Quantum Critical Dynamics of S = 1/2 Antiferromagnetic Heisenberg Chains Studied in CuPzN by ESR

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Abstract. We found the dramatic crossover of the quantum critical dynamics of the chain antiferromagnet CuPzN which manifests itself in a change of symmetry properties of the ESR lineshape at low temperatures. We argue that such a crossover reveals the subtle interplay of two different perturbations of the isotropic Heisenberg model: i) the exchange anisotropy and ii) the staggered magnetic field induced by alternating g-factors of nonequivalent Cu sites of the unit cell of this compound. We estimate the magnitude of these perturbations, which drive the system from the ideal Tomonaga-Luttinger-Liquid state to the state with the field-induced gapped spin excitation spectrum.

1. Introduction

Quantum spin chains have attracted much interest for a long time since the effect of quantum fluctuations is more significant than in higher dimensional systems [1, 2], resulting in many interesting phenomena. In addition to comprehensive theoretical analysis, based on the exact solutions, the progress in various experimental techniques provides a growing opportunity to study physics of one-dimensional systems. We report the systematic ESR investigations of S = 1/2 quantum antiferromagnetic chain compound copper pyrazine dinitrate (Cu(C₄H₄N₂)(NO₃)₂ or CuPzN) [3]. This quasi one dimensional material is an excellent example of the isotropic Heisenberg system (the intra-chain exchange \( J \approx 10.7 \) K), which remains disordered down to \( \sim 100 \) mK [4]. As a result the quantum critical behavior typical for isotropic low dimensional systems will take place down to very low temperature before being destroyed by different perturbations. Among them the most effective are those which violate the chains’ spin symmetry or transfer the spin excitations to another chains. In the second case the special role belongs to interchain interaction. To analyze these processes one needs local information concerning the spin state of the individual chains. One of the powerful methods for this purpose is ESR which is capable of distinguishing different spin states within the same unit cell. Since CuPzN is a system with nonequivalent Cu ions in adjacent linear chains crossing the same unit cell it is an especially valuable object for study of interchain coupling effects by means of ESR.

2. Experimental

For our measurements we used the plate-like CuPzN single crystals which were grown by evaporation of aqueous solutions of Cu nitrate and pyrazine. The typical sizes of plates were about \( 2 \times 1 \) mm² with

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a thickness of 0.1 mm. The CuPzN structure shown schematically in Fig. 1 corresponds to the orthorhombic space group Pnma with two formula units per cell with constants \(a=0.6712 \text{ nm}, b=0.5142 \text{ nm} \) and \(c=1.1732 \text{ nm}\). Each Cu ion is 4+2 coordinated. The basal plane is formed by two nitrate oxygen atoms and two pyrazine nitrogen atoms. Two remaining sites are occupied by additional nitrate oxygen atoms with the out of plane CuO bond making an angle of 29° with the normal to the CuN_2O_2 basal plane. The planes for the two Cu sites are canted by temperature dependent angles \(\pm \phi (\phi = 2.6^\circ \text{ at 168 K})\) from the crystallographic ac plane, thus making these sites inequivalent with the different molecular coordinate systems. The difference of \(g\)-factors for sites 1 and 2 (shown as viewed along the a axis in the bottom of Fig. 1) may result in different Zeeman splittings in the external magnetic field \(H\).

In a wide temperature range our measurements of Cu ESR at a frequency of 9.4 GHz revealed a single Lorentzian line as expected for an exchange-coupled system. The observed linewidth is small and shows no indication of line broadening due to spin diffusion. A small orientation dependence of the linewidth is due to the anisotropy containing contributions from the \(J\) anisotropy and of the dipole–dipole interaction. The \(g\)-factor and linewidth have the same orthorhombic symmetry with respect to the magnetic field \(H\) orientation. Fig. 2 shows the angular dependence of the \(g\)-factor measured by ESR at room temperature. We find \(g_a = 2.2053, g_b = 2.265, g_c = 2.063\), which are in good agreement with previously published ESR [4] and susceptibility [5] data. But at temperatures \(T \sim \frac{J}{k_B}\) drastic symmetry changes in the linewidth \(\Delta H\) angular dependence upon \(H\) rotating in the bc crystal plane have been found (See Fig. 3a), whereas its angular dependence around other axes reveal no symmetry changes (See Fig. 3b). The most impressive is also the fact that the characteristic temperature

![Figure 1](image1.png)  
**Figure 1.** The schematical structure of CuPzN. The canting of basal planes (shown by dashed line) of inequivalent Cu sites gives rise to different Zeeman splitting for them (bottom of the figure).

![Figure 2](image2.png)  
**Figure 2.** The \(g\)-factor angular dependence upon \(H\) rotating in the ab, bc and ac planes at 4.2 K (a); the decomposition of the \(g\)-factor angular dependence in to the sum of individual contributions of inequivalent Cu sites.
dependence of the linewidth $\Delta H$ becomes extremely sensitive to the magnetic field orientation: at low temperatures for $H$ along the $b$ or $c$ axis it decreases upon cooling proportional to $T$, whereas for the direction making an angle $45^\circ$ with these axes it diverges as $\Delta H \sim 1/T^2$ (See Fig. 4).

3. Results and discussion

To explain the observed behaviour one has to note that according to the CuPzN structure (Fig. 1) both of the nonequivalent Cu sites have the same symmetry respect to the magnetic field $H$, when it is oriented along $b$ or $c$ axis. For the orientations between these axes the symmetry difference which is especially noticeable for the orientation near $45^\circ$, takes place. This results in a difference in the $g$-factor values ($\Delta g = g_1 - g_2$) having the maximum for $H$ lying at $45^\circ$ with respect to the $b$ or $c$ axis. The observed $g$-factor corresponds to integrated signal which is the superposition of two lines from different sites. Assuming tetragonal symmetry for each molecular system we can fit the observed $g$-factor angular dependence by two contributions each having the same $g_{\perp}$ and $g_{\parallel}$ in the corresponding molecular system tilted by different ($\pm \phi$) angles from the basal planes. As a result in the $abc$ coordinate system $g$-factor for different sites will be written as nondiagonal matrices with nonzero $g_{bc}$ elements with alternating signs for neighboring chains, giving rise to staggered magnetic field in the system.

We believe that due to the interchain coupling ($J_1$) which is schematically shown by the wavy lines in Fig. 1 the corresponding difference in a Zeeman frequency has a strong impact on the ESR line. Depending on the relation between this difference and the rate of interchain jumps one may have various regimes of ESR beginning from the line narrowing due to the fast interchain exchange and finishing with the resolved spectrum for both of the nonequivalent sites in the regime of slow

![Figure 3](image1.png)

**Figure 3.** The linewidth $\Delta H$ angular dependence in the $bc$ plane at different temperatures (a); at 4.2 K upon external field $H$ rotating around different axes: $a$, $b$ and $c$ (b).

![Figure 4](image2.png)

**Figure 4.** Linewidth $\Delta H$ temperature dependence at different $H$ orientations in the $bc$ crystal plane: along the $b$ axis; for orientation of $45^\circ$ with the $b$ axis.
exchange fluctuations (with a typical lifetime $\tau$). The corresponding crossover between these regimes reflects the slowing down of fluctuations upon lowering the temperature. For the ESR at 9.4 GHz we deal with the line narrowing regime. (Our measurements at 50-330 GHz enabled us to observe a quasistatic regime with the resolved spectra of two sites; the details will be published elsewhere). After straightforward calculation it is possible to write the corresponding contribution to the linewidth: $\Delta H \sim (\Delta g H) \tau$, which diverges as $1/T^2$ upon cooling. Such a temperature dependence follows from the observation that in a frames of perturbation theory it is possible to consider the exchange field generated by a neighboring chain as a staggered staggered field. According to [2] the temperature dependence of the perturbations generated by the staggered field is given by $1/T^2$. The fit which is shown in Fig. 4 gives the magnitude of interchain exchange $J_1$ as $5 \cdot 10^{-2}$ K. Note, that this value is in reasonable agreement with the estimations of exchange of chains in CuPzN obtained from its AF ordering temperature as $4 \cdot 10^{-2}$ K. The ESR line behavior indicates the importance of interchain coupling for low temperature spin dynamics. Note, that CuPzN as a system with nonequivalent Cu ions in adjacent linear chains is a useful object for the study of this coupling by means of ESR. As we mentioned above its influence becomes negligible for $H$ along b and c axes. As there are no other sources of the staggered field for this system we believe that the linewidth for these orientations is due to the perturbation of the quantum critical regime by the anisotropy of intrachain exchange (or by the dipolar coupling). For this case the linewidth is proportional to the temperature $[2] \Delta H \sim (\delta/J)^2 T$. The fit of this formula to the experimental data which is shown in the inset to Fig. 4 enable us to estimate the effective anisotropy parameter $\delta \sim 3.2 \cdot 10^{-2}$ K. Note, that our estimations of the exchange anisotropy and of interchain coupling give evidence of the small magnitude of perturbations, which drive the system from the ideal Tomonaga-Luttinger-Liquid state to the state with the field-induced gapped spin excitation spectrum.

In conclusion we would like to point out, that while for the static properties the interchain exchange is irrelevant, in the dynamics it already manifests itself and induces the crossover from one critical regime to another. Our finding of the strong impact of the interchain coupling on the quantum dynamics indicates that the simplest model for description of CuPzN spin system is a zigzag spin ladder with two legs and $J$ being the interaction between the spins from the same leg whereas $J_1$ corresponds to the interaction of spins from the different legs. In its turn this model can be converted [7] to the 1D spin chain model with the interaction between the next nearest neighbors ($J_1$) in addition to that of nearest neighbors ($J$). The phase diagram of such a system which was obtained in [8] reveals the possibility of very interesting magnetic phases, some of them being incommensurate.

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5. References

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