Low Energy Dynamics in Spin-Liquid and Ordered Phases of S=1/2 Antiferromagnet Cs$_2$CuCl$_4$

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Abstract. Cs$_2$CuCl$_4$ realizes spin-1/2 quantum antiferromagnet on a distorted triangular lattice. It remains in a quantum spin-liquid state far below Curie-Weiss temperature 4 K and exhibits an incommensurate spin ordering at $T_N=0.6$ K. We studied Cs$_2$CuCl$_4$ by means of electron spin resonance (ESR) at temperatures down to 0.05 K in the frequency range $9<f<140$ GHz. An unexpected energy gap of 14 GHz and a splitting of ESR were found in the spin-liquid phase. We quantitatively describe both the shift and the splitting of the ESR line for different orientations of the applied magnetic field by accounting for the effect of a uniform Dzyaloshinskii-Moriya (DM) interaction on spinon excitations of weakly coupled Heisenberg chains. At cooling below $T_N$, we observe at lower frequency $f<40$ GHz a gradual crossover of the signal from the above spinon-type ESR toward a resonance of a spiral-AFM type. However, for higher frequency $f>60$ GHz, we observe that the above spinon-type ESR survives deep in the ordered phase. These novel phenomena are consequences of fractionalized spinon excitations of spin chains, which are effectively decoupled in Cs$_2$CuCl$_4$ due to strong geometric frustration.

1. Introduction

Magnetic crystals with $S=1/2$ ions coupled by antiferromagnetic exchange provide numerous quantum phases with specific spin structures and excitations. A quasi 2D antiferromagnet Cs$_2$CuCl$_4$ has stacked layered magnetic structure with distorted triangular lattice in the layers. It was thoroughly investigated by means of elastic and inelastic neutron scattering, which, in particular, uncovered an extensive two-spinon continuum [1, 2]. The spinon continuum was observed below the Curie-Weiss temperature $T_{CW}=4$ K but, however, still above the Néel temperature $T_N=0.62$ K, below which the system orders into a two-dimensional incommensurate spiral in the $bc$-plane. The two-spinon continuum was uncovered in a $q$-space region near the Brillouin zone boundary. This continuum, which is a distinctive feature of a quantum critical S=1/2 spin chain, was found to survive well below the ordering temperature and to coexist with the low-energy spin-wave excitations. The 1D nature of excitations in this layered structure is attributed to a special structure of exchange bonds, with the strongest exchange bond (J=0.375 meV) coupling magnetic ions along $b$-direction, parallel to the bases of isosceles triangles of the lattice. A weaker exchange integral $J'=0.34J$ corresponds to $c$-direction (lateral sides of the
triangles). The interlayer exchange $J''=0.045J$ is the weakest one. The spin chains along $b$-axis should be practically decoupled due to the geometric frustration of the exchange bonds $J'$, as shown in numerical simulation [3] and analytical approach [4]. This decoupling is the reason for the quasi-1D character of the spectrum of spin excitations. It also makes the system very sensitive to remaining weak interlayer and Dzyaloshinsky-Moriya interactions [5].

![Figure 1](image1.png)

**Figure 1.** 27 GHz ESR line at $T=1.3$ K for $H \parallel a$. Circles are experimental points, solid line is a two-Lorentzian fitting, dashed lines represent separate Lorentzians.

![Figure 2](image2.png)

**Figure 2.** Frequency-field diagram for $T=1.3$ K and $H \parallel a$. Dashed lines correspond to the theory, eqs. 3,4. Dotted line is the paramagnetic resonance frequency for $g=2.20$.

![Figure 3](image3.png)

**Figure 3.** Continuum of transversal spin excitations in a magnetic field $H = 0.5J/(g\mu_B)$ for 1D spin chain modified by the uniform Dzyaloshinsky-Moriya interaction. Note a considerable width of the continuum at $q=0$.

In this paper we describe the investigation of spin excitations in Cs$_2$CuCl$_4$ in the low-energy range by means of electron spin resonance (ESR) spectroscopy. A new kind of ESR signals of a spin $S=1/2$ antiferromagnet was found both in the spin-liquid and ordered phases.

2. Experiment

2.1. Spin-liquid phase

The magnetic resonance signals were recorded as dependence of the transmitted microwave power on the magnetic field, using the resonator type microwave spectrometers for the range 9-140 GHz, combined with the cryostats with $^4$He and $^3$He pumping and a dilution refrigerator Kelvinox-400. The ESR signal at $T >10$ K is a typical single mode resonance corresponding to $g$-factor values of $g_{a,b,c} = 2.20, 2.08, 2.30$ for the orientation of the magnetic field along the
crystallographic axis $a$, $b$ and $c$ correspondingly. This kind of resonance is typical for magnetic crystals containing $S=1/2 \ Cu^{2+}$ magnetic ions.

On cooling the sample below the temperature of about 6 K a strong evolution of the ESR line occurs. At $H \parallel b$, the single ESR mode is observed in the frequency range above 20 GHz, with the frequency shifted to lower fields. The frequency of this spin resonance may be fitted by a standard gapped antiferromagnetic resonance form

$$2\pi f = \sqrt{(g\mu_B H)^2 + \Delta^2}. \quad (1)$$

At $T = 1.3K$ the value of the gap is $\Delta/2\pi h = 14$ GHz

At $H \parallel a, c$ the ESR line splits into a doublet which is resolved below 4 K. The splitting of 27 GHz ESR lines is of about 0.5 T at $T=1.3$ K, as shown in Fig.1. The frequency-field dependence for these split ESR resonances is given in Fig.2. The details of the temperature evolution of the ESR signals and of the ESR spectra are described in Ref.[8]. The observation of the nonzero gap in zero field and of the splitting of the ESR line in the paramagnetic phase is unusual for $S=1/2$ chains. In the ideal case of Heisenberg chain the ESR frequency is not renormalized and remains at the standard Zeeman energy value $2\pi f = g\mu_B H$. In presence of perturbations such as staggered $g$-factor, alternating Dzyaloshinski-Moriya interaction or an anisotropic exchange, a field-induced gap may occur due to the generation of a staggered magnetic field in the presence of external magnetic field (see theory [9] and experiment, e.g, [10] ). In contrast to these known cases we observe a gap in the absence of external magnetic field and, even more strangely, the splitting of the ESR line.

2.2. Ordered phase

The next point of our investigation is to follow the transformation of the unusual ESR shift and splitting at cooling through the ordering temperature $T_N=0.62$ K. We consider the temperature evolution of ESR signals for the most simple case of $H \parallel a$. Here the magnetic field is perpendicular to the spiral plane and the structure should obey only gradual transformation to the cone configuration and further saturation without intermediate phase transitions, in contrast to the cases of $H \parallel b; c$ [11]. We observed two kinds of temperature evolution: i) For low frequencies ($f < 40$ GHz) the doublet described above is frozen out and at low temperature the antiferromagnetic resonance mode is formed as shown in Fig.4. ii) For higher frequencies, $f > 60$ GHz, the doublet found in the spin-liquid phase survives deep in the ordered phase. Thus, in addition to the antiferromagnetic resonance, a spin-liquid mode continues to exist (see the evolution on Fig.5). The frequency-field dependence for the resonance modes of the ordered phase is shown in Fig.6.

3. Discussion

The observations in the spin-liquid phase may be explained and quantitatively described by the consideration of the influence of the in-chain uniform Dzyaloshinsky-Moriya (DM) interaction on the spinon continuum. This interaction is a distinct feature of $Cs_2CuCl_4$ [5]. The uniform DM interaction in a classical antiferromagnet should result in a spiral ground state (compare to the canted antiferromagnetic ground state due to the alternating DM interaction). In a simple model case when the magnetic field is parallel to the DM vector $D$, this interaction modifies the spinon continuum of $S=1/2$ chains by simply shifting the spectral density by the amount of $D/J$ along the $q$-axis [7, 8], see Fig.3 (the initial, i.e. unshifted, spectrum has zero energy as a lower limit at $qa = \pi$). As a result, the ESR absorption, which is determined by $q = 0$ transitions, acquires maxima at two frequencies, corresponding to the upper and lower boundaries of continuum. (See [6] for the most recent theoretical investigation of this striking phenomenon.) Note that in the absence of the uniform DM interaction this continuum collapses to a single frequency. Detailed
Figure 4. Temperature evolution of the ESR signal at low frequency ($f < 40$ GHz).

Figure 5. Temperature evolution of the ESR signal at a high frequency ($f > 60$ GHz).

Figure 6. Frequency-field dependence for ESR in Cs$_2$CuCl$_4$ at $T <0.1 \; \text{K}$ and $\mathbf{H} \parallel \mathbf{a}$. Filled symbols correspond to the intensive ESRE modes, empty symbols present resonances of a weak intensity.

Theoretical interpretation [7, 8] is based on the following spin Hamiltonian:

$$H = \sum_{x,y,z} (JS_{x,y,z} \cdot S_{x+1,y,z} - D_{y,z} \cdot S_{x,y,z} \times S_{x+1,y,z} + -g\mu_B \mathbf{H} \cdot \mathbf{S}_{x,y,z}) + ...$$

(2)

Here the first term describes intrachain exchange $J$ ($x$ runs along crystal $b$ axis), the second – uniform DM interaction $D_{y,z}$ between chain spins, and the third is a Zeeman term, allowing for anisotropic $g$-factor. The dots correspond to the omitted interchain exchange and DM interactions on interchain bonds. Detailed symmetry analysis of the allowed DM interactions [5] shows that there are four different orientations of the DM vector (see Fig. 6 in [5]) depending on chain’s integer coordinates $y, z$: $D_{y,z} = D_a(-1)^y \hat{a} + D_c(-1)^y \hat{c}$. Here $z$ indices magnetic $bc$ layers, while $y$ numerates chains within a layer. The crystal symmetry forbids DM vector from having a component along the $b$ axis [5].
This Hamiltonian results in the following ESR frequencies:

\[
(2\pi \hbar f_1)^2 = (g_b \mu_B H_b)^2 + (g_a \mu_B H_a + (-1)^z \pi D_a/2)^2 + (g_c \mu_B H_c + (-1)^y \pi D_c/2)^2,
\]

\[
(2\pi \hbar f_2)^2 = (g_b \mu_B H_b)^2 + (g_a \mu_B H_a - (-1)^z \pi D_a/2)^2 + (g_c \mu_B H_c - (-1)^y \pi D_c/2)^2.
\]

These equations explain the difference between \( \mathbf{H} \parallel \mathbf{a, c} \) and \( \mathbf{H} \parallel \mathbf{b} \) situations. For \( \mathbf{H} \parallel \mathbf{b} \) the external field \( \mathbf{H} \) and the internal DM field are mutually perpendicular and lead to a single ESR frequency \( f_1 = f_2 \) of the form (1). For \( \mathbf{H} \parallel \mathbf{a, c} \) the DM field has a component along \( \mathbf{H} \) and the frequencies of the two spin excitations are different.

The theoretical \( f(H) \) dependencies derived from these equations are plotted in Fig.2 by dashed lines and correspond to the values of \( D_a/(4\hbar) = 8 \) and \( D_c/(4\hbar) = 11 \) GHz. These extracted numerical values describe well the value of the ”energy gap” of 14 GHz, observed at \( \mathbf{H} \parallel b \), as well as the angular dependence of the resonance field reported in Ref.[8].

In the ordered phases one could expect a formation of the standard ESR spectrum of a planar spiral spin structure with two axes of the anisotropy, which should have two gapped resonance modes and a third mode with zero frequency, at least in low magnetic fields. These expected frequencies, derived from a macroscopic analysis of low frequency dynamics of such a system [12], are plotted in Fig.6. The experiments show that our expectations are indeed true at sufficiently low frequencies. As described above in Section 2.2, at higher frequencies comparable to the main exchange energy \( J=90 \) GHz, we observe an additional mode which may be interpreted as a component of the ”spinon doublet”, which survives deep in the ordered phase and coexists with a mode of the antiferromagnetic resonance. This observation is probably related to a similar feature of the inelastic neutron scattering experiments of Ref.[2]. In this experiment the spinon continuum was found to remain practically unchanged at the ordering transition, and to coexist with the spin-wave mode at the temperature far below \( T_N \). In our experiments we observe that the spinon-type ESR remains approximately undistorted at high frequency, while it freezes out (disappears) at low frequency.

4. Conclusion
We observe splitting of the electron spin resonance line, originating from the modification of the spinon continuum by the uniform Dzyaloshinsky-Moriya interaction, in frustrated 2D antiferromagnet \( \text{Cs}_2\text{CuCl}_4 \). The spinon-type resonance at zero wavevector was found to coexist with the low frequency mode of the antiferromagnetic resonance at the temperature far below the Néel point.

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