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ESR Probing of Quantum Critical Phenomena in Doped $S = 1/2$ AF Quantum Spin Chain*

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Abstract. The results of high-frequency (60–315 GHz) electron spin resonance (ESR) studies of $CuGeO_3$ single crystals containing 0.9% Mn impurity are reported. The quantitative ESR line shape analysis shows that the low-temperature ($T < 40$ K) magnetic susceptibility of Cu^{2+} chains diverges as $\chi \sim 1/T^{\alpha}$ with the critical exponent $\alpha = 0.81 \pm 0.03$ and therefore indicates the onset of a quantum critical (QC) regime. A scenario in which the disorder caused by the Mn impurity in quantum spin chains of $CuGeO_3$ may lead to the coexistence of the quantum critical regime and the spin-Peierls dimerization is discussed. For the quantitative description of the temperature dependences of the line width and g-factor, a model assuming a crossover from the high-temperature semiclassical Nagata and Tazuke limit to the low-temperature quantum case described by Oshikawa and Affleck's theory is suggested.

1 Introduction

Recently it has been shown [1–5] that doping of the spin-Peierls compound $CuGeO_3$ with magnetic impurities such as iron and cobalt gives rise to disorder-driven quantum critical (QC) phenomena. The insertion of magnetic ions with $S = 3/2$ (Co) or $S = 2$ (Fe) at a concentration level $x = 1$–2% into antiferromagnetic (AF) Cu^{2+} quantum spin chains ($S = 1/2$) has led to a reduction of both the spin-Peierls and Neel transitions at least down to 1.8 or 0.5 K in the cases of Co and Fe, respectively [1–5]. The ground states for $CuGeO_3$:Fe and $CuGeO_3$:Co are expected to be a Griffiths phase (GP) [1–5], for which the theory [1, 6, 7] predicts a power law for magnetic susceptibility,

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$$\chi \sim 1/T^{\alpha}, \qquad (1)$$

different from the Curie–Weiss or Bonner–Fisher laws. In Eq. (1) the critical exponent satisfies the condition $\alpha < 1$ and is nonuniversally dependent on the random field characteristics [7].

For $CuGeO_3$:M (M = Fe, Co), the power law Eq. (1) with $\alpha = 0.34$ (Fe) and $\alpha = 0.9$ (Co) has been observed at $T < T_G \sim 40$ K [1–5] and holds down to the lowest temperature. Thus the experimental data [1–5] show that the transition into the GP occurs at temperatures which considerably exceed all characteristic temperatures on the x–T phase diagram expected in the standard scenario of doping [8].

The aim of the present work is to study the magnetic properties of $CuGeO_3$ single crystals doped with Mn magnetic impurity ($S = 5/2$) by the electron spin resonance (ESR) technique. ESR provides a possibility of direct monitoring of the magnetic properties of Cu^{2+} quantum spin chains, whereas the use of the static magnetization measurements implies an ambiguous procedure of the separation of the chains and possible paramagnetic impurities contributions. In the first paper, where the $CuGeO_3$:Mn system has been mentioned [9], no details on physical properties of this material have been reported. A short note about our ESR experiments on $CuGeO_3$:Mn has been published [10]. Here we will present a detailed report about high-frequency (60–315 GHz) measurements focused on QC phenomena and ESR parameters.

2 Experimental Details

The ESR experiments were carried out in the temperature range of 1.8–70 K on a cavity spectrometer (frequency range of 60–100 GHz and magnetic field B up to 7 T) using a quasioptical setup (frequency range of 100–315 GHz and magnetic field B up to 12 T). In the latter case, the transmission of the microwave radiation through the sample was measured as a function of the magnetic field. $CuGeO_3$ single crystals containing 0.9% Mn impurity have been studied. The quality of samples was controlled with X-ray and Raman scattering techniques. The actual content of impurity in the sample was checked by chemical analysis. From analysis of the structural data, it was possible to conclude that Mn impurity substitutes cooper in chains similarly to Fe and Co [1–4]. The synthesis technique details can be found elsewhere [11]. In ESR measurements the magnetic field was aligned along the crystallographic a-axis.

3 Experimental ESR Spectra

The observed ESR spectrum is represented by a single Lorentzian line. No extra lines, which can be attributed to the AF resonance mode expected in the standard scenario of doping [8], were found in the whole temperature–frequency–magnetic field domain studied. At fixed temperature, the resonance shifts almost lin-

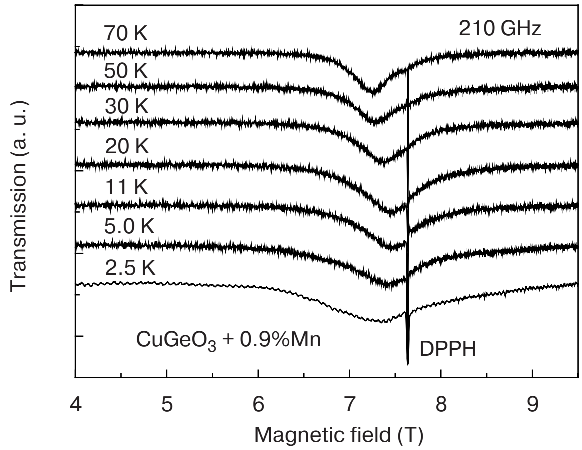

Fig. 1. ESR spectra of $CuGeO_3$ containing 0.9% Mn impurity obtained at 210 GHz with a quasioptical technique.

early with frequency in the range of 60–15 GHz. As long as the ESR line is relatively broad, the best spectra were obtained at frequencies exceeding 200 GHz (Figs. 1 and 2). Figures 1 and 2 show that this line broadens and shifts with lowering temperature and for this frequency range all spectroscopic parameters such as the line width, *g*-factor and integrated intensity were obtained as a function of temperature. Although the ESR line can be attributed to collective ESR on Cu^{2+} chains modified by doping with Mn^{2+} ions, for $B \parallel a$ and $T > 70$ K the *g*-factor value is only about 2.10, which is considerably lower than the *g*-factor of 2.15 noticed for the undoped $CuGeO_3$ [1–5]. Below we consider the possible reason

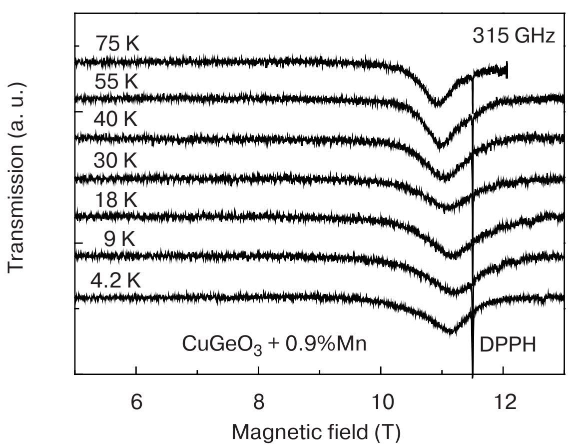

Fig. 2. ESR spectra of $CuGeO_3$ containing 0.9% Mn impurity obtained at 315 GHz with a quasioptical technique.

for this discrepancy, as well as the temperature dependence of the integrated intensity and other ESR parameters.

4 Discussion

4.1 Integrated Intensity and QC Behavior

Analogously to previous results obtained for $CuGeO_3$ doped with Fe and Co impurities [1–5], on the basis of proportionality of the integrate intensity I to the magnetic susceptibility $I(T) \sim \chi(T)$, it is possible to expect a power law Eq. (1) describing the temperature dependence $I(T)$. As follows from Fig. 3, the asymptotic power law Eq. (1) with $\alpha = 0.81 \pm 0.03$, which is a fingerprint for the disorder-driven QC regime, begins at $T_G \sim 40$ K. This is in agreement with the temperatures observed for the GP transition in $CuGeO_3$:Fe and $CuGeO_3$:Co [1–5]. In the vicinity of the characteristic temperature $T_D = 16$ K, the integrated intensity starts deviating from the power law Eq. (1) (Fig. 3). The value of T_D is close to the spin-Peierls transition temperature $T_{SP} = 14.5$ K in pure $CuGeO_3$ but slightly higher.

It is interesting that below $T \sim 7$ K at the frequency of 210 GHz and below $T \sim 5$ K at the frequency of 315 GHz the power law Eq. (1) with the same α is restored and holds up to the lowest temperature studied (Fig. 3). The observed $I(T)$ dependence is different from that reported for $CuGeO_3$:Fe and $CuGeO_3$:Co [1–5] and thus reflects a characteristic effect of the Mn impurity.

Such an unusual behavior may be qualitatively explained as follows. As long as at T_D the integrated intensity (and hence $\chi(T)$) starts to decrease, this characteristic temperature may be attributed to dimerization of the quantum spin chains.

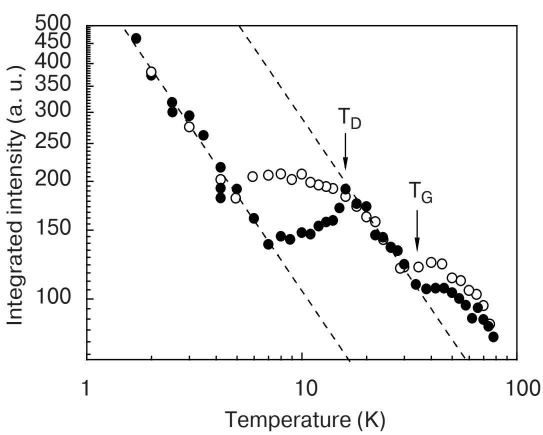

Fig. 3. Temperature dependences of the integrated intensity at 210 GHz (solid circles) and 315 GHz (open circles). Dashed lines represent a power asymptotic behavior of the magnetic susceptibility with $\alpha = 0.81$ [Eq. (1)]. Arrows mark the temperature of GP transition T_G and dimerization temperature T_D.

The condition $T_D < T_G$ means that a possible spin-Peierls transition in $CuGeO_3$:Mn occurs within the GP, i.e., when the magnetic subsystem is divided into spin clusters with different coupling constants [6, 7]. As long as the temperature lowering leads to an increase of the cluster size [6, 7], a transition into the dimerized state may be allowed for the chains belonging to clusters with sizes exceeding the coherence length. Below T_D, the magnetic contribution from dimerized Cu^{2+} chains vanishes rapidly due to the opening of a spin gap, and only the chains in the QC state contribute to the susceptibility. Therefore, a power law for $\chi(T)$ and $I(T)$ may be restored at $T < T_D$. As long as in the disorder-driven QC regime the index α only depends on the space dimension and dynamic exponent connecting the time and length scales [12], it is possible to expect a reentrant quantum criticality at $T < T_D$ with the same value of the critical exponent as observed experimentally (Fig. 3). Moreover, the fact that the condition $T_D > T_{SP}$ is fulfilled in our case may be a consequence of the change of the phonon–magnon interaction in finite spin clusters.

4.2 Line Width and g-Factor

The experimental spectra suggest that the *g*-factor for $CuGeO_3$:Mn varies with temperature in a nonmonotonous way (Figs. 1 and 2). For $T < 70$ K the *g*-factor decreases until about 10 K and then starts to increase (Fig. 4). It is worth noting that the magnitude of the low-temperature *g*-factor growth is more pronounced at the frequency of 210 GHz and considerably damped at the frequency of 315 GHz (Fig. 4).

The observed temperature dependence of the *g*-factor is different from the cases of $CuGeO_3$:Fe and $CuGeO_3$:Co, where the *g*-factor increases with lowering

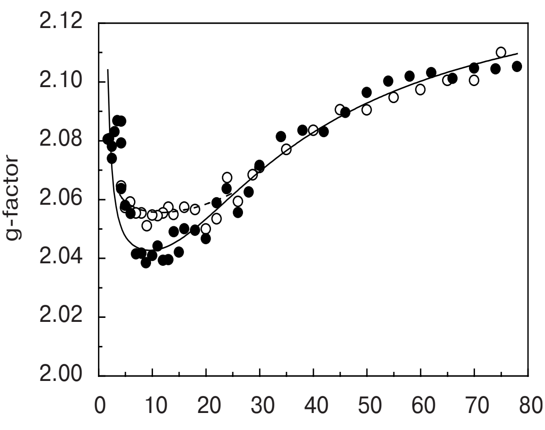

Fig. 4. Temperature dependences of the *g*-factor at 210 GHz (solid circles) and 315 GHz (open circles). Solid line corresponds to the model calculation (see text), dashed line is a guide to the eye.

temperature [1–5]. The quantitative analysis of the ESR spectra [13, 14] has shown that this effect may be explained in the Oshikawa and Affleck (OA) theory for ESR in one-dimensional $S = 1/2$ AF quantum spin chain [15, 16] by assuming the influence of the staggered field (SF). A possible mechanism of the appearance of the staggered component of magnetization in $CuGeO_3$ doped with magnetic impurities was considered in ref. 17.

Therefore the data in Fig. 4 suggest that for $CuGeO_3$:Mn the g-factor may be represented as the sum of two temperature-dependent parts,

$$g(T) = g_0 + \Delta g_{SF}(T) + \Delta g_1(T), \tag{2}$$

where Δg_{SF} denotes the contribution from the SF, Δg_1 stands for the term responsible for the g-factor increase with temperature and g_0 denotes the "bare" g-factor value without any corrections. Taking into account the character of the expected temperature dependence $\Delta g_1(T)$ and the fact that in our case the magnetic field is perpendicular to the chain direction, it is possible to use the Nagata and Tazuke mean field theory [18, 19]. If the spin correlations are not so strong, it is possible to express $\Delta g_1(T)$ as [18–21]

$$\Delta g_1(T) = a \cdot M(T)/M_{sat}, \tag{3}$$

where $M(T)$ and M_{sat} are the magnetization for the resonance field and the saturation value, respectively, and a denotes a numerical coefficient.

In the frame of this assumption the line width w should be also considered as the superposition of two terms,

$$w(T) = w_{SF}(T) + w_1(T), \tag{4}$$

having the same physical origin as in the case of g-factor [Eq. (2)]. Theories predict that both w_{SF} and w_1 should increase with decreasing temperature [15, 16, 19].

The experimental data for the line width in $CuGeO_3$:Mn are shown in Fig. 5. In agreement with theoretical expectations, this parameter increases with lowering temperature. The increase of frequency also leads to the broadening of the ESR line; however, at the frequency of 315 GHz the section of the low-temperature growth of the line width at $T < 10$ K is damped. As long as this temperature range is likely controlled by the SF effects, the simultaneous decrease of the g-factor and the line width magnitudes in the low-temperature region at 315 GHz should correspond to the field-induced damping of the SF component of magnetization. This effect was investigated in detail in ref. 14 for $CuGeO_3$:Fe and can be qualitatively explained by the competition between the staggered Zeeman energy and AF interactions in $CuGeO_3$ doped with magnetic impurities.

At the frequency of 210 GHz, we attempted to check the above model quantitatively, when the SF contribution could not be neglected. In the OA theory, the line width in the presence of the SF should diverge as $w_{SF} \sim 1/T^2$ [15, 16].

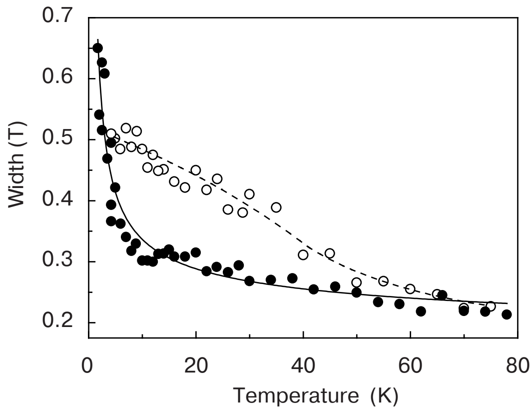

Fig. 5. Temperature dependences of the line width at 210 GHz (solid circles) and 315 GHz (open circles). Solid line corresponds to the model calculation (see text), dashed line is a guide to the eye.

At the same time, the temperature dependence of the staggered magnetization, which is supposed to be important in doped $CuGeO_3$ [14, 17], may change the temperature asymptotic of the line width to $w_{SF} \sim 1/T$ [17]. For that reason, we have chosen the model form as $w_{SF} = A/T^n$ (where $n = 1, 2$) for the SF contribution in Eq. (4). For the simplicity of calculations, a similar expression for $w_1 \sim b/T^{\beta}$ has been used instead of the exact one [19].

It is found that the experimental data in Fig. 5 could be fitted for $n = 1$ only, which is in agreement with the expected temperature dependence of the staggered magnetization caused by the competition with AF interactions [14, 17]. The solid line in Fig. 5 shows the result of the three-parameter fit well describing the shape of the experimental curve with the dominating low-temperature contribution from the w_{SF}.

A characteristic feature of the OA theory is the universal relation between w_{SF} and Δg_{SF} [13]:

$$\frac{w_{SF}}{\Delta g_{SF}} = 1.99\frac{k_B T}{\mu_B}, \qquad (5)$$

which does not depend on the SF magnitude. The dependence $w_{SF}(T)$ obtained from fitting the data in Fig. 5 has been used to calculate $\Delta g_{SF}(T)$ in Eq. (2) and thus this quantity has no free parameters. Following Eq. (3), a simple model form $\Delta g_1(T) = a \cdot \tanh(C/T)$ was chosen, and consequently another three-parameter fit was required to reproduce a complicated $g(T)$ dependence. The outcome of the aforementioned procedure is given in Fig. 4 by the solid line; the good representation of the experimental data is evident. It is interesting that fitting has provided a value $g(T \to \infty) = 2.14 \pm 0.02$, which is in agreement with the g-factor $g = 2.15$ in undoped $CuGeO_3$ for the studied experimental geometry of $B \parallel a$.

5 Conclusion

In conclusion, we have shown that the magnetic properties of Cu^{2+} quantum spin chains in $CuGeO_3$ doped with Mn are qualitatively different from the properties observed for the Fe- and Co-doped chains. An unusual coexistence of the QC regime described by the universal critical exponent $\alpha = 0.81 \pm 0.03$ and spin-Peierls dimerization is suggested. Checking of this scenario, as well as an additional verification of the possible size effect on the dimerization temperature, requires more theoretical and experimental studies.

The suggested approach, assuming the crossover of the high-temperature semiclassical Nagata and Tazuke limit with the low-temperature quantum case described in OA theory, allows a simultaneous description of the line width and g-factor in the frequency range of about 200 GHz. The deviations from this model at higher frequencies in $CuGeO_3$:Mn may be explained by an enhancement of AF interactions in high magnetic fields. Further examination of this model requires ESR measurements with the magnetic field applied along the chains direction, which are considered as a task for future investigations.

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