K¹. The lithium ions in $\text{Li}_2\text{CuZrO}_4$ occupy two different types of positions: *4b* (Li_{II}) with occupancy about 100 % and *8l* (Li_{I}) with occupancy 50 % (fig 1.). X-ray and neutron diffraction data² reveals two contiguous crystallographic *8l* positions for the Li_{I} ion between which it can hop.

Below we report the results of ^7Li NMR, Cu^{2+} ESR, and dielectric measurements for the powder sample of $\text{Li}_2\text{CuZrO}_4$ which was oriented in magnetic field along *a*-axis and fixed in the epoxy (for the chemical synthesis, see Ref. 2). The ^7Li ($I = 3/2$) NMR spectra of $\text{Li}_2\text{CuZrO}_4$ samples were measured at a frequency of 38 MHz in the temperature range 6 - 300 K in magnetic field parallel to the *Cu*-planes by point-by-point sweeping of magnetic field. The quadrupole splitting which is estimated to be of the order of 0.05 MHz^3 ($\approx 0.003 \text{ T}$ in our experiment) is unresolved in spectrum of our oriented powder samples and line shape can be described by a single Gaussian profile. The frequency dependent dielectric measurements were performed with the pressed powder pellet of $\text{Li}_2\text{CuZrO}_4$ in the temperature range 4 - 300 K. Finally, we have also performed a temperature dependent high field electron spin resonance (HF-ESR) measurement at a frequency of ~ 350 GHz with the home-made spectrometer (for technical details, see Ref. 4)

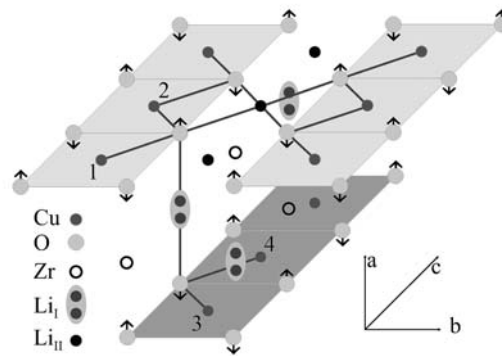


Fig. 1. Fragment of slightly idealized $\text{Li}_2\text{CuZrO}_4$ structure with the super-transferred Cu-O- $\text{Li}_{I,II}$ bonds. Arrows point to the oxygen ion displacements in a real structure.

3. Results and discussion

We start with the ^7Li NMR measurements which proved to be a very instructive tool to study both the Li ion mobility and the magnetic ordering in the cuprates. Well inside the paramagnetic state ($T > 150\text{K}$) the ^7Li NMR response of $\text{Li}_2\text{CuZrO}_4$ (Fig. 2) seemingly presents a single line, however, the lineshape and the T_2^{-1} nuclear relaxation rate analysis reveals a hardly resolved superposition of two Lorentzian lines with a full width of 0.01 T, which may be ascribed to the response of two lithium species with mobile Li_I ions and immobile Li_{II} ions, respectively. Lowering the temperature allows for a clear separation of two NMR signals. Below a characteristic temperature $T_g \sim 100\text{K}$ we observe two well separated lines with a different temperature behavior. The critical growth of the relaxation parameters (not shown) near magnetic phase transition temperature 5.5K and the temperature dependence of linewidth of the high-field (right) line allows us to assign it to the NMR response of the Li_{II} ions nuclei. Strong and unusual temperature dependent shift of the low-field (left) line position from 2.315T at 100K to 2.28T at 6K and inhomogeneous broadening of the left line (Fig. 3) clearly associated with the NMR response of mobile Li_I ions.

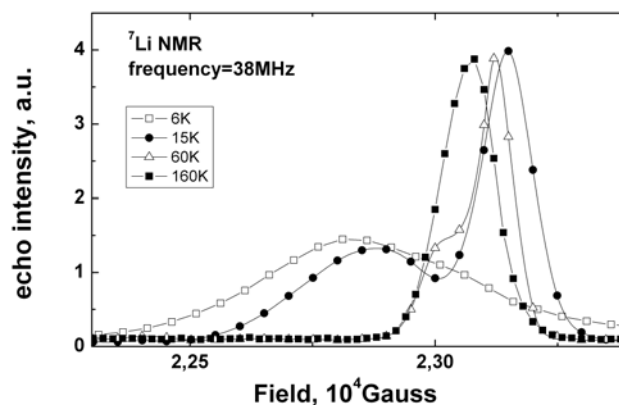


Fig. 2. The ^7Li NMR spectrum of the oriented $\text{Li}_2\text{CuZrO}_4$ sample with the resonance frequency of 38.0MHz at several temperatures

One should note that the temperature dependence of the Li NMR linewidth for immobile Li_{II} ions (high-field right line) shows up a rather conventional low-temperature rise that can be ascribed to the development of the critical spin fluctuations by the approach of the spin ordering. Assuming roughly the same spin fluctuation contribution for the both NMR signals we can single out the additional contribution to the inhomogeneous broadening of the left line. The difference between the magnitudes of two linewidths (shown by dashed line in fig.3) reflects the temperature dependence of the

additional contribution to the width of the left line. This additional broadening can be concerned with a slowing down of Li_I motion between two equivalent half-occupied positions when the temperature decreases. The onset temperature for the motional narrowing of the NMR line with a temperature growth is usually correlated with the glass transition temperature T_g (in our case $T_g \approx 100\text{K}$) that can be hence associated with a glass-like ordering of the Li_I sublattice in $\text{Li}_2\text{CuZrO}_4$.

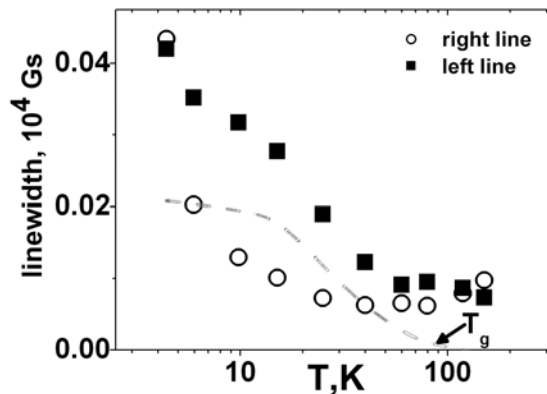


Fig. 3. Temperature dependence of the NMR linewidth for low- and high-field NMR lines. Dashed line shows the difference between the values of two linewidths reflecting an additional contribution to the inhomogeneous broadening of the left line.

Further evidence of a glass-like structural ordering can be provided by dielectric measurements. As it was expected from the NMR data, the temperature dependence of a dielectric constant shown in Fig. 4 reveals a frequency-dependent behavior (both real ϵ' and imaginary ϵ'' parts) at temperatures around $T_g \sim 100\text{K}$ which is typical for a glass-like transition. Interestingly, our dielectric measurements point to some intriguing high- and low-temperature features. The high-temperature rise of the real part of the dielectric constant evidences most likely a contribution of Li_I to ionic conductivity. The low-temperature features of ϵ' could be due to a possible coupling of the glass-like Li_I system to the quantum critical behavior that develops in the CuO_2 spin-1/2 chains at low temperatures¹.

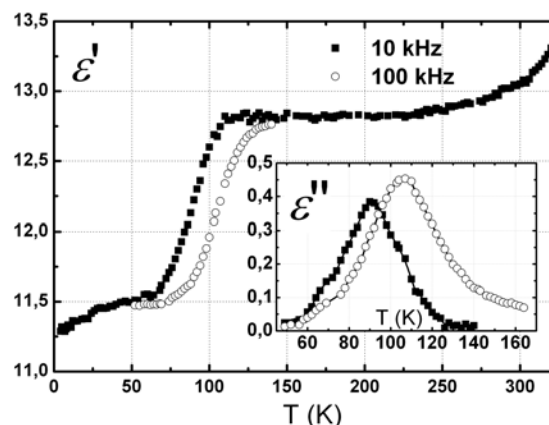


Fig. 4. Temperature dependence of real (ϵ') and imaginary (ϵ'') parts of a dielectric constant for a pressed sample of $\text{Li}_2\text{CuZrO}_4$.

In fact, indications of the influence of the electric Li_I sublattice on the subsystem of Cu spins have been found in the high-field ESR experiment that we performed at a field of $\sim 12\text{T}$. Upon cooling the

sample below $T_g \sim 100\text{K}$ the otherwise single-line high temperature ESR spectrum begins to split into two lines (not shown). This suggests a temperature driven development of two nonequivalent Cu sites with slightly different g-factors. Since the split Li_I position is situated close to the Cu site (Fig. 1) the positively ($1+$) charged mobile Li_I obviously contributes to the crystal field potential acting on the orbital states of the Cu ion and thus to the orbital part of the g-factor. Hence the occurrence of two ESR lines suggests a particular freezing pattern of the electrical Li_I sublattice below T_g , that may intervene with the low temperature quantum magnetism of the CuO_2 spin chains.

5. Conclusion

We have measured ^7Li NMR, Cu^{2+} ESR, and dielectric constants of a frustrated quantum spin-1/2 chain cuprate $\text{Li}_2\text{CuZrO}_4$. The examination of the temperature behavior of the ^7Li NMR line shape together with dielectric constant measurements evidences the glass-like structural ordering of the mobile Li ion electrical sublattice at $T_g \sim 100\text{K}$. The interplay between the subsystem of mobile Li ions and the spin subsystem is suggested by an observation of a local Cu^{2+} site nonequivalence by ESR at temperatures below T_g .

Acknowledgements

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