Magnetic Resonance of Spin Clusters and Triplet Excitations in a Spin-Peierls Magnet with Impurities

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The magnetic resonance spectrum of spin clusters formed in spin-Peierls magnets in the vicinity of impurity ions was investigated. The observed temperature dependences of the effective g-factor and the linewidth of the electron spin resonance (ESR) in crystals of Cu$_{1-x}$Ni$_x$GeO$_3$ are described in the model of the exchange narrowing of the two-component spectrum with one component ascribed to spin clusters and exhibiting an anomalous value of the g-factor and the other related to triplet excitations. An estimation of the size of the suppressed dimerization region around the impurity ion is obtained (this region includes about 30 copper ions). The dependence of the effective g-factor and the ESR linewidth on the impurity concentration at low temperatures indicates the interaction of clusters.

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I. INTRODUCTION

Crystals of quasi-one-dimensional magnet CuGeO$_3$ exhibit magnetic and crystallographic properties characteristic to spin-Peierls magnets. The magnetic structure of this compound is based on one-dimensional chains of Cu$^{2+}$ ions ($S = 1/2$) extended along the c-axis of the orthorhombic crystal structure. The value of the exchange integral along these chains is 10.4 meV.

Below the temperature of the spin-Peierls transition $T_{SP} = 14.5$ K, the dimerization of chains occurs: i.e., magnetic ions approach each other with the formation of pairs. The dimerization is accompanied by the alteration of the exchange integral, which in turn takes one of two values $J_{1,2} = J(1 \pm \delta)$. An energy gap $E \sim \delta J$ opens between the ground singlet state and triplet excitations. Due to the presence of the gap in the energy spectrum, the magnetic susceptibility decreases, and the pure crystal without defects becomes almost nonmagnetic at low temperatures. The lattice transformation due to the dimerization is correlated in space, and the dimers are located on a regular sublattice.

Interchain exchange interaction in CuGeO$_3$ is rather large (the value of the exchange integral along the two directions orthogonal to the chain is only by a factor of 10 and 100 less than the exchange integral along the chain). For this reason, in the absence of the spin-Peierls transition, antiferromagnetic ordering had to be observed. However, the spin-Peierls state is more preferable and is conserved down to very low temperatures.

CuGeO$_3$ is the only inorganic spin-Peierls compound in which a controlled substitution of magnetic ions is possible. The introduction of impurities results in a local suppression of the dimerization in the vicinity of the defect. As a result, the temperature of the spin-Peierls transition decreases, and at low temperatures the long-range antiferromagnetic order appears.

The occurrence of the antiferromagnetic order and the suppression of the dimerization order is explained in Refs. 10, 11. A cluster of antiferromagnetically correlated spins is formed around the impurity ion. In the chain of spins $S = 1/2$ with alternating exchange interaction, the antiferromagnetic correlations decay (see Ref. 12) thus forming wings of the cluster. As we recede from the defect, the mean value of the z-projection of the spin decreases exponentially. Overlapping of the clusters’ wings results in the expansion of the region of antiferromagnetic correlations and in the long-range antiferromagnetic order.

Substitution of the part of the Cu ions by Ni has two significant differences compared to other dopants.

First, in the antiferromagnetically ordered phase, the easy axis of anisotropy is directed along the a axis, whereas for other substituting impurities the easy axis of anisotropy is aligned along c. Second, an anomalous temperature dependence of the g-factor is observed in the dimerized phase. At the diminishing of the temperature below the transition point $T_{SP}$, the value of the effective g-factor begins to decrease and achieves the value
of 1.4 at low temperatures for $H \parallel c$. The anomalous value of the $g$-factor can be explained by the existence of the antisymmetric Dzyaloshinski–Moriya interaction in the vicinity of the defect. In a multispin system consisting of more than two spins, the existence of the Dzyaloshinski–Moriya interaction along with the symmetric Heisenberg exchange results in a strong anisotropy of the effective $g$-factor and in the decrease of its value. Calculations based on the six-spin model show that the existence of the antisymmetric exchange interaction with the value of the exchange integral of about 30% of the value of the intrachain exchange interaction is sufficient for the description of the observed deviation of the $g$-factor.

The present paper continues the study started in Ref. 8. Its purpose is to investigate high-quality samples of CuGeO$_3$ doped with nickel including those with a low content of the impurity ($x < 1\%$). The study of samples with a small concentration of the impurity (when the average distance between the impurity ions exceeds the characteristic cluster size) makes it possible to observe the magnetic resonance of isolated clusters. A noticeable difference of the $g$-factor of clusters from the $g$-factor of excitations of the spin-Peierls matrix makes it possible to differentiate between their ESR signals. In turn, this fact opens the possibility to investigate the interaction of clusters with the environment and between themselves. The analysis of the experimental data allowed us to determine the characteristic size of the cluster that is formed around the impurity ion, namely, the size of the region where the dimerization is destroyed and that of the region in which the antisymmetric exchange interaction exists.

II. EXPERIMENTAL TECHNIQUE AND SAMPLES

For the experiment, high-quality samples of Cu$_{1-x}$Ni$_x$GeO$_3$ with the impurity concentration $x = 0.2\%$ and $x = 0.8\%$ were grown. In order to analyze the dependence of the $g$-factor on concentration, samples with higher concentrations of the impurity ($x = 1.9\%$ and 3.0\%) were also used.

To control the quality of the samples, a single crystal of the pure compound grown following the same technology was used. At the temperature of 4 K, the magnetic susceptibility of this sample determined by the integral intensity of the ESR signal was about 4\% of the susceptibility at the transition temperature $T_{SP}$. This value corresponds to the residual concentration of the magnetic defects per a copper ion equal to 0.05\%.

The investigations were performed at the frequency of 36 GHz and the temperatures in the range 1.8–20 K with the help of an ESR spectrometer with a transmission type cavity. The magnetic resonance line was registered as the dependence of the intensity of the microwave power transmitted through the resonator on the magnetic field applied. In this case, the variation of the signal is proportional to the imaginary part of the magnetic susceptibility.

III. EXPERIMENTAL RESULTS

At the diminishing of the temperature below the spin-Peierls transition point (which is equal to 13.5 K for $x = 0.2\%$ and 12.0 K for $x = 0.8\%$), the field of the resonance absorption starts to increase. The temperature of the spin-Peierls transition was determined from the beginning of the decrease of the integral intensity of the ESR signal. The increase of the resonance absorption field corresponds to the decrease of the $g$-factor. The evolution of the ESR line with temperature is shown in Figs. 1 and 2.

The temperature dependences of the $g$-factor are presented in Figs. 3 and 4. At low temperatures ($T < 4K$), the values of the $g$-factor remain constant and equal $g_a = 1.75$, $g_b = 1.87$, and $g_c = 1.43$ (for $x = 0.2\%$).

For the sample with the impurity concentration $x = 0.2\%$, the magnetic resonance line splits into two components at the temperature $T' = 7$ K (Fig. 1). As the temperature decreases, one of those components continues to move to the higher fields, and its intensity increases. The second component remains in the field close to the ESR field above $T_{SP}$, but its intensity decreases and it almost vanishes as the temperature decreases further. The width of the magnetic resonance line has its maximum at the temperature close to the splitting temperature $T'$ (Fig. 5). A similar splitting was observed at other orientations of the sample with respect to the field for $x = 0.2\%$; however, we were able to follow it down to low temperatures only for $H \parallel c$ (this is due to the fact that for this orientation there is the maximal difference of the $g$-factors of two spectral components, which makes it possible to distinguish the weak absorption line on the wing of the strong one).

For the sample with the impurity concentration $x = 0.8\%$, the magnetic resonance line consists of the single component at all temperatures; the maximum of the linewidth is observed in the vicinity of $T'$ (Fig. 5).

In the paramagnetic phase the value of the $g$-factor is also different from the value characteristic for the pure compound. The dependence of the $g$-factor value on the impurity concentration at $T > T_{SP}$ is shown in Fig. 6. As the impurity concentration increases, the value of the $g$-factor decreases for all orientations of the magnetic field.

For samples with the impurity concentration $x = 1.9\%$ and 3.0\%, the long-range antiferromagnetic order takes place, the ordering manifests itself in the transition from the gapless ESR spectrum with a linear frequency-field dependence to a spectrum that is typical to antiferromagnets with orthorhombic symmetry. The Néel temperatures are $T_N = 2.5$ K for $x = 1.9\%$ and $T_N = 3.5$ K.
for \(x = 3.0\%\).

Comparison of the ESR lines at the minimal temperature (Fig. 7) shows that the field of resonance absorption and the width of the line of magnetic resonance are different for samples with different concentration of impurity. Dependences of the linewidth and the \(g\)-factor value on impurity concentration are presented in Fig. 8. For samples that exhibit the antiferromagnetic ordering, the data were taken at \(T = T_N\). For small \(x\), the width of the ESR line linearly depends on the concentration. Dependences of the ESR linewidth and of the \(g\)-factor value on the orientation of the magnetic field at \(T = 1.8\) K for the sample with \(x = 0.8\%\) are shown in Fig. 9.

**IV. DISCUSSION**

Before considering the quantitative analysis of the experimental data, we will present a qualitative description.

According to the concept developed in Refs. [10,11], a cluster of exchange-correlated spins is formed around the impurity ion in the spin-Peierls matrix. Due to the existence of the antisymmetric exchange interaction in this cluster, the ESR of clusters is characterized by an unusually small value of the \(g\)-factor \(g_{cl}\). Clusters are surrounded by a dimerized spin-Peierls matrix which is nonmagnetic in the ground state. Triplet excitations of the dimerized matrix are characterized by the value of the \(g\)-factor of copper ions \(g_{Cu}\) close to 2. Due to the exchange interaction of clusters with excitations an ESR line with an intermediate value of the \(g\)-factor is observed (the so-called exchange narrowing). At temperatures close to the spin-Peierls transition temperature, when the concentration of spin-Peierls excitations is large, an ESR line with the \(g\)-factor close to the values characteristic to copper ions is observed. As the temperature decreases, the concentration of triplet excitations decreases due to the existence of an energy gap, and the ESR line shifts to the value characteristic of isolated clusters. As the temperature decreases further, the effectiveness of the interaction of clusters with excitations decreases, and the ESR line splits into two components. A similar phenomenon was observed for the magnetic resonance of temperature-activated spins in radicals [12].

At last, at low temperatures, when triplet excitations are practically frozen out, the ESR line consists of two components — a strong one, characterized by the \(g\)-factor of clusters, and a weak one, which represents the residual triplet excitations and magnetic defects. This description corresponds to the observed evolution of the magnetic resonance line for the samples with the impurity concentration of 0.2%.

Similarly, one can explain the dependence of the \(g\)-factor on impurity concentration at temperatures greater than the transition temperature. In this case, one should consider the closest neighborhood of the impurity ion in which antisymmetric interaction exists as a cluster characterized by the anomalous value of the \(g\)-factor \(g_{cl}\). The ESR of copper ion chains is characterized by the \(g\)-factor \(g_{Cu}\). Due to the exchange interaction of the cluster with the surrounding copper matrix, the ESR line with an intermediate value of the \(g\)-factor is observed. The more is the number of clusters, the more the magnetic resonance line is shifted from \(g_{Cu}\) to \(g_{cl}\). Thus, the value of the effective \(g\)-factor must decrease as the impurity concentration increases.

In this reasoning, we assumed that the \(g\)-factor is the same for all clusters. This is actually true if the interaction between clusters is negligible. In this case the parameters of the ESR line would depend only on the interaction of clusters with triplet excitations. However, the fact, that the resonance absorption fields for the samples with \(x = 0.2\%\) and \(x = 0.8\%\) differs, shows that even for these impurity concentrations the interaction between clusters must be taken into account. Clusters interact due to the fact that their wings overlap, this makes it possible to obtain a coarse evaluation of the cluster size (assuming that clusters do not interact at \(x = 0.2\%), and that the interaction leads to the widening and shift of the line at \(x = 0.8\%\):  

\[
L \sim 1/0.008 \sim 100.
\]

(1)

This result is overestimated since the distance between the majority of clusters is less than the average one. Since antiferromagnetic correlations at cluster wings are destroyed by thermal fluctuations, the influence of the cluster interaction on the ESR line should decrease with the increase of temperature.

We will assume that an isolated cluster is characterized by the values of the \(g\)-factor observed for the sample with \(x = 0.2\%\) at the minimal temperature \((g = 1.75, g = 1.87,\) and \(g = 1.43\)). The values of the \(g\)-factor for excitations correspond to the \(g\)-factor of copper ions in undistorted crystal environment, i.e., in pure \(\text{CuGeO}_3\) \((g = 2.15, g = 2.26,\) and \(g = 2.06,\) and they are practically independent of temperature [13].

In the subsequent analysis we use the following simplified model. We assume that in the close neighborhood of the impurity ion of size \(L_{dim}\) the dimerization is suppressed and triplet excitations of the spin-Peierls matrix do not reach this region. Antiferromagnetic correlations exponentially decay with distance from the defect. This attenuation is characterized by the magnetic correlation length of dimerized chains \(\xi \sim v/\Delta\) where \(v\) is the speed of spin excitations and \(\Delta\) is the energy gap, (see Ref. [2]). In addition, there exists the antisymmetric Dzyaloshinski–Moriya exchange interaction in a certain neighborhood of the impurity ion due to a local reduction of symmetry. The size of this region is \(L_{DM} < L_{dim}\). The values of \(L_{DM}\) and \(L_{dim}\) are measured in interatomic distances along the chains.

The analysis of the dependence of magnetic susceptibility on temperature for a similar model was conducted in Refs. [14,15]. The advantage of the ESR method is in the fact that a noticeable difference in \(g\)-factors of clus-
ters and excitations makes it possible to separate their contributions.

A. Interaction of Clusters with Excitations in the Molecular Field Approximation

First, we will consider the case $T < T_{SP}$ when spin chains are dimerized. In the vicinity of the impurity ion, a cluster of exchange-coupled spins with the total spin $S = 1/2$ is formed. At a large distance from the defect, the spin-Peierls matrix remains unperturbed, and its magnetic properties are described by triplet excitations, which are separated by a gap from the ground state.

The prolongation of antiferromagnetic correlations from the cluster into the dimerized matrix results in the appearance of an interaction between the cluster and excitations. Since this interaction appears due to the exchange interaction between spins, the average energy of the interaction can be written in the form

$$E_{int} = \sum_{i=1,..,n} J_{eff}(<S_{cl}> \cdot <S_{Cu}(i)>)$$  \hspace{1cm} (2)

Here $J_{eff}$ is the effective exchange integral, $<S_{cl}>$ is the average total spin value of the cluster, $<S_{Cu}(i)>$ is the average spin value on the copper ion located away from the cluster (it occurs due to triplet excitations). The summation is performed over $n$ effective neighbors of the cluster (since the major role is played by the interaction along spin chains, we assume that $n = 2$).

Following the molecular field theory, we obtain the following system of self-consistent equations for average magnetization of a cluster and a copper ion in the dimerized matrix:

$$<\mu_{cl}> = \chi_{cl}(0) (H + n \frac{J_{eff}}{g_{cl}g_{Cu}\mu_B} <\mu_{Cu}>)$$  \hspace{1cm} (3)

$$<\mu_{Cu}> = \chi_{Cu}(0) (H + \frac{J_{eff}}{g_{cl}g_{Cu}\mu_B} <\mu_{cl}>)$$

Here $\chi_{cl}(0)$ and $\chi_{Cu}(0)$ are susceptibilities per one cluster and per one copper ion in the absence of the interaction.

From Eqs. (3) one can derive following equations for the magnetizations with regard for the interaction:

$$\chi_{cl} = \chi_{cl}^{(0)} \frac{1 + n\eta\chi_{Cu}^{(0)}}{1 - n\eta^2\chi_{cl}(0)\chi_{Cu}^{(0)}}$$ \hspace{1cm} (4)

$$\chi_{Cu} = \chi_{Cu}^{(0)} \frac{1 + \eta\chi_{cl}^{(0)}}{1 - n\eta^2\chi_{cl}(0)\chi_{Cu}^{(0)}}$$

where $\eta = \frac{J_{eff}}{g_{cl}g_{Cu}\mu_B}$.

The magnetic susceptibility of a single isolated cluster obeys the Curie law

$$\chi_{cl}^{(0)} = \frac{g_{cl}^2\mu_B^2S(S+1)}{3kT}$$  \hspace{1cm} (5)

For the susceptibility due to triplet excitations, we will use the results obtained in Ref. [16,17]. In those studies, an approximation of the magnetic susceptibility of pure CuGeO$_3$ crystals at temperatures below $T_{SP}$ was obtained experimentally. This approximation of the molar susceptibility at $H \parallel c$ has the form

$$F(t) = (a_0 + a_1 t + a_2 t^2) \exp(-\frac{A}{t}), \quad t = T/T_{SP},$$  \hspace{1cm} (6)

where $a_0 = 26.0 \times 10^{-3}$ cgs units/mol, $a_1 = -41.6 \times 10^{-3}$ cgs units/mol, $a_2 = 28.2 \times 10^{-3}$ cgs units/mol, and $A = 2.39$.

Then, we have for the magnetic susceptibility per copper ion in the dimerized matrix:

$$\chi_{Cu}^{(0)} = \left(\frac{g_{Cu}^{(0)}}{g_{Cu}^{(e)}}\right)^2 \frac{F(T/T_{SP})}{N_A}.$$ \hspace{1cm} (7)

Here $g_{Cu}^{(i)}$ is the $g$-factor of the copper ion in the corresponding direction.

If the impurity concentration is $x$, then the number of clusters is $xN_A$ and the number of copper ions in the dimerized matrix is $(1-xL_{dim})N_A$. Assuming that clusters do not interact, we obtain the following formulas for the total susceptibility of clusters and excitations:

$$\chi_{cl} = xN_A\chi_{cl},$$ \hspace{1cm} (8)

$$\chi_{Cu} = (1 - xL_{dim})N_A\chi_{Cu}.$$  

Equations (4)-(8) allow one to determine the contribution of clusters and triplet excitations to the susceptibility for all temperatures below the spin–Peierls transition temperature. We will use this result later.

The case $T > T_{SP}$ can be treated in a similar way. As it has already been mentioned above, in this case the neighborhood of an impurity ion in which the Dzyaloshinskii–Moriya exchange interaction exists should be considered as a cluster; hence, the characteristic size in Eq. (3) is $L_{DM}$. Since the susceptibility of spin chains weakly depends on temperature above the transition temperature, we must set $T = T_{SP}$ in Eq. (3).

B. Dependence of the $g$-factor on Temperature

As it has already been mentioned above, the evolution of the ESR line with the Ni concentration equal to 0.2% (Fig. 1) has the form typical of the exchange-narrowed two-component spectrum of the magnetic resonance with the frequency of exchange jumps dependent on temperature.

Following Refs. [3,15], we assume that the influence of the exchange interaction on the magnetic resonance spectrum of the system can be considered as random transitions with the characteristic frequency $\omega_{c}$ between the states with different Zeeman’s frequencies $\omega^{(0)}_{1} > \omega^{(0)}_{2}$. 


The location of the center of gravity of the magnetic resonance spectrum is independent of \( \omega_c \) and is determined by the formula
\[
\overline{\omega} = \frac{\omega_1^{(0)} \chi_1 + \omega_2^{(0)} \chi_2}{\chi_1 + \chi_2},
\]
(9)

where \( \chi_{1,2} \) are the susceptibilities of the corresponding states with regard for the interaction between them.

Analysis of these random transitions by statistical methods (see Ref. 13) show that the frequencies of the spectral components and their widths are determined by the formulas
\[
\omega_{1,2} = \overline{\omega} + Im(\lambda_{1,2})
\]
(10)
\[
\Delta \omega_{1,2} = Re(\lambda_{1,2}),
\]

where
\[
\lambda_{1,2} = \frac{1}{2} - \{ -[\omega_c - \imath \delta] \pm \sqrt{\omega_c^2 - \Delta^2 - 2 \omega_c \delta} \},
\]
(11)
\[
\Delta = \omega_2^{(0)} - \omega_1^{(0)}, \quad \delta = \omega_1^{(0)} + \omega_2^{(0)} - 2 \overline{\omega}.
\]
(12)

In the limit of \( \omega_c \gg \Delta \), we have
\[
\omega_1 = \overline{\omega} - \frac{\delta^2 + \Delta^2}{4 \omega_c^2} \quad \Delta \omega_1 = \frac{\delta^2 - \Delta^2}{4 \omega_c}
\]
(13)
\[
\omega_2 = \overline{\omega} + \delta \quad \Delta \omega_2 = \omega_c.
\]

Thus, the ESR spectrum consists of a narrow line close to \( \overline{\omega} \) and a wide background line.

In the absence of the interaction (\( \omega_c = 0 \)), we have
\[
\omega_{1,2} = \omega_{1,2}^{(0)} \quad \Delta \omega_{1,2} = 0
\]
(14)

which corresponds to two narrow spectral components at the frequencies \( \omega_{1,2}^{(0)} \) and \( \omega_{2,2}^{(0)} \).

Qualitatively, this corresponds to the observed transition from the ESR line consisting of a single component to the two-component line. In this model, we neglect the intrinsic widths of lines in both states of the system.

Magnetic properties of the doped spin-Peierls system at \( T > T_N \) correspond to free spins of clusters and triplet excitations of the dimerized matrix. The difference in \( g \)-factors of clusters and excitations lead to differences in Zeeman’s frequencies.

The presence of an energy gap leads to a dependence of the concentration of triplet excitations on temperature. In this case, the frequency of exchange jumps \( \omega_c \) also depends on temperature as
\[
\omega_c(t) = \Omega_c \exp\left\{ -\frac{E(t)/T_{SP}}{t} \right\}, \quad t = T/T_{SP}.
\]
(15)

The dependence of the energy gap on temperature can be approximated as follows (see Refs. 13-17):
\[
E(t) = E(0)(1 - t)^a, \quad a \approx 0.1, \quad t = T/T_{SP}.
\]
(16)

The magnitude of the energy gap at \( T = 0 \) K is related to the transition temperature by the equation (see Ref. 16)
\[
E(0) = 1.76kT_{SP}.
\]
(17)

Equations (11)-(12), (13) and (15)-(17) make it possible to obtain temperature dependences of the resonance absorption frequencies (\( g \)-factors) and widths of spectrum components. To take into account the interaction of clusters with triplet excitations, we use the molecular field approximation (4)-(8).

The temperature dependences of the \( g \)-factor and the width of the magnetic resonance line are described with the help of three fitting parameters – the size of the region of suppressed dimerization \( L_{dim} \), the effective exchange integral value \( J_{eff} \), and the preexponential coefficient of the exchange frequency \( \Omega_c \).

This model assumes that clusters do not directly interact. As it has been mentioned above, the influence of interaction of the clusters decreases with increasing temperature. For this reason, when choosing the parameters, we used the temperature dependence of the \( g \)-factor at \( T > T' = 7 \) K for all basic orientations of both samples and the temperature dependence of the \( g \)-factor below \( T' \) for the sample with the impurity content 0.2% for \( H \parallel c \).

Thus, the following values of the fitting parameters were obtained:
\[
L_{dim} = 32 \pm 2, \quad J_{eff} = -(13 \pm 1)K, \quad \Omega_c = (2.2 \pm 0.3) \times 10^{12} \text{sec}^{-1}.
\]
(18)

Note that \( \hbar \Omega_c/k \sim 16 \) K, which is close to \( J_{eff} \). This result could be expected since \( \Omega_c \) and \( J_{eff} \) must be determined by the magnitude of the intrachain exchange integral.

The comparison of the theoretical and experimental results is illustrated in Figs. 3, 4. The theoretical dependences provide an accurate description of the experimental data for the sample with the impurity concentration 0.2%; however, for the sample with \( x = 0.8 \%), there is a disagreement at low temperatures, which we attribute to the interaction of clusters.

The value of the suppressed dimerization region obtained here coincides with the result of Ref. 17 which was obtained by the analysis of static susceptibilities.

We also can make a coarse evaluation of the impurity concentration at which the long-range spin-Peierls order must be completely destroyed: \( x_C = 1/L_{dim} \sim 0.03 \), which is in good agreement with the result obtained in Ref. 21.

C. Dependence of the Width of the Magnetic Resonance Line on Temperature

On the basis of the model described above, we can derive the dependence of the width of the ESR line on
temperature. The comparison with experimental data is presented in Fig. 5. For convenience, the width of the line at the spin-Peierls transition point is added to the theoretical dependences. No additional adjustable parameters were used.

For the sample with the impurity concentration 0.2%, the agreement of the theory with the experiment is very good. The theory provides correct location of the maximum of the linewidth and correct value of it at this point. The best agreement between the theory and the experiment is observed. The location of the maximum is determined rather well; however, the behavior of the linewidth at low temperatures is different from that predicted by the model. We attribute this fact to interaction between clusters.

**D. Dependence of the g-factor on Concentration above the Temperature of the Spin-Peierls Transition**

Approach developed above can be also applied to the description of the dependence of the g-factor value on impurity concentration above \( T_{SP} \). In this case, we consider as a cluster the neighborhood of the impurity ion of size \( L_{DM} \) where the Dzyaloshinski-Moriya exchange interaction exists.

At temperatures close to \( T_{SP} \), the condition \( \omega_c \gg \Delta \) (\( \omega_c \sim \Omega_c \sim 10^{12} \text{sec}^{-1}, \Delta \sim 10^{10} \text{sec}^{-1} \)) holds. Hence, simplified Eqs. (13) can be used. Neglecting the terms of order \( \Delta^2/\omega_c^2 \), we obtain the following equation for the mean value of the g-factor (this equation is similar to (11)):

\[
\overline{g} = \frac{g_{el} \chi_d + g_{Cu} \chi_{Cu}}{\chi_d + \chi_{Cu}}.
\]  

As before (see Eqs. (3)), susceptibilities \( \tilde{\chi} \) are determined in the molecular field approximation. We assume that in the absence of interaction, the cluster susceptibility is described by the Curie law (3), and the susceptibility of the copper ions surrounding the cluster is independent of temperature and equals the susceptibility at the point of the spin-Peierls transition (3).

We do not present the expression for the dependence of the g-factor value on concentration because it is too cumbersome. This expression includes two parameters: the effective exchange integral \( J_{eff} \) and \( L_{DM} \). The parameter \( J_{eff} \) has already been determined earlier. This leaves us a single adjustable parameter to describe the dependence of the g-factor on impurity concentration for all orientations of the sample with respect to the magnetic field. As it has already been mentioned, the value of the impurity concentration at which clusters can be considered as uninteracting increases with temperature. Thus, at high temperatures our approach can be applied even in the case of large concentrations. Figure 6 presents data for samples with nickel concentrations up to 3.3% at the temperature of 15 K along with theoretical curves. The experimental dependences correspond to \( L_{DM} = 18 \pm 2 \).

**E. Dependence of the ESR Linewidth on Concentration at Low Temperatures. Interaction of Clusters**

The difference of the ESR lines of samples with the impurity concentration 0.2% and 0.8% (Fig. 7) indicates that clusters interact. The dependence of the linewidth on impurity concentration for small \( x \) is linear (Fig. 8). A linear dependence of the ESR linewidth on the concentration of magnetic centers was observed in experiments with diluted paramagnets (paramagnetic centers in a diamagnetic crystal) (see, e.g., Ref. 24).

As a possible cause of the observed linewidth one can suggest long-range dipole–dipole interactions or exchange interactions occurring due to overlapping of wings of nearby clusters.

In order to estimate the contribution of the dipole–dipole interaction to the linewidth, we notice that the dipole field magnitude is about 10 Oe at the distance of 10 Å from the magnetic moment \( \mu_B \). Thus, the observed ESR linewidth \( \sim 1 \text{ kOe} \) cannot be explained by the existence of the dipole–dipole interaction between impurity ions.

Therefore, the linewidth must be determined by the antisymmetric or anisotropic exchange interaction of clusters. Reorientation of clusters due to thermal fluctuations leads to the appearance of a random effective field \( H_{eff} \), which determines the linewidth.

Due to the random distribution of the impurities, the number of closely-spaced clusters constitutes a noticeable part of the total number of clusters. In the one-dimensional case, the probability to have an impurity ion at the distance of \( n \) interatomic distances from the given ion at the impurity concentration \( x \) is

\[
p(n) = x(1-x)^n.
\]

Then, the probability that the distance between impurity ions is less than \( N \) is

\[
P(n < N) = \sum_{n=0}^{N-1} p(n) = 1 - (1-x)^N.
\]  

In the limiting case \( x \ll 1 \) we obtain \( P(n < N) \approx Nx \). Thus, if the impurity concentration is 1% (and the average distance between impurity ions in a chain is 100 interatomic distances) the part of the clusters that are closer to each other than \( L_{dim} = 32 \) is about of 30%.
On the basis of the observed values of the width of the magnetic resonance line, we can give a coarse evaluation of the magnitude of the random effective magnetic field generated by clusters.

Since antiferromagnetic correlations decrease exponentially when moving away from the defect into the dimerized matrix, we assume that the average value of the effective field depends on the distance \( L \) from the region of the destroyed dimerization according to the law

\[
H_{\text{eff}} = H_0 \exp(-L/\xi),
\]

where \( \xi \) is the magnetic correlation length and \( H_0 \) is the effective field on the boundary of the suppressed dimerization region.

Averaging over \( L \) with the help of distribution (24) and taking into account that \( x \) is small, we obtain the following estimate for the width of the ESR line:

\[
\Delta H \sim \sum_{L=0}^{\infty} H_{\text{eff}}(L)p(L) = \frac{xH_0}{1 - (1 - x)\exp(-1/\xi)} \approx \xi xH_0.
\]

Hence, setting \( \xi \approx 10 \) (see Ref. 23) and taking into account that at \( x \approx 1\% \) the linewidth \( \Delta H \approx 1 \text{ kOe} \) (see Fig. 8), we obtain for \( H_0 \) the estimate \( H_0 \approx 10 \text{ kOe} \).

Such a magnitude of the effective field corresponds to the energy of order of 1 K, which is about 1\% of the intrachain exchange integral.

Additional information on the nature of the interaction that determines the width of the magnetic resonance line can be obtained with the help of the angular dependence of the linewidth. The dependences of the effective \( g \)-factor and the ESR linewidth on the orientation of the magnetic field in the plane \( bc \) of the crystal with \( x = 0.8\% \) are presented in Fig. 9. The angular dependence of the \( g \)-factor is accurately approximated by the function

\[
g_{\text{eff}}^2 = g_c^2 \cos^2 \phi + g_b^2 \sin^2 \phi,
\]

where \( \phi \) is the angle in the plane \( bc \) measured from the axis \( c \). Thus, the anisotropy of the \( g \)-factor can be described in terms of the principal values of the \( g \)-tensor.

The contribution of the antisymmetric exchange interaction to the angular dependence of the linewidth is \( \pi \)-periodic, and the contribution of the anisotropic symmetric interaction is \( \pi/2 \)-periodic. In the case under consideration, both contributions are present. Figure 9 illustrates fitting of experimental data for the ESR linewidth by the function \( A + B \cos(2\phi) + C \cos(4\phi) \). However, one must take into account the fact that the anisotropy of the \( g \)-factor also affects the angular dependence of the linewidth, and this influence is periodic with the period equal to that of the angular dependence of the \( g \)-factor, \( \pi \).

The magnitude of the parameter \( D \) of the anisotropic exchange interaction is related to the isotropic exchange integral \( J \) by the equation (see Ref. 24)

\[
D \sim \frac{(\Delta g)^2}{g} J,
\]

where \( \Delta g = g - 2 \). In \( \text{CuGeO}_3 \), \( (\Delta g/g) \approx 0.1 \), which yields an estimate of 1 K for \( D \). Thus, it is possible that the observed magnitude of the ESR line is explained by the existence of the symmetric anisotropic exchange interaction.

V. CONCLUSIONS

When studying high-quality samples of the spin-Peierls magnet \( \text{CuGeO}_3 \) doped with nickel with a small impurity concentration \( x <1\% \), it was found that the \( g \)-factor decreases with temperature to unusually small values (down to 1.4). This fact is due to formation of the clusters of antiferromagnetically correlated spins with antisymmetric exchange interaction around impurity ions. Above the transition temperature, the value of the \( g \)-factor decreases as the impurity concentration increases.

The dependence of the \( g \)-factor on temperature and concentration can be explained in the framework of the model of exchange narrowing. An analysis of data allows one to evaluate the size of the region around an impurity in which the dimerization is suppressed (\( L_{\text{dim}} \approx 30 \text{ interatomic distances} \)) and the size of the region in which the antisymmetric exchange interaction exists (\( L_{\text{DM}} \approx 20 \text{ interatomic distances} \)).

Experimental data show that even at small impurity concentrations, the interaction between clusters plays an important role at low temperatures. The magnitude and the angular dependence of the width of the magnetic resonance line suggest the existence of an anisotropic exchange interaction in \( \text{CuGeO}_3 \).

VI. ACKNOWLEDGMENTS

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Fig.1 The temperature evolution of the ESR line at $x = 0.2\%$, $\mathbf{H} \parallel c$, and $f = 36$ GHz. The vertical segments in figures $a$ and $b$ correspond to the same amplitude of the signal.

Fig.2 The temperature evolution of the ESR line at $x = 0.8\%$, $\mathbf{H} \parallel c$, and $f = 36$ GHz.

Fig.3 Dependence of the effective $g$-factor on temperature for the sample with the impurity content $x = 0.2\%$: $\bullet - \mathbf{H} \parallel a$, $\Box - \mathbf{H} \parallel b$, $\bigtriangledown - \mathbf{H} \parallel c$. Solid curves correspond to the theoretical calculation.

Fig.4 Dependence of the effective $g$-factor on temperature for the sample with the impurity content $x = 0.8\%$: $\bullet - \mathbf{H} \parallel a$, $\Box - \mathbf{H} \parallel b$, $\bigtriangledown - \mathbf{H} \parallel c$. Solid curves correspond to the theoretical calculation.

Fig.5 Dependence of the half-width of the ESR line on temperature for $x = 0.2\%$ (a) and $x = 0.8\%$ (b). $\mathbf{H} \parallel c$, $f = 36$ GHz. Solid curves correspond to the theoretical calculation.

Fig.6 Dependence of the effective $g$-factor on impurity concentration at $T = 15$ K: $\bigcirc - \mathbf{H} \parallel a$, $\Box - \mathbf{H} \parallel b$, $\bigtriangledown - \mathbf{H} \parallel c$. Solid curves correspond to the theoretical calculation, and black symbols correspond to the data of the study.

Fig.7 Comparison of the ESR lines for $x = 0.2\%$ and $x = 0.8\%$ at $T = 1.8$ K, $\mathbf{H} \parallel c$, and $f = 36$ GHz.

Fig.8 Dependence of the half-width of the ESR line on impurity concentration for $\mathbf{H} \parallel c$: $T = T_N = 2.5$ K for $x = 1.9\%$, $T = T_N = 3.5$ K for $x = 3.0\%$, and $T = 1.8$ K for $x = 0.2\%$ and $x = 0.9\%$.

Fig.9 Angular dependence of the width of the magnetic resonance line ($\bigcirc$) and the effective $g$-factor ($\Box$) for the field applied in the plane $bc$. Solid curves correspond to the dependence $A + B \cos(2\phi) + C \cos(4\phi)$, $x = 0.8\%$, $T = 1.8$ K, and $f = 36$ GHz; $\phi = 0^\circ$ corresponds to $\mathbf{H} \parallel c$.

**VII. FIGURE CAPTIONS**

Fig.1 The temperature evolution of the ESR line at $x = 0.2\%$, $\mathbf{H} \parallel c$, and $f = 36$ GHz. The vertical segments in figures $a$ and $b$ correspond to the same amplitude of the signal.

Fig.2 The temperature evolution of the ESR line at $x = 0.8\%$, $\mathbf{H} \parallel c$, and $f = 36$ GHz.

Fig.3 Dependence of the effective $g$-factor on temperature for the sample with the impurity content $x = 0.2\%$: $\bullet$ - $\mathbf{H} \parallel a$, $\Box - \mathbf{H} \parallel b$, $\bigtriangledown - \mathbf{H} \parallel c$. Solid curves correspond to the theoretical calculation.

Fig.4 Dependence of the effective $g$-factor on temperature for the sample with the impurity content $x = 0.8\%$: $\bullet - \mathbf{H} \parallel a$, $\Box - \mathbf{H} \parallel b$, $\bigtriangledown - \mathbf{H} \parallel c$. Solid curves correspond to the theoretical calculation.

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- $\mathbf{H} \parallel a$, $\Box - \mathbf{H} \parallel b$, $\bigtriangledown - \mathbf{H} \parallel c$. Solid curves correspond to the theoretical calculation.
Glazkov et al., Figure 1
Glazkov et al., Figure 2
Glazkov et al., Figure 3
Glazkov et al., Figure 5

(a) 

(b)
Glazkov et al., Figure 6
Glazkov et al., Figure 7
Glazkov et al., Figure 8

The diagrams show the relationship between \( x, \% \) and two parameters: \( \Delta H, \text{kOe} \) and \( g \). The upper graph illustrates a linear increase of \( \Delta H \) with \( x \), while the lower graph displays a linear increase of \( g \) with \( x \), accompanied by error bars indicating the uncertainty in the measurements.
Glazkov et al., figure 9