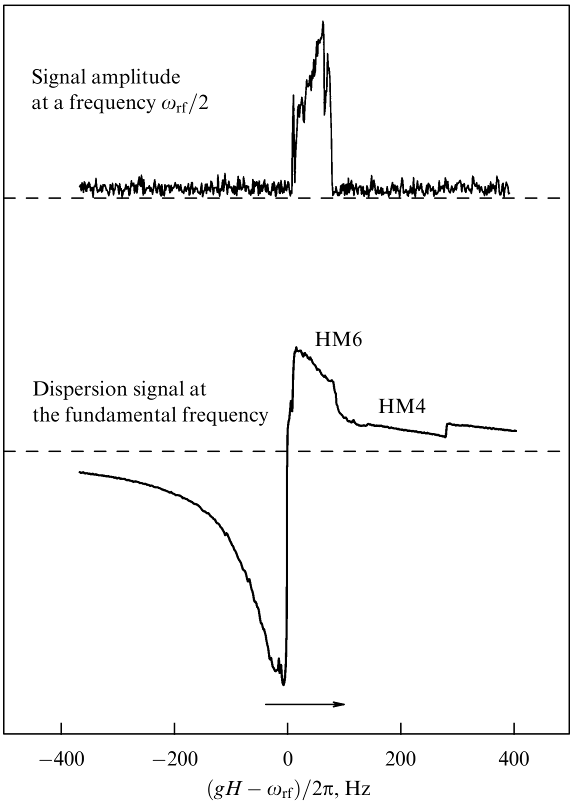

Figure 3. Dispersion signal at a frequency ω_{rf} (lower curve) and the signal amplitude at a fractional ($\omega_{rf}/2$) frequency (upper curve). The arrow indicates the direction of the variation of the scanning field. $\omega_{rf}/2\pi = 1699$ kHz; the Q factor of the cold circuit is 7000, $T \approx 0.98T_c$.

which leads to the formation of uniformly precessing domains [12].

I am very grateful to all my colleagues who participated in the above-described experiments.

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References

1. Leggett A J *Rev. Mod. Phys.* **47** 331 (1975)
2. Volovik G E *J. Phys.: Cond. Matter* **5** 1759 (1993)
3. Fomin I A *J. Low Temp. Phys.* **31** 509 (1978)
4. Vollhardt D, Wölfle P *The Superfluid Phases of* ^{3}He (London: Taylor & Francis, 1990)
5. Brinkman W, Smith H *Phys. Lett. A* **53** 43 (1975)
6. Kharadze G, Vachnadze G *Pis'ma Zh. Eksp. Teor. Fiz.* **56** 474 (1992) [*JETP Lett.* **56** 458 (1992)]
7. Dmitriev V V et al. *Phys. Rev. Lett.* **78** 86 (1997)
8. Sonin E B *Zh. Eksp. Teor. Fiz.* **94** 100 (1988) [*Sov. Phys. JETP* **67** 1791 (1988)]
9. Eltsov V B et al. *J. Low Temp. Phys.* **113** 645 (1998)
10. Dmitriev V V, Kosarev I V, Ponarin D V *Pis'ma Zh. Eksp. Teor. Fiz.* **69** 200 (1999) [*JETP Lett.* **69** 215 (1999)]
11. Kharadze G A, Suramlishvili N G, Vachnadze G E *Fiz. Nizk. Temp.* **23** 803 (1997) [*Low Temp. Phys.* **23** 405 (1997)]
12. Borovik-Romanov A S et al. *Zh. Eksp. Teor. Fiz.* **88** 2025 (1985) [*Sov. Phys. JETP* **61** 1199 (1985)]; Fomin I A *Zh. Eksp. Teor. Fiz.* **88** 2039 (1985) [*Sov. Phys. JETP* **61** 1207 (1985)]

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Magnetic resonance of intrinsic and extrinsic defects in a spin-Peierls magnet $CuGeO_3$

A I Smirnov

1. Introduction

A spin-Peierls transition is a brilliant phenomenon in the physics of low-dimensional magnets. This transition was revealed in crystals containing chains of magnetic ions with spin $S = 1/2$ coupled through an antiferromagnetic exchange interaction. The interchain interaction should be much weaker than the intrachain one. The phase transition into the spin-Peierls state consists in the dimerization of magnetic atoms into chains; in this process, the spins are grouped to form pairs in which the ion separation is shorter than between ions of neighboring pairs. The exchange interaction becomes alternating, i.e., the exchange integral alternately takes on the values $J(1+\delta)$ and $J(1-\delta)$. This transition is accompanied by a gain in the exchange energy that exceeds the loss in the elastic energy of the crystal [1]. The rearrangement of the lattice turns out to be correlated in all three dimensions, i.e., the dimers are located on an ordered sublattice. Below the point of the above transition, a so-called spin energy gap appears because of the alternation of the exchange interaction; this gap separates the ground singlet state from the spectrum of triplet excitations. Thus, the crystal becomes nonmagnetic at low temperatures; below the transition point, the susceptibility should exponentially vanish.

In spite of the great variety of quasi-one-dimensional magnetic structures, the spin-Peierls transition has been revealed only in a few organic compounds and one inorganic compound. The first and so far the only inorganic substance that exhibits the spin-Peierls transition is $CuGeO_3$ [2]. This compound can be obtained in the form of perfect single crystals, which permits one to perform exhaustive crystallographic and magnetic investigations, including elastic and inelastic neutron scattering. In addition, this compound allows substitution of nonmagnetic ions such as Zn^{2+}, Mg^{2+} or magnetic ions such as Ni^{2+} for the magnetic Cu^{2+} ions.

The main parameters that determine the magnetic properties of $CuGeO_3$ are as follows (see, e.g., Ref. [3]): the exchange integral inside the chains is $J_c = 10.2$ meV; the spin-Peierls temperature is $T_{SP} = 14.5$ K; dimerization in the chains of Cu ions located along the c axis of the orthorhombic crystal leads to the alternation of the exchange interaction with a parameter $\delta \approx 0.04$; and the spin energy gap at zero temperature is $\Delta \approx 2$ meV. The magnetic structure of $CuGeO_3$ is not ideally one-dimensional; the interchain exchange integrals are $J_b = 0.1J_c$ and $J_a = -0.01J_c$ [4]. It has also been supposed that there is an exchange interaction with next-nearest neighbors with an exchange integral approximately equal to $0.36J_c$ [5].

If the lattice of $CuGeO_3$ were rigid, this crystal would suffer a transition into an antiferromagnetic state at a Néel temperature $T_N \sim (J_cJ_b)^{1/2} \sim 10$ K [6]. However, the spin-Peierls state proves to be energetically more favorable. Doping $CuGeO_3$ with both magnetic and nonmagnetic impurities stimulates the formation of long-range antiferromagnetic order in the compound at low temperatures [7]. In this case, the dimerization and the long-range antiferromagnetic order prove to coexist at small impurity concentrations. The mechanism of induction of antiferromagnetic ordering by impurities was explained in Refs [5, 8]. It was shown that, in the vicinity of an impurity or a defect, regions of antiferromagnetically correlated spins of copper ions arise in the form of clusters or frozen solitons. The edges of these solitons overlap, which leads to the extension of antiferromagnetic correlations over the whole crystal owing to intrachain and interchain interactions. These solitons represent multispin objects with a microscopic value of the total spin.

In this report, we describe experiments on the magnetic resonance of spin clusters caused by the presence of impurity atoms and on the investigation of antiferromagnetic resonance in the ordered phase stimulated by impurities. We also describe the investigations of signals of magnetic resonance in pure crystals, which are related to dimerization defects in the form of boundaries of spin-Peierls dimerization domains.

2. Electron spin resonance of magnetic clusters that are formed around impurity ions of Ni^{2+} in the spin-Peierls matrix of $CuGeO_3$

In accordance with the formation of a spin gap, the intensity of the EPR signal from pure stoichiometric samples of $CuGeO_3$ at temperatures below the transition point decreases and becomes significantly lower than the intensity at the T_{SP} temperature. In the $CuGeO_3$ samples grown at low ('minimal') rates of crystallization, the minimum susceptibility and intensity of the EPR signal (observed at a temperature of 4 K) were no more than 5% of the corresponding values at 14.5 K. Such an intensity corresponds to a concentration of free spins of about 10^{-3} per copper ion. This residual signal is related to the presence of residual structural defects and will be discussed below.

Upon partial substitution of Ni^{2+} ions for copper at low temperatures the intensity of the EPR signal increases. This intensity corresponds to a concentration of free ions approximately equal to the concentration of the introduced impurities. For the range of Ni concentrations 0.2–4% taken in this work, the intensity of the EPR signal at low temperatures significantly exceeds the signal of residual defects in pure samples. Figure 1 displays the dependence of the *g* factor of the EPR signal in samples with different concentrations of nickel. It is seen that the variation of the *g* factor upon the introduction of an impurity is quite significant and has an apparently anomalous character: with decreasing temperature (i.e., with decreasing concentration of triplet excitations of the spin-Peierls phase), the *g* factor significantly decreases and at low temperatures goes far beyond the region limited by typical values of the *g* factor for Cu^{2+} and Ni^{2+} ions (2.1 and 2.3, respectively). Thus, the EPR signal with a *g* factor equal to 1.42 observed at temperatures below 4 K cannot be associated with isolated nickel or copper ions or exchange pairs of these ions. We believe that this signal should be related to the formation of multispin clusters. The *g* factor of the signal of these clusters turned out to be much more anisotropic than the signal from the paramagnetic phase.

The strongly anisotropic and anomalously small value of the *g* factor can be explained based on the consideration of a multispin object in which the spins of copper ions are coupled with the nickel spin located in the center of a cluster through a symmetric exchange Heisenberg interaction and an antisymmetric Dzyaloshinskiĭ–Moriya exchange interaction. The allowance for the Dzyaloshinskiĭ–Moriya interaction and the consideration of a system consisting of more than three spins permits one to obtain a value of the effective *g* factor strongly differing from 2 for the direction of the magnetic field perpendicular to the Dzyaloshinskiĭ–Moriya vector. In the model that allows for the interaction of six spins [9], the value of the *g* factor observed in our experiments is obtained for a Dzyaloshinskiĭ–Moriya exchange equal to approximately $0.3J_c$. The structure of a spin cluster calculated on the basis of the above model is shown in Fig. 2. This model, which takes into account six spins (*1–6*) and the Dzyaloshinskiĭ–Moriya interaction, pretends to only a qualitative description

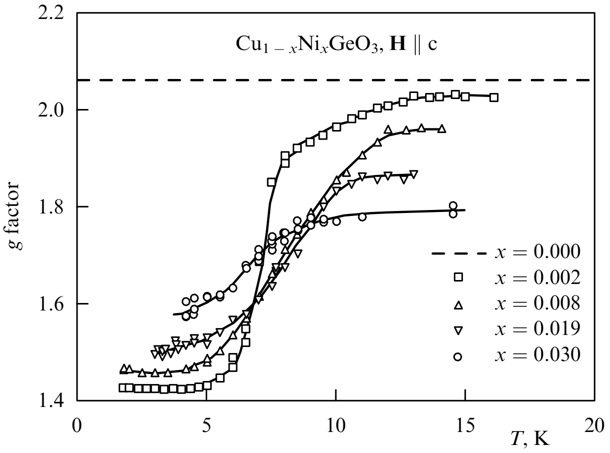

Figure 1. Variation of the *g* factor (g_c) for $CuGeO_3$ samples doped with nickel as a function of temperature.

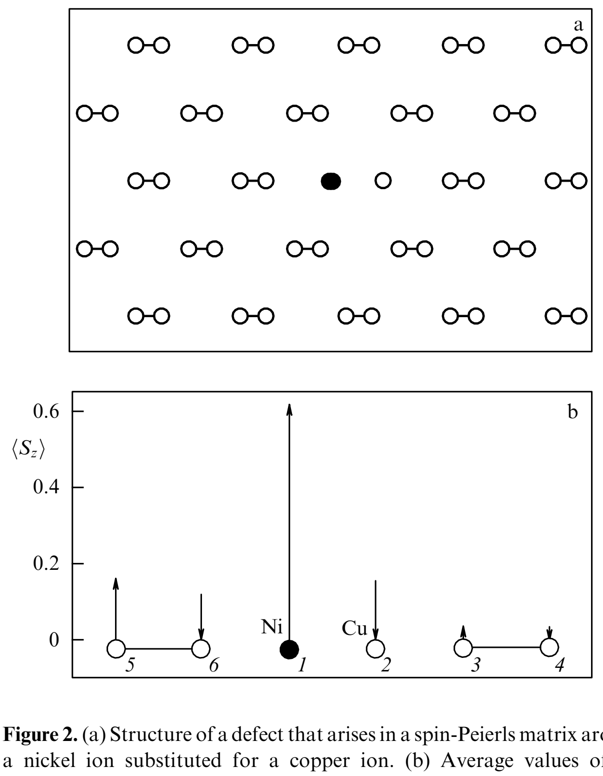

Figure 2. (a) Structure of a defect that arises in a spin-Peierls matrix around a nickel ion substituted for a copper ion. (b) Average values of the projections of spins on lattice sites in the vicinity of an impurity spin. The Hamiltonian and the model parameters are given in Ref. [9].

and illustrates the multispin character of the behavior of the observed EPR signal.

3. Antiferromagnetic resonance in the antiferromagnetic phase stimulated by impurities

Figures 3 and 4 display antiferromagnetic resonance spectra of single-crystal samples of $Cu_{0.968}Ni_{0.032}GeO_3$ at a temperature of 1.8 K and of $Cu_{0.98}Zn_{0.02}Ge_{0.02}O_3$ at a temperature of 1.3 K. In the first case, the spin-Peierls magnet is diluted with foreign magnetic ions. In the second compound, the spin-Peierls matrix is diluted with a diamagnetic impurity. The spectrum of frequencies of resonance absorption in both cases is typical of an antiferromagnet with two axes of anisotropy and indicates the induction of a magnetic order by impurities in a spin-Peierls crystal.

For the samples with impurity concentrations more than 3%, the antiferromagnetic resonance spectrum corresponds well to the dependences (calculated by the standard method) of the resonance frequencies on the magnetic field for conventional antiferromagnets (solid and dashed lines in Figs 3 and 4). These results permit one to determine the magnitudes of the gaps in the resonance absorption spectrum and of the field of the spin-flop transition (in this field, the frequency has a value close to zero for the field oriented along the easy axis of antiferromagnetism). Note that in samples doped with nickel and zinc the directions of the easy axes of antiferromagnetism differ: this is the c axis in samples doped with zinc and the a axis of the orthorhombic structure in the crystals doped with nickel.

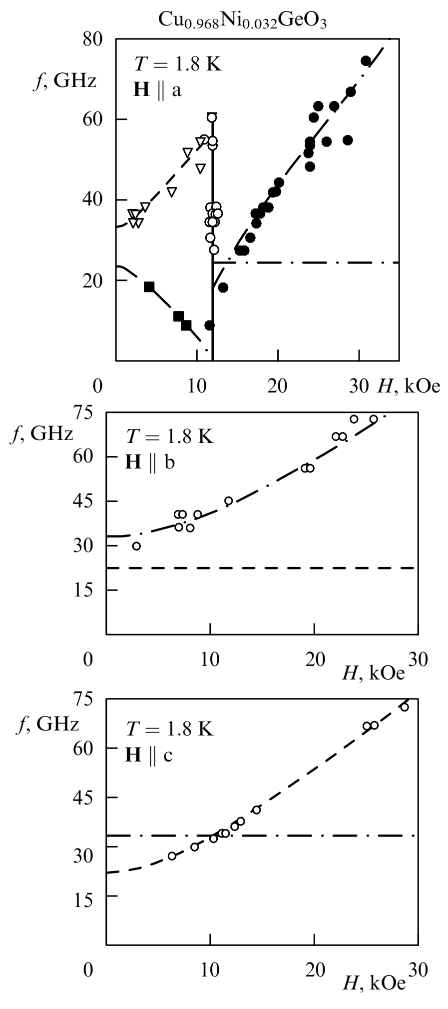

Figure 3. Spectrum of antiferromagnetic resonance in $Cu_{0.968}Ni_{0.032}GeO_3$ at a temperature of 1.8 K.

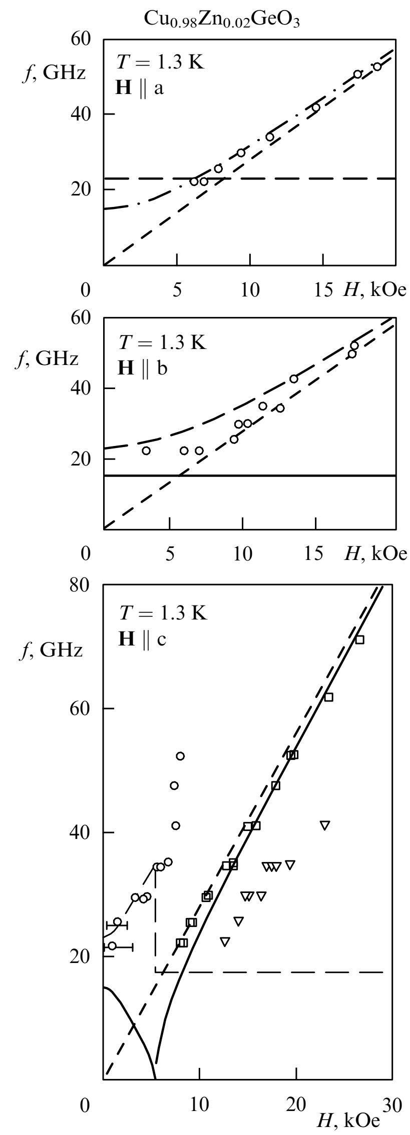

Figure 4. Spectrum of antiferromagnetic resonance of $Cu_{0.98}Zn_{0.02}GeO_3$ at a temperature of 1.3 K.

For samples with a zinc concentration of 0.02 and nickel concentration of 0.019, the correspondence of the spectrum of magnetic resonance to the standard dependence of the frequency on the antiferromagnetic resonance field is violated (see Fig. 4). This appears to be due to the occurrence of dimerization, which vanishes at a certain critical concentration, as was shown in Ref. [10].

4. Intrinsic defects of a spin-Peierls magnet

The dimerized state of a spin-Peierls crystal is twofold degenerate, since there are two ways of division into dimers in the chains. In each of the halves of Fig. 5, two domains are shown schematically, dimerized according to the first or the second fashion. On the left-hand and right-hand sides of Fig. 5, two types of boundaries of these domains are shown. The domain boundaries contain nondimerized spins. The existence of such domain boundaries is energetically unfavorable, just as the existence of the boundaries of

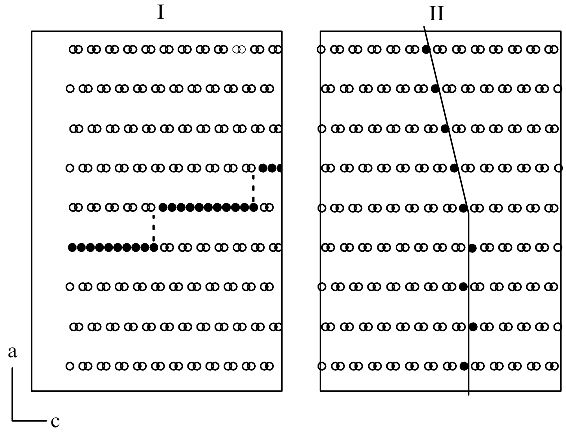

Figure 5. Domains and domain boundaries of a spin-Peierls phase.

crystallites that are formed upon crystallographic structural transitions or as the existence of boundaries of domains of the antiferromagnetic phase. However, both the crystallographic and antiferromagnetic domains (and domain boundaries) exist owing to the pinning of domain boundaries at point defects. Thus, because of the presence of a single point defect, a whole plane of defects arises. This explains the relatively high residual susceptibility of pure spin-Peierls crystals.

In the case of a spin-Peierls magnet, several types of boundaries containing nondimerized spins can exist, which should contribute to the residual magnetic susceptibility and can be identified by their magnetic resonance signals. The domain boundaries of the first type (shown on the left in Fig. 5) contain nondimerized chains of spins, whereas the boundaries of the second type contain nondimerized spins from different chains. In accordance with what was said in the Introduction and with the results of Refs [5, 8], a soliton-type spin cluster should arise around each of the nondimerized spins located in a boundary of the second type. At the steps in a boundary of the first type, breaks in the nondimerized chains occur and exchange-coupled pairs of copper ions with a total spin $S = 1$ are formed at the expense of the ferromagnetic exchange in the a direction.

Investigation of the EPR of pure perfect $CuGeO_3$ crystals at temperatures below 4 K revealed the existence of a weak EPR signal with a total intensity corresponding to a concentration of free spins of 10^{-3} per copper ion. Measurements of the concentrations of residual impurities such as Fe, Ni, Mn, and Co using plasma spectroscopy showed that their concentration did not exceed 10^{-4} per copper ion.

At low temperatures, the spectrum of this signal contains three closely located lines (a, b, c) and a line d located apart, at a higher field (Fig. 6). A thorough investigation of these signals over a wide range of frequencies was performed in Ref. [11]. The ratios of intensities of these lines in different samples suggest that the line b, a doublet of lines a and c, and the line d refer to various types of defects. The g factor of the line b and the absence of the initial splitting indicate that this signal originates from isolated Cu^{2+} ions with spin $S = 1/2$ which exist at the ends of broken chains. This line may also be related to nondimerized chains of Cu^{2+} ions. The initial splitting of the frequencies of the resonance lines a and c and the related g factor indicate the origin of this signal from pairs of Cu^{2+} ions with a total spin $S = 1$ coupled by exchange interaction.

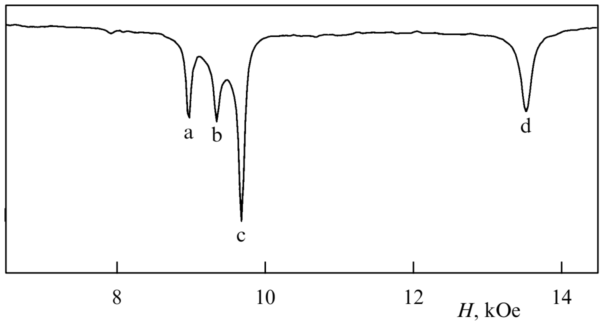

Figure 6. Record of an EPR line at a frequency of 26.7 GHz. Magnetic field is parallel to the c axis, $T = 1.3$ K.

The values and the angular dependence of the components of the g factor tensor are analogous to the above-described case of the EPR of spin clusters based on Ni ions. A qualitative description of the resonance frequency of this line was obtained in Ref. [11] on the basis of a cluster model containing 5 spins (one nondimerized spin in the center and two dimers on the sides). To obtain the correspondence to the observed magnitude $g_c = 1.44$, the presence of the antisymmetric Dzyaloshinskiĭ-Moriya exchange may be suggested. The related constant in this case turns out to be $0.2J_c$.

5. Two-dimensional magnet at a domain boundary of the spin-Peierls phase

The EPR line d possesses a nonlinear high-frequency susceptibility atypical of paramagnetic resonance. Figure 7 displays the records of the resonance absorption lines of a pure sample of $CuGeO_3$ at a temperature of 1.3 K at various values of the microwave power. These data show that the imaginary part of the high-frequency magnetic susceptibility increases in a threshold fashion (in the microwave power). The effect of the saturation of the resonance line usually observed in the paramagnetic resonance of isolated ions leads to the reverse effect of the power: the imaginary part of susceptibility decreases with increasing power.

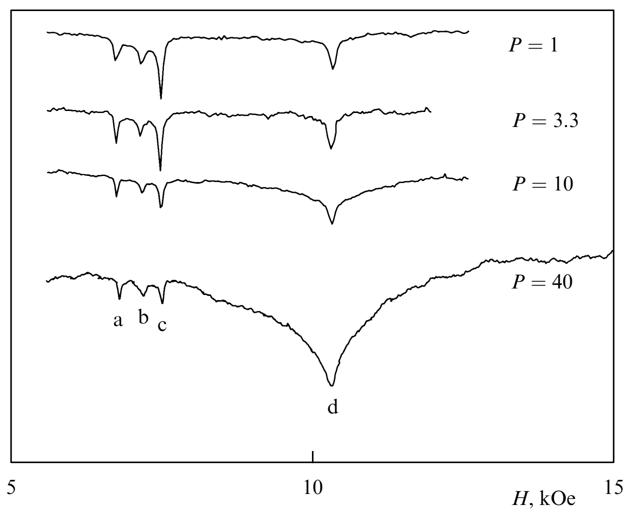

Figure 7. EPR line (relative change in the signal passed through a resonant cavity with a sample) at various values of the power at a frequency of 20.2 GHz. The power P is given in arbitrary units. The magnetic field is parallel to the c axis, $T = 1.3$ K.

The threshold effect observed can be explained by parametric excitation (see, e.g., Ref. [12) of spinons in a two-dimensionally correlated magnet, which represents a domain boundary of the second type. In this case, one quantum of the uniform spin precession splits into two spinons with opposite wave vectors. The conservation laws admit such a process of decomposition, since in a low-dimensional antiferromagnet there is a branch of spin vibrations with a zero gap in the presence of a magnetic field [13].

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References

1. Pytte E *Phys. Rev. B* **10** 4637 (1974)
2. Hase M, Terasaki I, Uchinokura K *Phys. Rev. Lett.* **70** 3651 (1993)
3. Regnault L P et al. *Phys. Rev. B* **53** 5579 (1996)
4. Nishi N, Fujita O, Akimitsu J *Phys. Rev. Lett.* **50** 6508 (1994)
5. Khomskii D, Geertsma W, Mostovoy M *Czech. J. Phys.* **46** Suppl. S6 3239 (1996)
6. Hennessy M J, McElwee C D, Richards P M *Phys. Rev. B* **7** 930 (1973)
7. Regnault L P et al. *Europhys. Lett.* **32** 579 (1995)
8. Fukuyama H, Tanimoto T, Saito M *J. Phys. Soc. Jpn.* **65** 1182 (1996)
9. Glazkov V N et al. *J. Phys.: Cond. Matter* **10** 7879 (1998)
10. Masuda T et al. *Phys. Rev. Lett.* **80** 4566 (1998)
11. Smirnov A I et al. *Zh. Eksp. Teor. Fiz.* **87** 1019 (1998) [*JETP* **87** 1019 (1998)]
12. Kveder V V, Kotyuzhanskiĭ B Ya, Prozorova L A *Zh. Eksp. Teor. Fiz.* **63** 2205 (1972) [*Sov. Phys. JETP* **36** 1165 (1973)]
13. Mueller G et al. *Phys. Rev. B* **24** 1429 (1981)