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Magnetic resonance of spinons in quantum magnets

A I Smirnov

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Contents

Abstract. A study is made of the spinon continuum fine structure which is observed to occur in the spin-liquid phases of chain- and triangular-lattice magnets at small wave vectors due to the action of a uniform Dzyaloshinsky–Moriya interaction. An ordered phase with a strongly quantum-reduced order parameter is found to exhibit the coexistence of magnon and spin type excitations, the former crossing over to the latter when the excitation energy exceeds that of the exchange interaction.

Keywords: spin chains, magnetic resonance, antiferromagnets, quantum magnets

1. Introduction. Continuum of excitations in antiferromagnetic spin chains

It was first shown by H Bethe [1] and subsequently by other theorists that, contrary to classic predictions, an antiferromagnetic Heisenberg chain of $S = 1/2$ spins has a strongly fluctuating ground state with the mean spin projection being zero at any lattice site. At the same time, this state is strongly correlated, its antiferromagnetic spin correlations showing a slow power-law falloff. Thus, a spin chain at a temperature of absolute zero is in a critical state in which conventional long-range magnetic order is absent, whereas the correlation radius is infinite.

The excited states of quantum spin chains also turn out to be a very interesting problem. Theoretical studies [2] have given evidence that the spin structure of an elementary excitation is similar to that of a domain wall in a Néel antiferromagnet — unlike the classic magnon, which has an inverted spin as its prototype structure.

Notice that a single inverted spin produces two domain walls a chain period apart. In a one-dimensional chain, these walls can move any distance away from each other without spending energy and without changing the total spin. Spin structures corresponding to the magnon and those corresponding to two domain walls are shown in Fig. 1. These

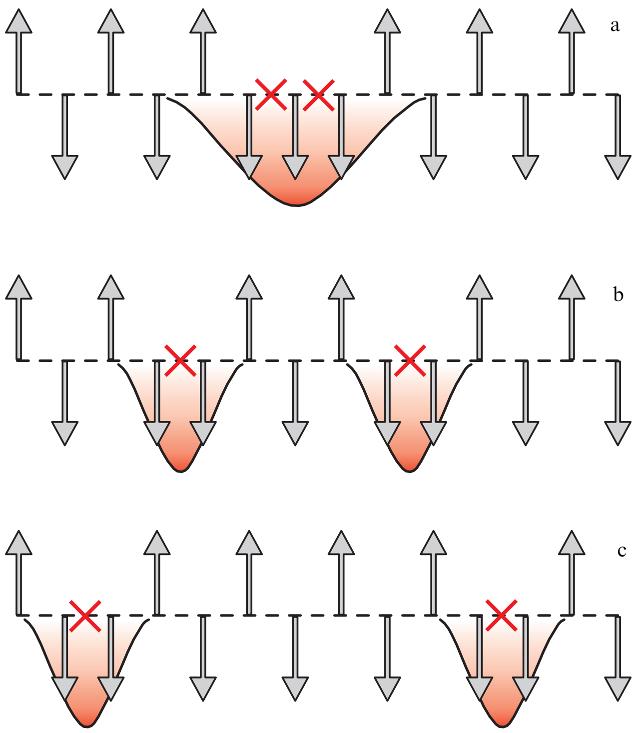

Figure 1. Schematic diagram of spin projections at spin chain sites. (a) Spin configuration corresponding to a magnon with spin $S = 1$. (b, c) Spin configurations with the same exchange energy, corresponding to an uncoupled spinon pair.

A I Smirnov Kapitza Institute for Physical Problems, Russian Academy of Sciences, ul. Kosygina 2, 119334 Moscow, Russian Federation
E-mail: smirnov@kapitza.ras.ru

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unusual excitations with a domain-wall spin structure were named spinons. All of such excitations carry a half-integer spin $S = 1/2$ and therefore arise and disappear in pairs when interacting with neutrons or photons (where such interactions can change the total spin projection of the crystal by one).

The excitation or absorption of spinon pairs results in emerging the spectrum of transferred energy and momentum q having the form of a two-particle excitation continuum with the upper $\epsilon_1(q)$ and lower $\epsilon_2(q)$ boundary energies related by $\epsilon_1(q) = 2\epsilon_2(q/2)$. One-particle excitations satisfy the dispersion relation

$$\epsilon_2(q) = \frac{\pi}{2} J \sin(qa) , \tag{1}$$

where q is the wave vector, a is the spin chain period, and J is the exchange integral.

The continuum region in the energy–wave vector plane is shown schematically in Fig. 2.

To date, a large number of crystals with intrachain antiferromagnetic exchange coupling have been studied. The existence of a two-spinon continuum has been confirmed by numerous neutron scattering experiments that revealed an absorption band distinctly bounded by the calculated values of $\epsilon_{1,2}$ (see, for example, Refs [3, 4]). A correspondence has been established between the experimental continuum spectral density and theoretical predictions based on notion of half-integer spin excitations. Due to some peculiarities of the neutron experiment, a distant-from-the-center part of the Brillouin zone was mainly explored in these measurements.

That spinons themselves actually exist as well defined quasiparticles was confirmed by observations of the large mean-free-path thermal conductivity [5, 6]. The idea of the spinon as a half-integer-spin particle received strong support from an inelastic neutron scattering experiment [7] which showed that the longitudinal spin fluctuation spectrum exhibits a fine structure in the form of soft modes that arise in a magnetic field as wave vector satellites at the Brillouin zone boundary. This fine structure is explained by considering transitions occurring in a magnetized one-dimensional Fermi liquid.

Our experiments reported here aim to show that spin-1/2 excitations in a quasione-dimensional antiferromagnet behave like Fermi particles in the region of small wave vectors, where the width of the continuum tends to zero and

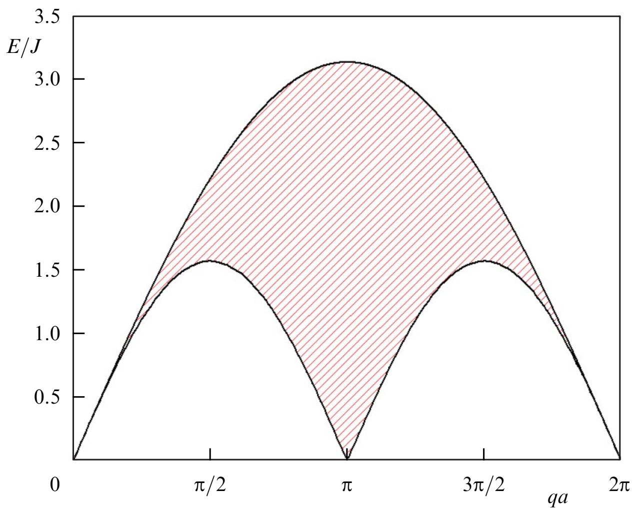

Figure 2. Two-spinon continuum in a zero magnetic field.

where the magnetic field affects most strongly the spectrum of transverse spin fluctuations. Still, the chirality of transverse spinon modes manifests itself in chains in which the magnetic ions have a low-symmetry local surrounding. It was shown theoretically [9] that if in addition to the Heisenberg exchange the chain also involves a much weaker uniform Dzyaloshinsky–Moriya interaction, then oppositely propagating spinons have different spectra provided the applied magnetic field is parallel to the vector $\mathbf{D}$ that determines the Dzyaloshinsky–Moriya interaction.

Following papers [9, 10], consider a spin chain Hamiltonian which includes the exchange interaction, the uniform Dzyaloshinsky–Moriya interaction, and the Zeeman interaction:

$$\mathcal{H} = \sum_i \left(J \mathbf{S}_i \mathbf{S}_{i+1} + \mathbf{D}\, \mathbf{S}_i \times \mathbf{S}_{i+1} + g\mu_{\mathrm{B}} \mathbf{S}_i \mathbf{H} \right) . \tag{2}$$

Here, g is the Lande factor, μ_{B} is the Bohr magneton, $\mathbf{S}_i$ are the spin operators at the sites of the one-dimensional lattice, and the vector $\mathbf{D}$ is the Dzyaloshinsky–Moriya interaction parameter [11, 12].

The uniform Dzyaloshinsky–Moriya interaction has the distinguishable feature that all the spin numbers i in the chain have their vectors $\mathbf{D}$ aligned in the same direction. A more typical form of the Dzyaloshinsky–Moriya interaction — known to occur in many antiferromagnets — is alternate and contains the factor $(i)^{-1}$ in the Hamiltonian. The alternate interaction leads to the well-known tilting effect between the sublattices in the ordered phase — the so-called weak ferromagnetism of antiferromagnets.

In our exotic case of the uniform Dzyaloshinsky–Moriya interaction, the classic form of ordering would be a spiral structure with wave vector $q_{\mathrm{DM}} = D/aJ$. In a quantum spin chain the classic ordering is absent. The uniform Dzyaloshinsky–Moriya interaction, if present, should theoretically shift the continuum spectrum by an amount q_{DM}, making the oppositely propagating spinons nonequivalent. To prove this, note that the uniform Dzyaloshinsky–Moriya interaction can in the first approximation be removed from the Hamiltonian by rotating all the spins by an angle dependent on the spin number, $i \arctan(D/J)$ [10, 13]. Figure 3 illustrates the form of the spinon continuum for transverse spin fluctuations in a magnetic field and how it is affected by the uniform Dzyaloshinsky–Moriya interaction. As a result, the region of nonzero continuum width includes the zero wave vector and is therefore accessible to magnetic resonance spectroscopy studies that probe excited states with a zero wave vector (or, more accurately, with a wave vector which is small in comparison with π/a).

Because of the spectral density singularities in the long-wavelength parts of the continuum at its lower and upper boundaries [14], a doublet of resonance lines is expected to be observed instead of a single line at the Larmor frequency [9, 10, 13]. Two factors — the spinon nature of the excitations and the presence of the uniform Dzyaloshinsky–Moriya interaction — determine the expected electron spin resonance splitting. The magnetic field dependences of the spinon doublet frequencies are, for the orientations $\mathbf{H} \parallel \mathbf{D}$ and $\mathbf{H} \perp \mathbf{D}$, as follows [9, 10, 13]:

$$2\pi\hbar\nu_{\pm} = \left| g_{\parallel} \mu_{\mathrm{B}} H \pm \frac{\pi D}{2} \right| , \tag{3}$$

$$2\pi\hbar\nu_{\pm} = \sqrt{(g_{\perp}\mu_{\mathrm{B}} H)^2 + \left(\frac{\pi D}{2}\right)^2} . \tag{4}$$

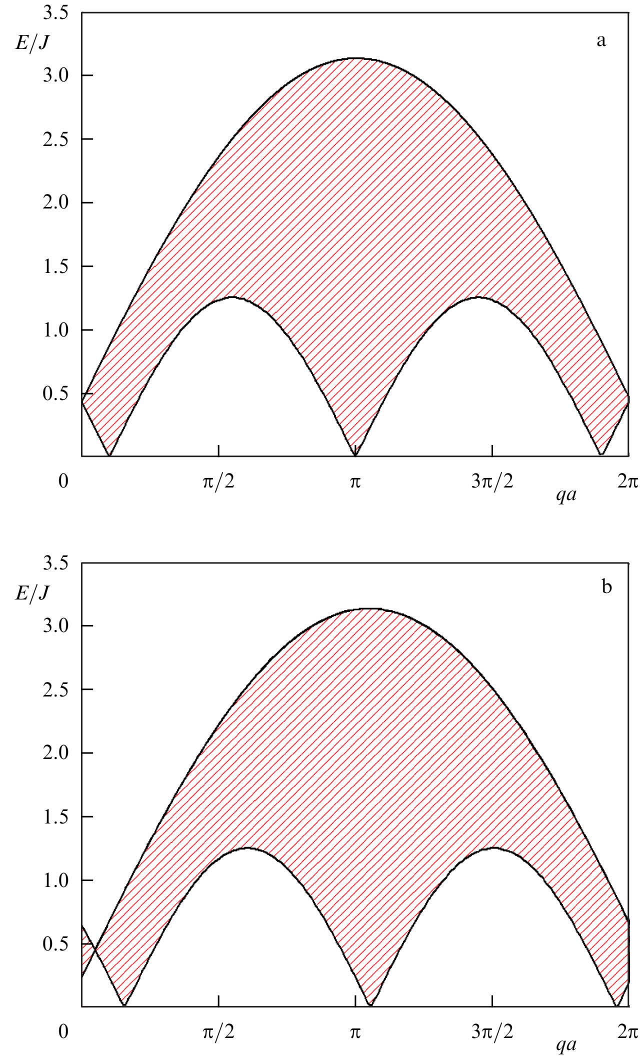

Figure 3. Continuum of transverse spin fluctuations in a magnetic field in the absence (a) and in the presence (b) of a uniform Dzyaloshinsky–Moriya interaction.

Here, $g_{\parallel,\perp}$ are the g-factors for a magnetic field parallel (perpendicular) to $\mathbf{D}$. These relations determine the zero field gap, $2\pi\hbar\Delta = \pi D/2$, and suggest the presence of a soft mode for $\mathbf{H} \parallel \mathbf{D}$ in a magnetic field $H_0 = \pi D/(2g_{\parallel}\mu_{\rm B})$, when the Zeeman energy is related in a certain specific way to the Dzyaloshinsky–Moriya interaction energy.

Among the recently studied chain type antiferromagnets there are two compounds — the chloride Cs_2CuCl_4 (see, for example Refs [15–17]) and the bromide $K_2CuSO_4Br_2$ studied in Ref. [18] — containing magnetic Cu^{2+} ions coupled by the antiferromagnetic Heisenberg exchange and by the uniform Dzyaloshinsky–Moriya interaction and exhibiting a distinct continuum of spinon excitations in neutron scattering experiments.

We have studied the electron spin resonance in the crystals of these compounds [8, 10, 19, 20] and have revealed that the above-mentioned spinon doublet is formed in them on cooling below the temperature of the formation of antiferromagnetic correlations, $T_J = J/k_{\rm B}$. Consistent with theoretical predictions, the doublet is most manifested for the magnetic field along the vector $\mathbf{D}$ determined by the crystallographic symmetry. The perpendicular orientation produces a single resonant line but opens a gap in the zero-field spectrum.

2. Experiment

The reported experiments used a multifrequency spectrometer in which several resonator measuring cells are combined with an ^{3}He pumping cryostat or dilution refrigerator and a 12-T cryomagnet. The resonant cells used cover the frequency range of 0.5–250 GHz. The experiment recorded the magnetic field dependence of the transmitted microwave power signal, the drastic reduction in the signal indicating that the magnetic resonance conditions are satisfied.

3. Magnetic resonance of spinons in a chain antiferromagnet with a uniform Dzyaloshinsky–Moriya interaction

Let us consider first, following work [8], the electron spin resonance in $K_2CuSO_4Br_2$. This compound exhibits very strongly its one-dimensional nature: the ratio of the intra-to-interchain exchange reaches 600 [18], and the ordering due to the interchange exchange and to other interactions weaker than the main exchange occur at a temperature of 70 mK, which is much lower than $T_J = 20$ K. Thus, there is a broad temperature range $T_{\rm N} < T \ll T_J$ (where $T_{\rm N}$ is the Néel temperature) which allows the existence of spin chains in a state near the ground state, whereas the interchain interaction is negligibly small, and the correlations induced by it are destroyed by a low temperature.

The crystal structure of $K_2CuSO_4Br_2$ is illustrated in Fig. 4. A characteristic feature of the structure is the absence of an inversion center between magnetic ions in the chain, the reason being the shift of the SO_4 group from the line connecting the copper atoms. This shift is the same throughout the chain, which ensures that the interaction at work is precisely the uniform Dzyaloshinsky–Moriya interaction. The vector $\mathbf{D}$ in the neighboring chain is opposite in direction, so that the up–down equivalence is not violated in the crystal as a whole.

In Fig. 5, the formation of a spinon doublet is presented by the temperature evolution of the electron spin resonance spectrum at 27.83 GHz.

At temperatures above T_J, one observes the usual paramagnetic resonance in a magnetic field, with the generator frequency equal to the Larmor frequency: $\nu_{\rm L} = g\mu_{\rm B}H/\hbar$. As the temperature is lowered, Fig. 5 shows that the line doublet $M_{\pm}$ forms for the magnetic field orientation $\mathbf{H} \parallel b$ (i.e., $\mathbf{H} \parallel \mathbf{D}$). Near the paramagnetic resonance field, we are left with a weak line P appeared due to the residual

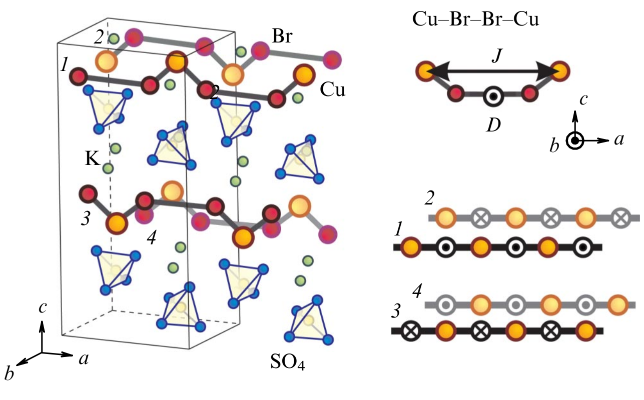

Figure 4. Crystal structure of $K_2CuSO_4Br_2$. (Courtesy of the authors of Ref. [8]. Copyright (2015) by the American Physical Society.)

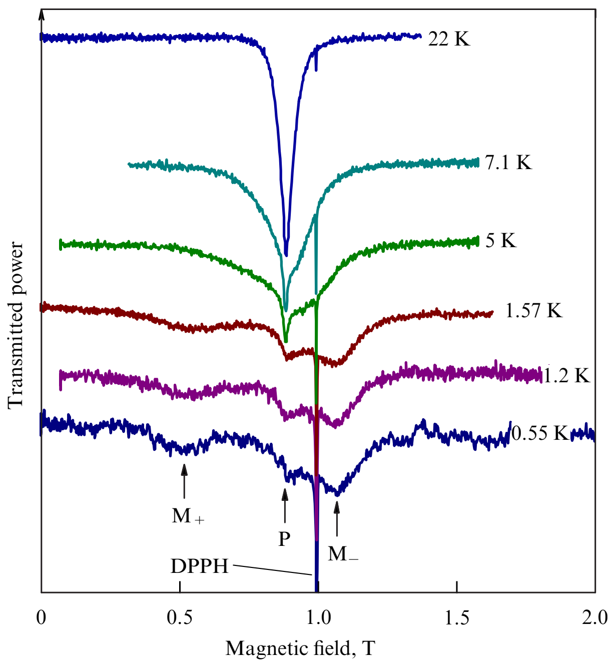

Figure 5. Temperature evolution of the electron paramagnetic resonance signal at a frequency of 27.83 GHz. DPPH stands for the reference signal of diphenylpicrylhydrazyl ($g = 2$). (Courtesy of the authors of Ref. [8]. Copyright (2015) by the American Physical Society.)

paramagnetic impurities and defects and exhibiting an increase in intensity under cooling, typical for materials with impurities. For the field orientation $\mathbf{H} \perp \mathbf{D}$, one single line is preserved which, however, shows a down-field shift from the paramagnetic resonance signal.

Figures 6 and 7 show the temperature dependences of the resonance fields for experiments at a frequency of 27.83 GHz. The curves suggest that the low-temperature spectrum starts forming on cooling to temperatures below T_J, but continues so at much lower temperatures; it is only at temperatures below 1 K where the resonance fields cease to change. Using the limiting values of the resonance field for $\mathbf{H} \perp \mathbf{D}$ and Eqn (4), we can determine the magnitude of the band gap, $\Delta = 8.7$ GHz, and then proceed to calculate the Dzyaloshinsky–Moriya interaction parameter: $D = 0.27$ K.

In order to verify the theoretical field–frequency dependences (3), (4), we measured the resonance fields over a wide range of frequencies both below and above the gap, concentrating on the search for a soft mode predicted to exist in a b-directed magnetic field of magnitude $H_D = D/g\mu_B$. The measured results are plotted in Figs 8, 9.

Figures 8 and 9 show by dashed lines the results calculated from Eqns (3), (4) using the parameter D determined above. The magnetic field orientation $\mathbf{H} \parallel a, c$ was observed to provide good agreement with theory. For $\mathbf{H} \parallel b$ and relatively low (up to 30 GHz) frequencies, good agreement is observed with theoretical predictions obtained with no fitting parameters (see the top inset to Fig. 8). Higher frequencies lead to a marked deviation of the theoretical prediction: the high-frequency component of the doublet disappears, whereas its low-frequency counterpart approaches the Larmor frequency. There are two possible reasons for these frequency–field dependences. One is that a strong magnetic field suppresses zero-point quantum spin fluctuations, including their associated continuum [20, 21], and the other is that in a strong field, when the Zeeman energy greatly exceeds the Dzyaloshinsky–Moriya interaction energy, the formation of a doublet may also prove problematic. This conjecture is also

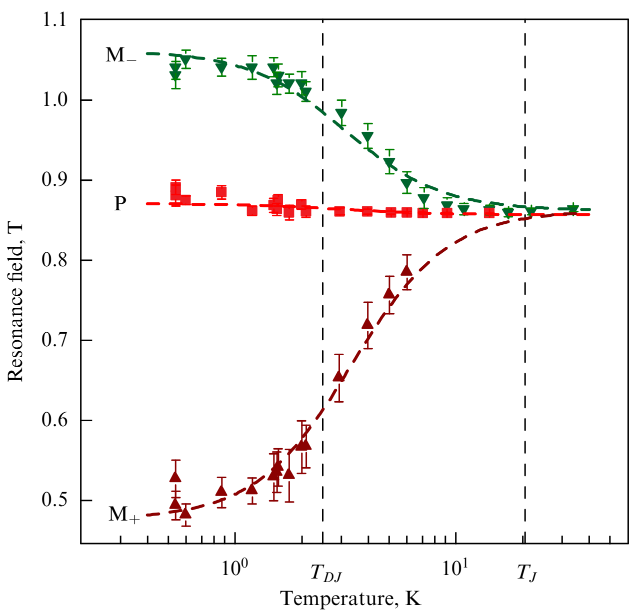

Figure 6. Temperature dependence of resonance fields at 27.83 GHz for $\mathbf{H} \parallel \mathbf{D}$. (Courtesy of the authors of Ref. [8]. Copyright (2015) by the American Physical Society.)

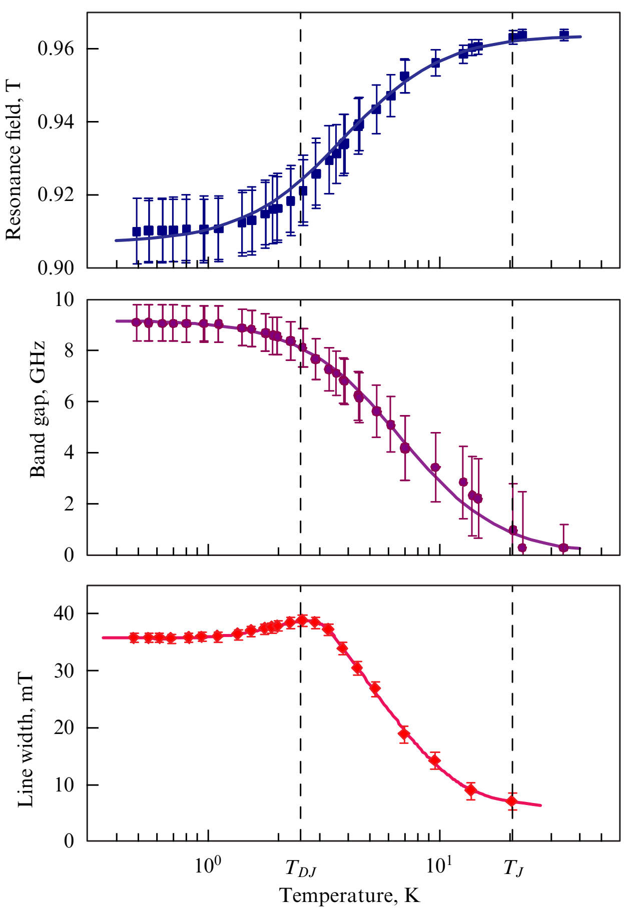

Figure 7. Temperature dependence of resonance fields, band gap, and line width at 27.83 GHz for $\mathbf{H} \perp \mathbf{D}$. (Courtesy of the authors of Ref. [8]. Copyright (2015) by the American Physical Society.)

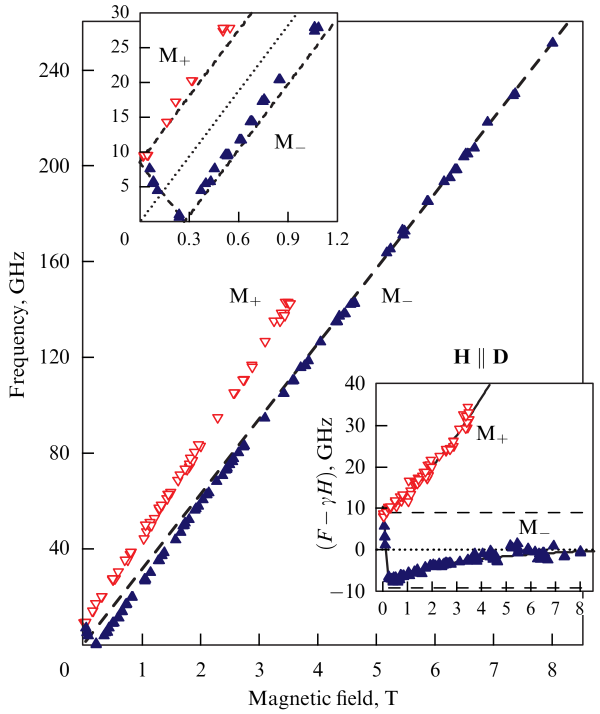

Figure 8. Frequency–field dependence of spin resonances for **H** ∥ *b*. Top inset: low-frequency range. Bottom inset shows the deviation of the resonance frequencies from the Larmor frequency, depending on the magnetic field. Dashed line: theoretical dependence (3). (Courtesy of the authors of Ref. [8]. Copyright (2015) by the American Physical Society.)

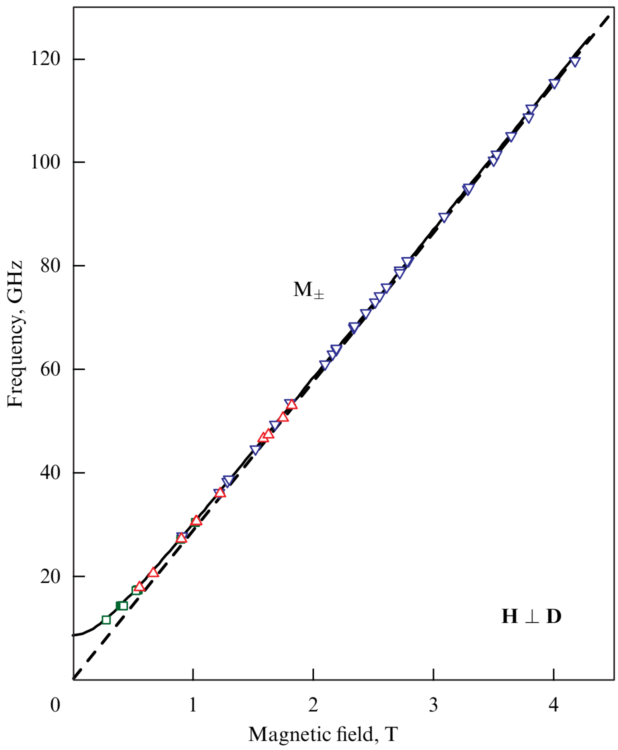

Figure 9. Frequency–field dependence of spin resonances for **H** ⊥ *b*. The solid line represents the theoretical dependence (4), and the dashed line corresponds to the paramagnetic resonance at a temperature above 20 K. (Courtesy of the authors of Ref. [8]. Copyright (2015) by the American Physical Society.)

favored by the temperature dependence of the band gap, whose vanishing temperature is not on the order of T_J, but is much lower (empirically, $T_{DJ} = \sqrt{JD}/k_B$).

By and large, the results reviewed point to the conclusion that the uniform Dzyaloshinsky–Moriya interaction modifies the two-spinon continuum in a chain-structured $S = 1/2$ antiferromagnet and the spectrum of magnetic excitations therewith shifts in k-space in such a way that the continuum region embraces the origin of coordinates. As a result, a fine structure develops in the magnetic resonance spectrum in the form of a doublet, whose components differ in frequency by an amount equal to the continuum width for the wave vector q_{DM} and which appear on each sides of the paramagnetic resonance frequency. Simultaneously, a soft mode develops in the field at which the Zeeman energy is balanced by the Dzyaloshinsky–Moriya interaction energy.

4. Magnetic resonance of spinons in a quasi-two-dimensional triangular-lattice antiferromagnet

We now turn to a more complex magnetic material, Cs_2CuCl_4, whose magnetic Cu^{2+} ions are located in the layers of isosceles triangle lattice and in which the interlayer exchange J^* is much weaker than both the exchange $J = 4$ K along the base of the structural triangle and the skewed exchanges $J' = 1.3$ K along the laterals. The scheme of exchange bonds is presented in Fig. 10. What is remarkable about this compound is that, while structurally quasi-two-dimensional, neutron experiments [15] give evidence that at temperatures $1 < T < 4$ K it reveals an excitation continuum which well corresponds, in terms of boundaries and spectral density, to the one-dimensional chains of $S = 1/2$ spins. The reason for this is the frustration of skewed exchange bonds J' [22, 23].

This indeed follows from the fact that within molecular field theory the correlations along the triangle bases should, in the limit $J \gg J'$, be antiferromagnetic, with the result that the molecular fields of the spins residing in th triangle base will compensate for one another as they act on the spin located at the vertex of the triangle. A quantum Monte Carlo investigation into this question [22] led to the conclusion that correlations in such a triangular system can retain its one-dimensional nature even if J' increases to the value that

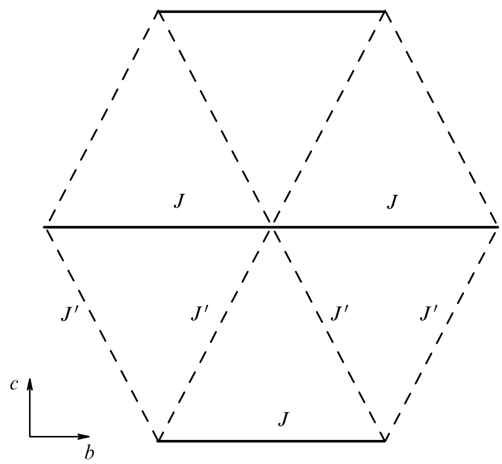

Figure 10. Structure of exchange bonds in the *bc* plane in a Cs_2CuCl_4 crystal. (Taken from Ref. [19].)

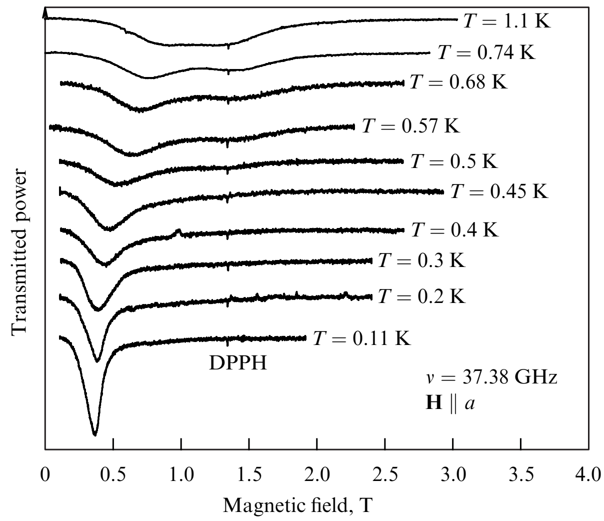

Figure 11. Temperature evolution of the 37.38-GHz magnetic resonance line in a Cs_2CuCl_4, **H** ∥ *a* crystal on cooling below the Néel point. (Courtesy of the authors of Ref. [19]. Copyright (2012) by the American Physical Society.)

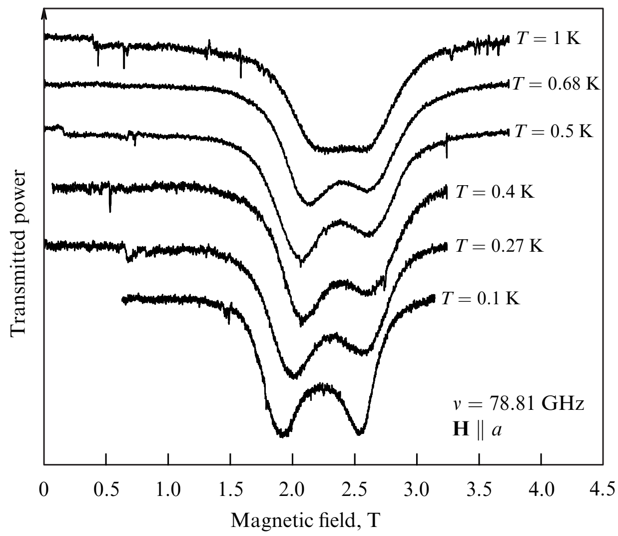

Figure 12. Temperature evolution of the 78.81-GHz magnetic resonance line in a Cs_2CuCl_4, **H** ∥ *a* crystal on cooling below the Néel point T_N. (Courtesy of the authors of Ref. [19]. Copyright (2012) by the American Physical Society.)

the exchange integral ratio becomes very large: $J'/J = 0.6$. Spin-liquid behavior (the presence of a spinon continuum in the absence of ordering) is observed in this compound in the temperature range of $0.6 < T < 4$ K. Cooling below $T_N = 0.62$ K causes ordering into a spiral magnetic structure, and above 4 K the spin–spin correlations are destroyed and the crystals exhibit magnetic properties characteristic of normal paramagnets.

Ordering at a temperature $T_N \ll T_J$ under conditions of frustrated exchange interaction is associated with the presence of weak interactions, namely, the interlayer exchange and the Dzyaloshinsky–Moriya interaction (the effect of the latter on magnetic ordering in Cs_2CuCl_4 was considered in Ref. [17]). Unlike ordering in usual antiferromagnets, here, the ordered spin component does not reach the nominal value of $S_z = 1/2$ even at absolute zero: the spin reduction due to quantum spin fluctuations is as large as a quarter of the nominal value [24].

Because of the presence in Cs_2CuCl_4 of the two-spinon continuum and because symmetry rules allow the presence of the uniform Dzyaloshinsky–Moriya interaction on exchange bonds, we can, in this compound as well, check the presence of the magnetic resonance spinon doublet and monitor how the spinon type magnetic resonance evolves as the material makes the transition to the ordered phase with the essential reduction in the ordered spin component.

In Fig. 11, the plot of the temperature evolution of the 37.38-GHz magnetic resonance line illustrates the emergence of the spinon doublet and its transformation into an antiferromagnetic resonance line as the Néel point is passed. At higher frequencies, however — for example, at 78.81 GHz — Fig. 12 demonstrates that the doublet line persists even on cooling to extremely low temperatures. The passage between these two frequency regimes, i.e., from the antiferromagnetic resonance at low frequencies to a spinon type resonance at high frequencies, occurs at a frequency close to 60 GHz, i.e., at the exchange order frequency $J/\hbar$. This passage is illustrated by the experimental data in Fig. 13, which show how the single antiferromagnetic resonance line transforms into a spinon doublet at high frequencies.

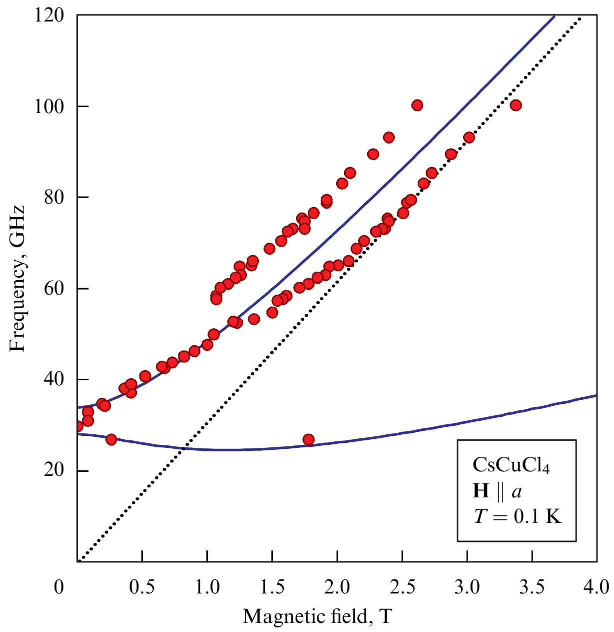

Figure 13. Frequency versus field diagram for major magnetic resonance signals for a Cs_2CuCl_4, **H** ∥ *a* crystal at $T = 0.1$ K. Solid lines: theoretical calculation of the antiferromagnetic resonance for a planar magnetic structure. Dotted line: paramagnetic resonance at $T = 10$ K. (Taken from Ref. [19].)

Such a coexistence of two types of magnetic resonance is extremely remarkable and shows that an ordered antiferromagnetic structure with a strongly reduced ordered spin component exhibits simultaneously spin–wave modes of spin vibrations characteristic of ordered systems and spinon modes characteristic of a quantum-disordered magnet.

5. Conclusion

An experimental study has been made of magnetic resonance in quantum magnets with a low-dimensional structure of antiferromagnetic exchange bonds. The two-spinon excitation continuum at small wave vectors is found to have a fine structure due to the uniform Dzyaloshinsky–Moriya interaction.

Acknowledgments

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