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New polarization effect and collective excitation in $S = 1/2$ quasi 1D antiferromagnetic quantum spin chain

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Anomalous polarization characteristics of magnetic resonance in $CuGeO_3$ doped with 2% of Co impurity are reported. For the Faraday geometry this mode is damped for the microwave field $\mathbf{B}_\omega$ aligned along a certain crystallographic direction showing that the character of magnetic oscillation differs from the standard spin precession. The observed resonance coexists with the ESR on Cu^{2+} chains and argued not to be caused by "impurity" EPR, as previously claimed, but to correspond to a previously unknown collective mode of magnetic oscillations in an $S = 1/2$ AF quantum spin chain.

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From the modern theoretical point of view [1, 2], magnetic resonances in $S = 1/2$ quasi 1D antiferromagnetic (AF) quantum spin chains should be treated as collective phenomena rather than a diffusive spin dynamics suggested by exchange narrowing [3] approach. In the case of the electron paramagnetic resonance (EPR), the collective nature develops in the specific temperature dependences of the line width and g-factor caused by an interplay of the staggered field and anisotropic exchange and in the damping of EPR at low temperatures accompanied by rising of the breather mode [1, 2]. In the latter case, the changes in the resonant spectrum also affect the experiment geometry; namely, EPR can be excited only in the Faraday geometry whereas the breather mode may be observed for both the Faraday and Voigt geometry [4]. These predictions have been well proven experimentally [4 – 6] for the cases of Cu-benzoate and doped $CuGeO_3$.

Another possible field, where a collective motion of spins may be found, is a polarization effect [2]. Both the field theory approach [2] and direct numerical simulation [7] suggest that an EPR line depends on the orientation of the microwave field $\mathbf{B}_\omega$, however the expected influence on the line width and g-factor is small. This result agrees well with the previous calculations in the frame work of exchange narrowing theory and with known experimental data [8 – 10].

Here we report an experimental observation of a strong polarization dependence for a magnetic resonance in $CuGeO_3$ doped with a Co impurity, which have not been foreseen by existing theories for a low dimensional magnets. We argue that the discovered effect reflects the appearance of the unknown before collective mode in an $S = 1/2$ quasi 1D AF quantum spin chain.

A cobalt magnetic impurity in $CuGeO_3$ ($S = 3/2$) substitutes copper in chains [11 – 13] and in contrast to other dopants induces an onset of the specific resonant mode, which accompanies EPR on Cu^{2+} chains [11, 12]. Therefore, an experimental spectrum of the resonant magnetoabsorption in $CuGeO_3$:Co is formed by two broad lines, which can be completely resolved for frequencies $\omega/2\pi \geq 100$ GHz. It was found [11, 12] that frequencies of both modes are proportional to the resonant magnetic field in a wide frequency range, 60–360 GHz. The analysis of the g-factor values have shown that the resonant mode corresponding to higher magnetic fields represents a collective EPR on Cu^{2+} chains, whereas the resonant mode corresponding to lower magnetic fields may be interpreted as an EPR on Co^{2+} impurity clusters embedded into $CuGeO_3$ matrix rather than as an antiferromagnetic resonance (AFMR) mode [12].

In the present paper, we performed polarization measurements in the Faraday geometry of the magnetic resonance spectrum of $CuGeO_3$ containing 2% of Co at frequency 100 GHz in a temperature range 1.8–40 K. The details about samples preparation, characterization, and quality control are given elsewhere [12]. It was established that for this concentration range Co impurity completely damp the spin-Peierls transition for the vast majority of Cu^{2+} chains and no Neel transition was found at least down to 1.8 K [11, 12]. The quantitative analysis of the EPR on Cu^{2+} chains parameters have shown that the line width and g-factor reflect properties of the chains with the damped spin-Peierls state and,

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moreover, the Cu^{2+} magnetic subsystem retains the one dimensional character in the aforementioned temperature interval [5, 12].

In polarization experiments, a single crystal of $CuGeO_3$:Co was located on one of the endplates of the cylindrical reflecting cavity tuned to the TE_{014} mode. A small DPPH reference sample was simultaneously placed in the cavity. The external field **B** up to 7 T was generated by a superconducting solenoid and was parallel to the cavity axis. Three cases, when **B** was aligned along the **a**, **b** and **c** crystallographic directions, were studied. In each case, two orientations of the oscillating microwave field along remaining axes were investigated; namely, the polarizations $\mathbf{B}_\omega \| \mathbf{b}$ and $\mathbf{B}_\omega \| \mathbf{c}$ for $\mathbf{B} \| \mathbf{a}$ and so on. (Hereafter we denote the Cu^{2+} chain direction as **c**; **b** axis is perpendicular to **c** marking a direction of the second strongest exchange in the chains plane and **a** axis is orthogonal to the chains plane). Correspondingly below we report the results for six experiment geometries. Measurements were repeated for ten single crystals and provided identical results.

It is worth noting that $\mathbf{B}_\omega$ is perpendicular to **B** in all cases studied and no effect in a convenient EPR on a single spin is expected. For the isotropic Heisenberg spin system, the spin Hamiltonian consisting of the exchange and Zeeman terms commutes with the magnitude of the total spin and its z-component. Thus in the absence of anisotropic terms in the Hamiltonian, which give rise to a finite line width, the EPR occurs at the same frequency $\omega = \gamma B$ as in single-spin problem [1, 2]. As a result, even in a strongly interacting system like quantum spin chain, it is possible to use a semiclassical language and describe magnetic resonance in terms of magnetization rotation along the field direction as one does for the single spin. Therefore for the quantum spin chain in "zero order", the excitation of EPR does not depend on the $\mathbf{B}_\omega$ direction in plane perpendicular to **B**. This speculation qualitatively explains why polarization effects may be only expected in the line width and polarization corrections to the g-factor that is in agreement with the exact results [2, 7 – 9].

The obtained experimental data, however, contradict to this picture. As can be seen from Fig.1 the low field mode A, which is presumed to be an "impurity" resonance in the previous studies [11, 12], can be excited for one polarization only. At the same time, the EPR on Cu^{2+} chains (resonance B) does not show any strong polarization dependence. For the mode A and $\mathbf{B} \| \mathbf{a}$, an "active" polarization is $\mathbf{B}_\omega \| \mathbf{c}$ and "non-active" polarization corresponds to the case $\mathbf{B}_\omega \| \mathbf{b}$ (Fig.1a). It is worth to note that in the case of "non-active" polarization the magnetic resonance A is almost completely

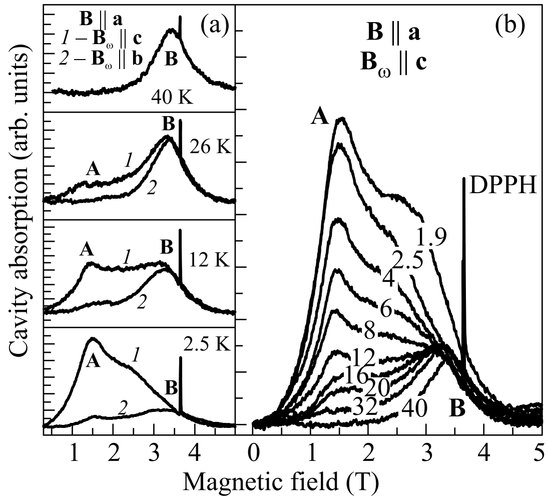

Fig.1. Comparison of "active" and "non-active" polarizations (panel a) and temperature evolution of the magnetoabsorption spectrum for "active" polarization (panel b) in geometry $\mathbf{B} \| \mathbf{a}$. Narrow line in panel a represents DPPH signal. Figures near curves in panel b correspond to temperatures in K

damped, and weak traces of this mode for $\mathbf{B}_\omega \| \mathbf{b}$, which are visible at low temperatures, are due to the finite sample size and related weak misalignment of $\mathbf{B}_\omega$ from **b** axis in cavity measurements. Another characteristic feature of the observed phenomenon is the peculiar temperature dependence. For the "active" case, mode A appears below 40 K and at $T \sim 12$ K becomes as strong as the resonance on Cu^{2+} chains. Further lowering of temperature makes the A resonance a dominating feature in the magnetoabsorption spectrum with amplitude considerably exceeding that of mode B (Fig.1b).

Similar behavior is observed for $\mathbf{B} \| \mathbf{b}$ geometry (Fig.2). In this case for mode A an "active" polarization is $\mathbf{B}_\omega \| \mathbf{a}$, and "non-active" polarization is $\mathbf{B}_\omega \| \mathbf{c}$, whereas the resonance B is not much affected by an orientation of the microwave field. In agreement with the case $\mathbf{B} \| \mathbf{a}$, the mode A is the strongest in the spectrum, however for $\mathbf{B} \| \mathbf{b}$ the main resonance A is accompanied by its second harmonic (Fig.2). Interesting that although the mode A is completely damped in $\mathbf{B}_\omega \| \mathbf{c}$ case, the second harmonic of this resonance retains the same amplitude for both "active" and "non-active" polarizations (Fig.2).

A dominating character of the resonance A at low temperatures is conserved in $\mathbf{B} \| \mathbf{c}$ case (Fig.3). The effect of polarization appears to be weaker, and the amplitude of the resonance A for $\mathbf{B}_\omega \| \mathbf{b}$ is only two times less than for $\mathbf{B}_\omega \| \mathbf{a}$. Nevertheless, the polarization dependence of this mode remains anomalously strong, especially as compared with the resonance on Cu^{2+} chains.

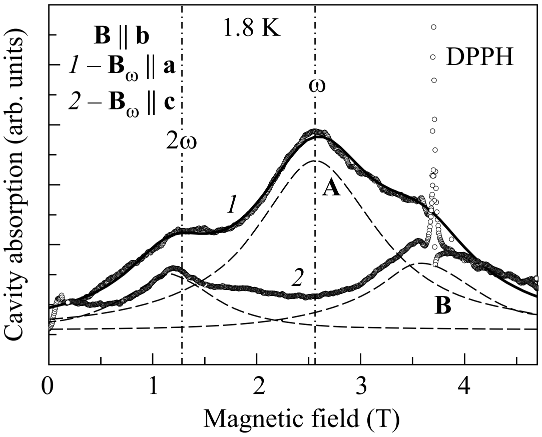

Fig.2. "Active" and "non-active" polarizations for **B**||**b**. Points correspond to experiment, solid line- fitting of the experimental spectrum assuming Lorentzian shapes of the resonances A, B and second harmonic of resonance A. Partial contributions of these resonances to the spectrum are shown by dashed lines

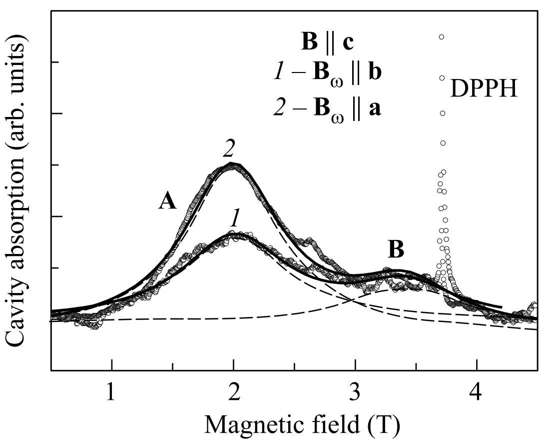

Fig.3. "Active" and "non-active" polarizations for **B**||**c**. Points correspond to the experiment, solid line- to fitting of the experimental spectrum assuming Lorentzian shapes of the resonances A and B. Partial contributions of these resonances to the spectrum are shown by dashed lines

Data in Figs.1–3 show that the resonance field for the mode A varies substantially, when a direction of the external magnetic field **B** is changed. The corresponding g-factor values are $g \approx 4.9$ (**B**||**a**), $g \approx 2.9$ (**B**||**b**), and $g \approx 3.7$ (**B**||**c**). Thus, the g-factor for this mode may differ by a factor of 1.7, while for the EPR on Cu^{2+} chains (resonance B) the g-factors for various crystallographic directions lie in the range 2.06–2.26 [6, 12] and, hence, vary only by 10%.

The experimental data obtained in the present work demonstrate that the resonant mode A in $CuGeO_3$:Co is an anomalous one. First of all, this mode shows extremely strong dependence on orientation of the oscillating microwave field $\mathbf{B}_\omega$ in the Faraday geometry. At the same time, no comparable effect for EPR on Cu^{2+} chains is observed in good agreement with theoretical expectations [7–10].

Secondly, the vanishing of the resonance A for certain polarizations means that the character of magnetic oscillations in this mode is completely different from the magnetization vector precession around a magnetic field direction described by Landau-Lifshits equation. Indeed, in case of precession, the magnetization vector end moves around a circle, whose plane is perpendicular to the magnetic field, and hence any linear polarization in Faraday geometry excites an EPR-like mode or a mode based on correlated precession of various magnetization components [14].

Thirdly, modes A and B coexist in a wide temperature range $1.8 < T < 40$ K and therefore the scenario giving a vanishing collective EPR (mode B) after an onset of the breather excitation like in Cu-benzoate [1, 2, 4] does not hold. The appearance of the mode A at relatively high temperatures $T \sim 40$ K (Fig.1) simultaneously eliminates applicability of the standard scenario of doping [15], where the coexistence of EPR and AFMR in doped $CuGeO_3$ may be expected only at temperatures below $0.3T_{SP} \sim 4$ K (AFMR coexisting with EPR in $CuGeO_3$ have been observed in experiments at $T < 2$ K [16]).

The above consideration does not allow explaining of mode A in terms of a single spin EPR problem. At the same time, the properties of this magnetic resonance is not possible to describe assuming either collective EPR or AFMR in a quantum spin chain system, as well by the other known to date collective modes like breather excitations. Thus, doping with Co of Cu^{2+} quantum spin chains in $CuGeO_3$ leads to formation of a novel unidentified magnetic resonance. Nevertheless it is possible to deduce that the observed excitation of a magnetic subsystem of $CuGeO_3$:Co has a collective nature. The first argument favoring this supposition is the magnitude of this magnetic resonance. Taking into account that in the samples studied only 2% of cooper ions are substituted by the cobalt impurity and no spin-Peierls transition affecting mode B happens, it is difficult to expect that any individual impurity mode considerably exceeds the magnitude of the magnetic resonance on Cu^{2+} chains (Figs.1–3). Therefore, in our opinion, mode A is likely a specific collective excitation of a quasi 1D Cu^{2+} chain, which properties are modified by doping.

The unusual polarization dependence of the mode A may be considered as another argument. Apparently, the observed behavior is forbidden for a single spin or

$S = 1/2$ AF spin chain with an isotropic Hamiltonian [1, 2]. However, in presence of anisotropic terms, the spin chain Hamiltonian does not commute with the total spin and its z-component, and hence, in principle, the magnetic oscillation modes different from the standard spin precession may become possible. It is worth to note that experimental data in Figs.1–3 suggest a selected character of **b** axis. Indeed, for $\mathbf{B}_\omega||\mathbf{b}$ the resonance A is completely damped ($\mathbf{B}||\mathbf{a}$) or its magnitude is reduced ($\mathbf{B}||\mathbf{c}$) and in case $\mathbf{B}||\mathbf{b}$ the second harmonic of the anomalous mode, which is missing in other geometries, develops. At the same time, the previous studies [5, 6] have shown that doping with magnetic impurities of $CuGeO_3$ leads to appearance of the staggered magnetization aligned predominantly along **b** axis [6]. Therefore, the observed mode A is likely related with the staggered field, which may be responsible for anomalous polarization characteristics. Apparently no such effects caused by a staggered field may be expected for a single spin resonance and thus the idea of a staggered magnetization controlled mode A agrees with its collective nature. From to date theoretical point of view, a staggered field is known to be anisotropic term in Hamiltonian, which is crucial for the EPR problem in the studied case [1, 2]. However the question whether this type of anisotropy is sufficient for the explanation of the observed phenomena remains open and a required extension of the theory [1, 2] is missing.

From the data presented in Figs.1–3 it is possible to deduce the character of magnetic oscillations for resonances A and B in $CuGeO_3$:Co. In a semiclassical approximation the magnetization in a given magnetic field **B** has the form $\mathbf{M} = \mathbf{M}_0 + \mathbf{m}$, where $\mathbf{M}_0$ denotes an equilibrium value and **m** stands for the oscillating part [14]. As long as magnetic resonances probe normal modes of magnetization oscillations described by vector **m**, for an excitation of some mode, vector $\mathbf{B}_\omega$ should have non zero projection on any **m** component [14], i.e., a condition $(\mathbf{B}_\omega, \mathbf{m}) \neq 0$ for the scalar product should be fulfilled. For geometry $\mathbf{B}||\mathbf{a}$ and a normal mode, when precession of magnetization around the field direction takes place, $\mathbf{m} = (0, m_b, m_c)$ and both projections of **m** on **b** and **c** axes are nonzero. Therefore any alignment of vector $\mathbf{B}_\omega$ in **bc** plane excites precession. The weak dependence of the resonance amplitude on $\mathbf{B}_\omega$ alignment corresponds to condition $m_b \approx m_c$. Thus, for the mode B and $\mathbf{B}||\mathbf{a}$, the trajectory of the vector **M** end is a circle lying in **bc** plane (a similar consideration is apparently applicable to mode B in geometries $\mathbf{B}||\mathbf{b}$ and $\mathbf{B}||\mathbf{c}$).

The same analysis can be applied for the resonance A. Data in Fig.1 suggest that in geometry $\mathbf{B}||\mathbf{a}$ the oscillating contribution to magnetization should acquire the form $\mathbf{m} = (0, 0, m_c)$ leading to "active" polarization $\mathbf{B}_\omega||\mathbf{c}$ and "non-active" polarization $\mathbf{B}_\omega||\mathbf{b}$ (Fig.1). Therefore in this case, the end of vector **M** should move along the line parallel to **c** axis. Analogously, $\mathbf{m} = (m_a, 0, 0)$ for $\mathbf{B}||\mathbf{b}$ and linear oscillation happens along **a** axis (Fig.2). For $\mathbf{B}||\mathbf{c}$, mode A can be excited in both polarizations and hence $\mathbf{m} = (m_a, m_b, 0)$. However, the decrease of the resonance magnitude for $\mathbf{B}_\omega||\mathbf{b}$ suggests condition $m_a \approx 2m_b$ (Fig.3). As a result, the trajectory of the vector **M** end will be an ellipse in **ab** plane elongated in **a** direction. The summary of the above consideration for mode A is given in Fig.4.

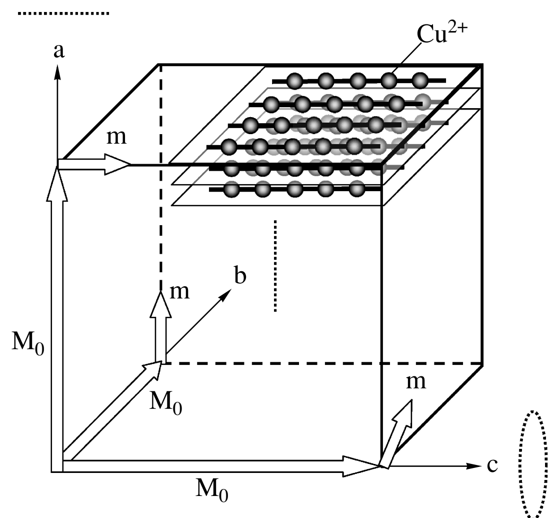

Fig.4. Schema of possible magnetic oscillations for normal modes responsible for anomalous polarization dependences of the mode A in three cases ($\mathbf{B}||\mathbf{M}_0||\mathbf{a}$, $\mathbf{B}||\mathbf{M}_0||\mathbf{b}$ and $\mathbf{B}||\mathbf{M}_0||\mathbf{c}$). Oscillating contribution **m** is assumed to vary harmonically with time in cases $\mathbf{M}_0||\mathbf{a}$ and $\mathbf{M}_0||\mathbf{b}$. For $\mathbf{M}_0||\mathbf{c}$ vector **m** rotates around the **c** axis. Dotted lines mark trajectories of the vector $\mathbf{M} = \mathbf{M}_0 + \mathbf{m}$ end

To our best knowledge, the modes with linear or elliptic oscillation trajectories have been neither reported for any magnetic resonance, nor foreseen by theoretical studies. Moreover, the current understanding of the whole field of magnetic resonance (including EPR, AFMR and ferromagnetic resonance) essentially exploits semiclassical magnetization precession in an external field, and hence leaves no space to the observed new polarization effect. Therefore, an adequate theory relevant to the studied case, including different polarization characteristics of magnetic resonance harmonics appears on the agenda.

In conclusion, we have shown that doping of $CuGeO_3$ with 2% of Co impurity induces an anomalous magnetic resonance mode possessing unique polarization characteristics. This resonance coexists with the EPR on Cu^{2+} chains and is likely caused by a new, unknown before, collective mode of magnetic oscillations in $S = 1/2$ AF quantum spin chain.

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