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Crossover to XXZ Chain Spin Liquid in the Frustrated Quantum Magnet Cs_2CoCl_4

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Abstract

We study 25–120 GHz electron spin resonance in a quasi-two-dimensional $S = 3/2$ antiferromagnet on an isosceles triangular lattice Cs_2CoCl_4. Due to the frustration of the exchange interaction along the lateral sides of the triangles, the exchange network may be viewed as a quasi-one-dimensional system of weakly interacting chains. The strong single-ion anisotropy of Co^{2+} allows a pseudospin $s = 1/2$ formulation of the problem. We observe in experiments a well-pronounced temperature crossover from the ESR of individual pseudospins with a g-factor of 3.3 (corresponding well to individual pseudospins s=1/2) to ESR spectrum shifted strongly down in frequency at the temperature range below 1 K. This shifted ESR spectrum corresponds well to the singularity at the lower boundary of the quasi-spinon continuum of an XXZ spin chain in a transverse field, calculated in theory by Bruognolo et al., in Phys Rev B 94:085136, 2016 and by Laurell et al., in Phys Rev Lett 127:037201, 2021.

1 Introduction

Low-dimensional spin systems with the antiferromagnetic exchange often demonstrate ground state which cannot be expected from the classical point of view. These ground states either completely fluctuate or have ordered spin components with a strong quantum reduction. The most bright examples are given by Heisenberg quantum chains of spins S=1/2 or S=1. For both these examples, the ground state is in a classic sense disordered, i.e., there is no ordered spin component at a lattice site, but, nevertheless, there are strong correlations and well-defined excitations corresponding to quantized quasiparticles. For $S = 1/2$ chain, the spin–spin correlations decay algebraically (ground state is quantum-critical) and quasiparticles, so called spinons, have fractionalized spin S=1/2, resulting in a gapless continuum of

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transferred energy for neutron or photon scattering, see, [1–4]. For S=1, the ground state is again disordered, but the correlation length is final. Quasiparticles are S=1 triplets separated from the ground state by a so-called Haldane gap [5]. Recently, many other quantum spin systems were found, both theoretically and experimentally, such as spin ladders, kagome lattices, etc. [6, 7].

Now we study experimentally the spectrum of excitations in a simple but very enlightening model which is intermediate between completely fluctuating system and partially ordered one—a spin $S = 1/2$ chain with an Ising type anisotropy (so-called XXZ chain). This system was extensively studied theoretically because of intriguing entangled states [8–11]. At the same time, it may be adequately realized in the target compound of our study Cs_2CoCl_4 which was tested in many aspects experimentally [9, 11–14]. The spin Hamiltonian of XXZ chain in a magnetic field is

$$\mathcal{H} = \sum_i (J(S_x^i S_x^{i+1} + S_y^i S_y^{i+1} + \Delta S_z^i S_z^{i+1}) + g_\alpha \mu_B H_\alpha S_\alpha^i), \tag{1}$$

here S_α^i are spin component operators for site i of the chain, g_α are g-factor tensor components and H_α are components of the magnetic field. g-factor tensor is proposed to be diagonal.

We will be interested in the case of positive Δ corresponding to the anisotropy of the easy plane type. This system has a remarkable ground state and field-induced phase transitions [8, 9, 11, 14]. In a zero field, there is a quantum-critical gapless spin liquid, in a transverse magnetic field H_x, the ground state is a 1D long-range ordered flopped antiferromagnet with sublattice magnetization strongly reduced by zero-point fluctuations. At a critical value of magnetic field $H_x = 1.6J/g_x\mu_B$, the ordered state disappears with restoration of a 1D spin-liquid state due to the non-commuting action of magnetic field and anisotropy, which causes the entanglement of states [11]. In this field, the magnetic moment should be of about of 90 percent of saturation. The saturation is expected only asymptotically in higher fields. Naturally, a 3D long-range order should occur at a low-temperature $T_N << J/k_B$ in a real quasi-1D antiferromagnet with the inevitable interchain coupling. Nevertheless, in a temperature range $T_N < T << J$, the spin configuration within chains should be close to that of a single XXZ chain at T=0. The adjacent chains should be not correlated because of the temperature exceeding weak interchain exchange. Note that the Nèel temperature of the quasi-1D antiferromagnet with the intrachain exchange $J_\|$ and interchain exchange $J_\perp$ may be approximately estimated from the expression [15]

$$k_B T_N \simeq J_\perp \sqrt{\ln \frac{J_\|}{k_B T_N}}. \tag{2}$$

In case of a quasi-1D antiferromagnet, i. e. at $J_\perp \ll J_\|$, this expression implies that $k_B T_N \ll J_\|$ and the above temperature interval should be really wide enough.

The remarkable fact is that XXZ 1D system may be in a good approximation realized in crystals of Cs_2CoCl_4 [9–11, 13, 14]. In this system, magnetic ions Co^{2+}

(S=3/2) are placed in *bc* planes of the orthorhombic lattice within the layers stacked along *a*-axis. Within each layer, magnetic ions form a sublattice of isosceles triangles. The bonds with exchange integral $J_{\frac{3}{2}}$=0.74 K are placed on bases of triangles along the *b*-axis. The lateral exchange as well as the interplane exchange coupling is estimated to be at least an order of magnitude weaker, see, [9, 13]. Taking in account the frustration of the lateral exchange [16], we can view the exchange network as almost ideal chain structure. A further reduction of the S=3/2 problem to the problem of effective pseudospin s=1/2 is described in [9, 13, 14]. Because of the energy split in 14 K of the crystal field sublevels with $S_z = \pm 3/2$ and $S_z = \pm 1/2$, in the low temperature approximation, magnetic ions may be considered as pseudospins $s = 1/2$. The pseudospin representation of the initial $S = 3/2$ Hamiltonian with the exchange parameter $J_{3/2}$=0.74 K, single-ion anisotropy $D = 7$ K, and isotropic g-factor $g_{3/2} = 1.94$ results directly in the Hamiltonian (1), see [14] with parameters $J = J_{1/2} = 4J_{3/2}$, $\Delta = 0.12$, and anisotropic g-factor with g_x component $g_{1/2} = 3.26$. Naturally, this representation is valid only for $k_B T \ll D$ and $g_{1/2}\mu_B H_x \ll D$. Here Δ and $g_{1/2}$ are calculated using the above values of of $J_{3/2}$ and D, see [14]. Thus, Cs_2CoCl_4 is a very promising model system for realization of XXZ chain states.

The previous studies of inelastic neutron scattering [10, 11] explore spectra of excitations in the ordered state below 0.2 K where many features of XXZ chain spectra were detected in a high-energy part of the spectrum. In the present work, we target the crossover of the excitation spectrum from the pseudospin paramagnet to the spin liquid (intrachain correlated but interchain disordered state) and further to the spectrum of the ordered phase. As a result of the multifrequency electron spin resonance (ESR) study in a wide temperature range, we observe a regime of decoupled pseudospins, and then a crossover to spin liquid of the decoupled but intra-correlated chains and finally—a transition to spin-wave-like spectrum of the ordered state.

2 Experiments

In our experiment, the absorption of microwave energy is detected in the sample placed in cylindrical cavity at the maximum of the microwave magnetic field. The microwave power transmitted through the resonator at a fixed frequency *vs* magnetic field was recorded. A set of the fixed frequencies covers the range between 25 and 125 GHz. The ESR fields correspond to the minima of the transmitted signal. A small amount of DPPH (2,2-diphenyl-1-picrylhydrazyl was placed near the sample which provides g=2.00 marker. Having the records taken at different frequencies, we reconstruct the frequency vs field dependencies of the ESR. The low temperature down to 0.1 K was produced in the homemade microwave spectrometer combined with a portable dilution cryostat insert [17]. Magnetic fields up to 80 kOe were generated by a superconducting solenoid. The resonator of the diameter of 15.5 mm and height of 10 mm has the frequency of the TE_{011} mode at the frequency f= 27 GHz, TE_{012} mode at 35 GHz and higher modes in the range 25–125 GHz.

3 Experimental results

Several examples of the ESR records present the temperature evolution of the 40.99 GHz ESR line in Fig. 1. We see a single rather broad ESR line in the temperature range between 7 and 4 K with a weak temperature dependence of the resonance field H_1 between 7.8 and 8.4 kOe. At the diminishing temperature between 3 and 0.9 K, the field H_1 is stabilized at 8.9 ±0.1 kOe. At the cooling in the interval from 2 to 0.4 K, the spectral density is partially transferred to a higher resonance field H_2 which varies in a narrow interval between 12.6 and 12.2 kOe. We note further these modes as H_1 and H_2 modes. Below T =0.9 K, most spectral weights are already placed near the field H_2 and continue to stay here till about 0.3 K where, at further cooling through the temperature 0.2 K, the resonance field of the main ESR line shifts slightly to lower field and several satellites appear both above and below H_2. These last transformations are observed near the transition to an ordered phase. According to the thermodynamic measurements of [13], in a magnetic field of 12.5 kOe, there are two phase transitions, at a temperature T_{c1}=0.35 K to a phase with an unknown order parameter and at a temperature of T_{c2} =0.2 K to a spin-flopped

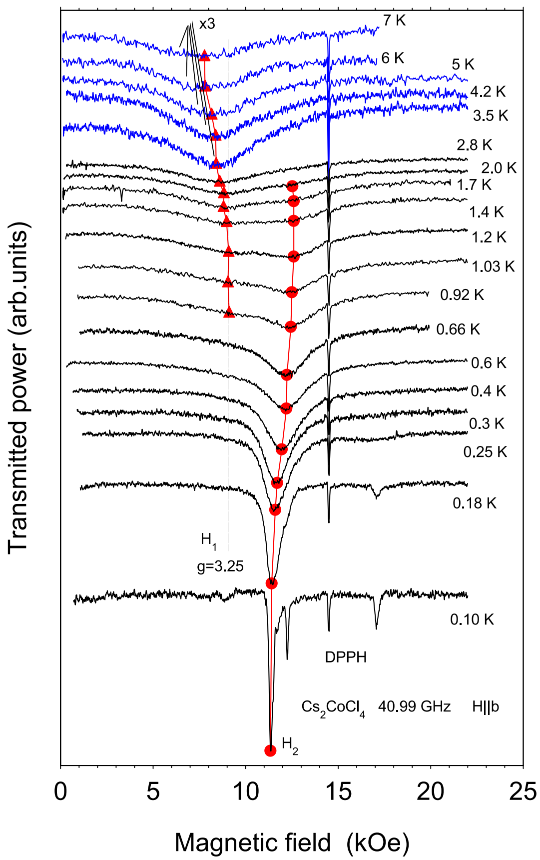

Fig. 1 Temperature evolution of 40.99 GHz ESR line in the range 7−0.1 K. For clarity, the five upper curves are stretched vertically three times. Magnetic field 9.02 kOe, corresponding to g=3.25, is marked by a vertical dashed line. The magnetic fields corresponding to the resonance of H_1-mode are marked by triangles and corresponding to H_2-mode by circles and joined by a solid line

antiferromagnetic phase. Near T_{c2}, the change in the ESR absorption is well-pronounced by an abrupt narrowing of the resonance line and drop of the intensity, as well as by emerging satellites. Near T_{c1} =0.35 K, intensity starts to drop, but we do not see significant changes between 0.4 and 0.3 K to fix a critical behavior.

The temperature dependencies of resonance fields, integral intensities, and linewidths of modes H_1 and H_2 at the frequency 40.99 GHz are presented in Fig. 2. The values presented here are extracted by a Lorentzian fit of the ESR curves. This figure illustrates the process of diminishing the intensity of the H_1 ESR and increasing of the H_2 intensity upon cooling. Also the temperature range of existence of both kind of ESR signals may be distinctly determined: H_1 ESR certainly exists at 2 K $< T <$ 4 K, while the high-field mode occurs at 0.3 K $< T <$ 2 K.

The transition of the resonance field from H_1 to H_2 occurs via a continuous spectral density flow to a new position, without the shift of the resonance field. Experiments on other frequencies of the range show that the fields H_1 and H_2 are frequency-dependent. We plot the values of H_1 and H_2 taken at different frequencies in

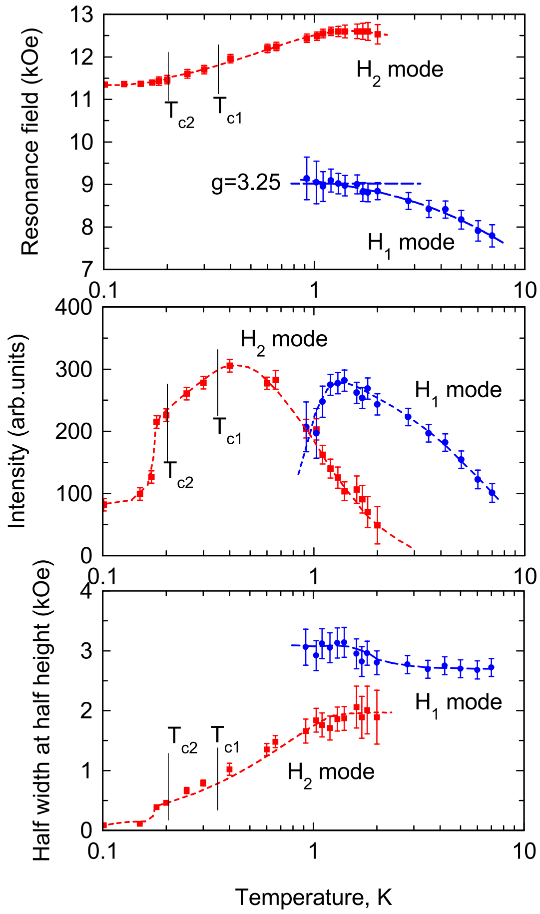

Fig. 2 Temperature dependencies of resonance fields, integral intensities and linewidths of 40.99 GHz ESR modes observed in fields H_1 and H_2. T_{c1} and T_{c2} are the critical temperatures observed in [13]

the range 25–125 GHz in Fig. 3. The upper resonance frequency (observed at H_1) is linear in magnetic field and crosses the zero field at the linear extrapolation to zero. The g-factor value determined by the linear fit

$$f = g\mu_B H/\hbar \tag{3}$$

corresponds to g=3.3±0.1. The lower-frequency resonance, observed at fields H_2 at lower temperatures $0.35 < T < 1K$ is shifted down in frequency approximately for 14 GHz with respect to H_1-resonance.

4 Discussion

The experimental value of g=3.3±0.1 corresponds well to the specific "pseudospin" value [14]

$$g_{1/2} = 2g_{3/2}\left(1 - \frac{3J_{3/2}}{2D}\right) = 3.26. \tag{4}$$

This g-factor points to the formation of the pseudospin s=1/2 state at the temperatures far below $2D/k_B$ = 14 K. The crossover to the H_2-resonance corresponds to the exchange correlations emerging at the temperature of the order of about 1 K, which is below the value of of intrachain exchange $J_{1/2}$= 3.0 K. Here we expect the excitation spectra of the XXZ chain in a transverse (noncommuting) field. These excitations were theoretically studied by the DMRG method [10, 11]. It was found that the excitations are analogous to spinons in a Heisenberg S=1/2 antiferromagnetic chain, and the correlation function determining the susceptibility has the ω, k-dependence in a form of continuum, evolving with the magnetic field in a spin wave-like branch. One can compare the continuum of transferred energy for neutrons or photons (with

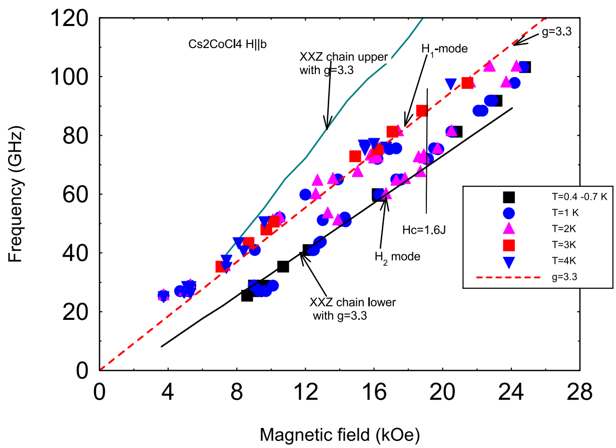

Fig. 3 Frequency-field diagram of H_1 and H_2 ESR modes. Different symbols correspond to different temperatures. Solid lines present the upper and lower maxima of $S(0, \omega)$ as calculated in [11], see text

ΔS=1) for Heisenberg chains and XXZ chains, looking at the intensity plots of [18] and [11]. The presentation of the corresponding dynamic structure factor $S^{\alpha\alpha}(k,\omega)$ in a false color form may be found in the Supplement of [11]. We used the results obtained in [11] for the structure factor averaged on the polarization of the exciting field presented in Fig.S12 of this work. Analogous results of [10] demonstrate that the dynamic structure factor calculated for Δ = 0.25 and Δ= 0.12 practically coincides. Thus, we can use the more detailed Δ = 0.25 results of [11] for the interpretation. These results show that the continuum of $S^{\alpha\alpha}(k,\omega)$ in a moderate field and in a long-wave limit has two maxima at the lower and the upper boundary energies. The lower maximum is more intense than the upper one. In Fig. 3, we plot the values of lower and upper limits of polarization-averaged structure factor $S(0,\omega)$ taken from Fig.S12 of [11]. For adopting the theoretical value of magnetic field, given in units of $J_{1/2}$, we use the value of g=3.3 derived in our experiments. One can see a good correspondence of the frequencies of the resonances observed at 0.4 K $< T <$ 2 K in the field H_2 to the frequency of the lower maximum at the boundary of the XXZ-S=1/2 chain continuum. From this correspondence, we conclude that at the temperature 0.4 K $< T <$ 2 K, the spin system of Cs_2CoCl_4 resembles the intra-correlated XXZ chains, which still do not have interchain correlation. Thus, the DMRG calculation of XXZ chain chain in a transverse field is satisfactory confirmed by ESR experiment in the long wave range, which is typically not tested by neutrons. We also observe the transformation of the ESR line at the phase transition T = 0.35 K and at the antiferromagnetic transition T = 0.2 K in accordance with the phase transitions reported in thermodynamic research [13]. This antiferromagnetic resonance will be reported elsewhere.

5 Conclusions

In a chain S=3/2 anisotropic antiferromagnet, we observe the low-temperature ESR response corresponding to uncorrelated pseudospins s =1/2 with a characteristic g-factor 3.3. At further cooling, we find a crossover from the ESR absorption of uncorrelated pseudospins s =1/2 to the absorption spectrum of the 1D S=1/2 XXZ-anisotropic antiferromagnet, and, finally at the temperature of the Nèel transition, we find a multimode antiferromagnetic resonance, which will be a subject of a future separate study.

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Availability of data and materials The source datasets are available on reasonable request.

Declarations

Ethical approval Not applicable.

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