Appl. Magn. Reson. (2008) 33, 3–9
DOI 10.1007/s00723-008-0051-6
Printed in The Netherlands

**Applied
Magnetic Resonance**

New Magneto-Optical Effect in Co-Doped $CuGeO_3$

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Received 25 August 2006

Abstract. We report the anomalous effect of the polarization dependence of electron paramagnetic resonance absorption in $CuGeO_3$ doped with 2% of Co. While the resonance line of Cu^{2+} chains is independent of the microwave polarization in the Faraday geometry, the resonant mode of Co impurity exhibits a strong polarization dependence for all directions of the external magnetic field. Possible reasons of such behavior are discussed.

1 Introduction

Recent electron paramagnetic resonance (EPR) experiments have shown that doping of $CuGeO_3$ with 2% Co leads to a unique low-temperature magnetic behavior [1, 2]. Indeed, most impurities like Zn, Si, Ni and Mg [3–5] change magnetic properties of $CuGeO_3$ in a similar way, when damping of the spin–Peierls transition is accompanied by establishing a long-range antiferromagnetic order. An impurity in this case influences only the properties of the Cu^{2+} chain magnetic resonance mode by modifying its parameters (line width, position and intensity). The Co-doped $CuGeO_3$ is the only known system for which an additional resonance absorption line caused by an impurity was observed [1, 2]. The resonant magnetic field of this line is proportional to the measuring frequency in the range of 60–360 GHz and the corresponding g-factor for $\mathbf{B} \parallel \mathbf{a}$ was found to be $g \approx 4.9$. In this work, we report on the anomalous polarization dependence of the impurity EPR line absorption on the direction of oscillating microwave field.

2 Experimental

Due to the large enhancement of the resonance line width revealed in EPR experiments of Co-doped $CuGeO_3$ in comparison with an undoped sample [1, 2], we have developed a 100 GHz cavity technique aimed at a detailed study of wide resonance lines. For this purpose a cylindrical cavity operating at the TE_{014} mode has been designed. To measure polarization effects, the sample was put on the end plate of the cavity in such way that the oscillating magnetic field was parallel to one of the crystallographic axes. A small diphenylpicrylhydrazyl (DPPH) reference sample was simultaneously placed in the cavity. This procedure was done for two axes perpendicular to the magnetic field for each of three directions of the magnetic field $\mathbf{B} \parallel \mathbf{a}$, $\mathbf{B} \parallel \mathbf{b}$ and $\mathbf{B} \parallel \mathbf{c}$. The experiments have been carried out in the temperature range of 1.8–60 K in magnetic fields up to 7 T. The polarization effect was also tested (for $\mathbf{B} \parallel \mathbf{a}$) on 10 samples of different size and shape. The information about the sample preparation was published previously and can be found in ref. 2. Measurements of the temperature dependence of the magnetic susceptibility on SQUID (superconducting quantum interference device) magnetometer have shown good agreement with previously published data [6].

3 Results and Discussion

The evolution of the resonance spectra with temperature decreasing for $\mathbf{B} \parallel \mathbf{a}$ exhibits a large growth of the resonance mode A below $T \sim 40$ K (Fig. 1). This mode in the previous study was interpreted as caused by the Co^{2+} impurity [2]. The second mode which is the only mode at higher temperatures (Fig. 1a) belongs presumably to Cu^{2+} chains [2]. As long as Cu^{2+} resonance is slightly temperature-dependent, the impurity mode A becomes dominant at low temperatures. The most remarkable effect of the polarization dependence of the Co^{2+} line intensity on the direction of the microwave oscillating field $\mathbf{B}_\omega$ is illustrated in Fig. 1a: for $\mathbf{B}_\omega \parallel \mathbf{c}$ the integrated intensity of the line is at least 10 times larger than that for $\mathbf{B}_\omega \parallel \mathbf{b}$ below 0 K. It is worth to note that it is impossible to reach the full suppression of the resonance in “nonactive” polarization in this experiment due to a rather big sample as well as because of small errors in the sample orientation. A more elaborated measurement of the polarization dependence with a smaller specimen has shown the almost full suppression of the resonance in a certain direction of polarization (Fig. 2).

A similar behavior has been observed for the $\mathbf{B} \parallel \mathbf{b}$ geometry (Fig. 3). In this case for the mode A an “active” polarization is $\mathbf{B}_\omega \parallel \mathbf{a}$, and “nonactive” polarization is $\mathbf{B}_\omega \parallel \boldsymbol{c}$, whereas the resonance B (on the Cu^{2+} chain) is not strongly affected by the microwave field orientation. In agreement with the case $\mathbf{B} \parallel \mathbf{a}$, the mode A is the strongest in the spectrum at low temperatures. However, for $\mathbf{B} \parallel \mathbf{b}$ the main resonance mode A has a more complicated structure and, according to the numerical analysis, consists of two lines of the Lorentzian shape (Fig. 3).

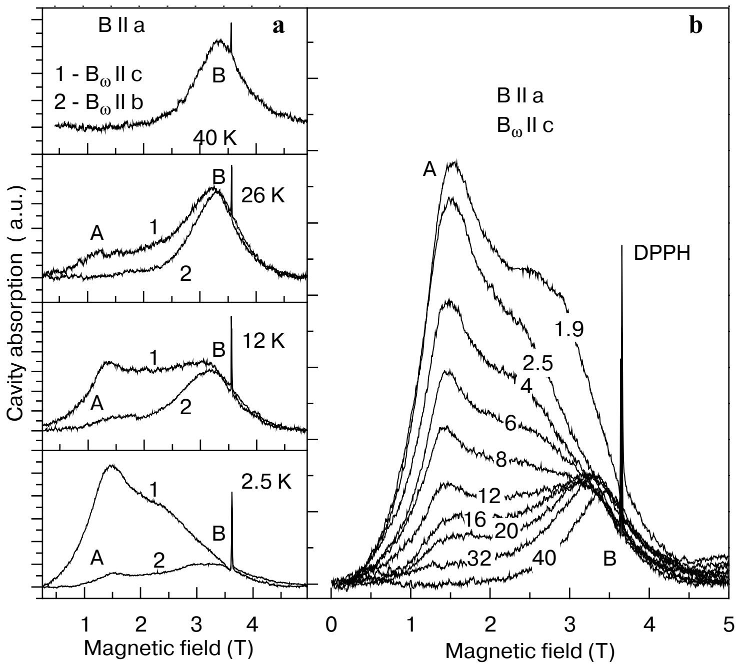

Fig. 1. Comparison of "active" and "nonactive" polarizations (**a**) and temperature evolution of the magneto-absorption spectrum for "active" polarization (**b**) in geometry **B** || **a**. **a** Narrow line represents DPPH signal. **b** Figures at curves correspond to temperatures in kelvins.

The resonance mode A remains dominant at low temperatures in the **B** || **c** case (Fig. 4) as well. However, the magnitude of the polarization effect appears to be weaker, and for $\mathbf{B}_\omega$ || **b** the amplitude of the resonance A is only two times lower than that for $\mathbf{B}_\omega$ || **a**. Nevertheless, the polarization dependence of this mode remains anomalously strong, especially in comparison with the resonance on Cu^{2+} chains.

According to the obtained results (Figs. 1, 3, 4), the g-factor of the impurity mode A is strongly anisotropic. The corresponding g-factor values are $g \sim 4.9$ (**B** || **a**), $g \sim 2.9$ (**B** || **b**) and $g \sim 3.7$ (**B** || **c**). The resonance mode of Cu^{2+} chains (resonance B) shows g-factor values in the range of about 2.06–2.26 for various crystallographic directions in good agreement with results known for pure $CuGeO_3$ [7].

The experimental data obtained in the present work demonstrate that the resonant mode A in $CuGeO_3$:Co is an anomalous one. Indeed, the observed behavior is forbidden as for a single spin or for $S = 1/2$ antiferromagnetic spin chain with the isotropic Hamiltonian [8, 9]. The vanishing of this resonance for a certain polarization means that the character of magnetic oscillations in this mode is completely different from the case of precession of magnetization vector around the magnetic field direction described by Landau–Lifshits-like equations. Indeed, in the case of the precession, the magnetization vector end moves

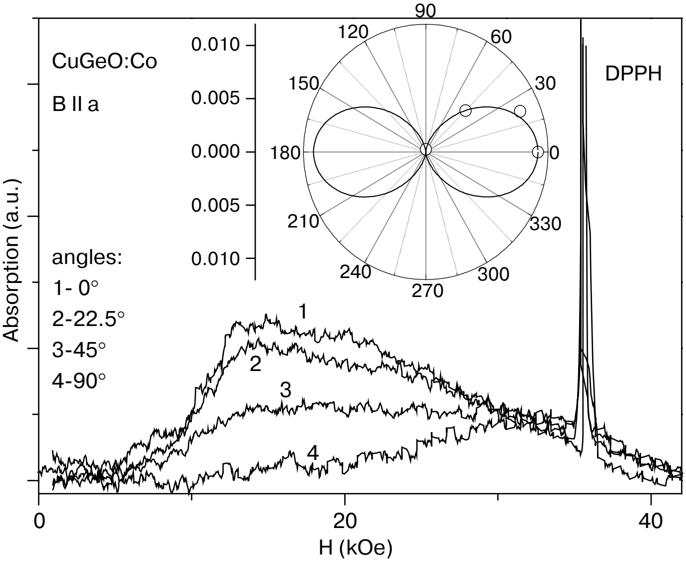

Fig. 2. Polarization dependence of the resonance spectra in geometry **B** || **a**. The inset shows the polar plot of the intensity of the resonance mode A. Solid line in the inset represents a cosine law for the polarization dependence.

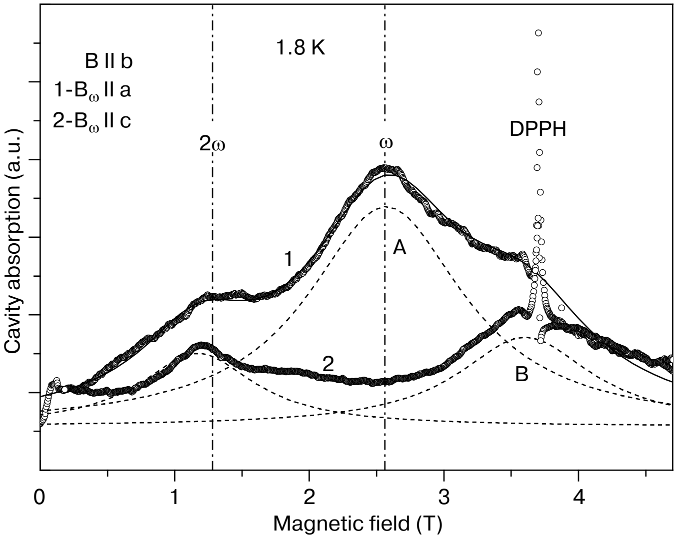

Fig. 3. "Active" and "nonactive" polarizations for **B** || **b**. Points, experiment; solid line, fitting of the experimental spectrum assuming Lorentzian shapes of the resonances A, B and second harmonic of resonance A. Partial contributions of these resonances to the spectrum are shown by dashed lines.

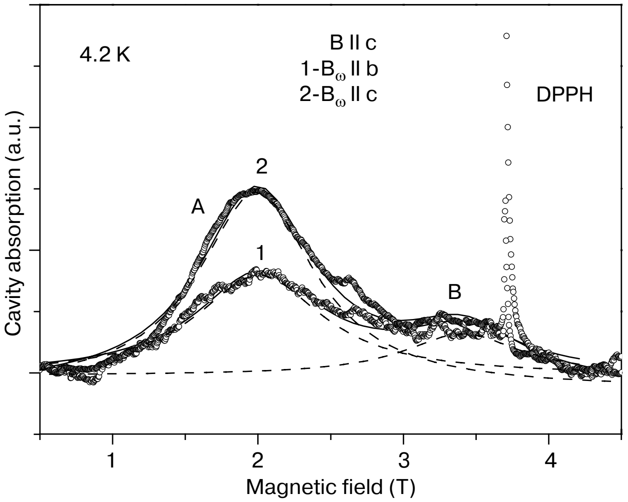

Fig. 4. "Active" and "nonactive" polarizations for **B** || **c**. Points, experiment; solid line, fitting of the experimental spectrum assuming Lorentzian shapes of the resonances A and B. Partial contributions of these resonances to the spectrum are shown by dashed lines.

around a circle with its plane perpendicular to the magnetic field, and hence any linear polarization in the Faraday geometry will excite an EPR-like mode or any mode based on correlated precession of various magnetization components [10].

However, in the presence of anisotropic terms, the spin chain Hamiltonian will no longer commute with the magnitude of the total spin and its z-component, and hence, in principle, the magnetic oscillation modes different from the standard spin precession may be excited. This may be the case of the strong magnetic anisotropy or an anisotropic term described as the staggered magnetic field [8, 9]. The role of the magnetic anisotropy in Co-doped $CuGeO_3$ was shown in magnetization measurements where the spin-flop transition was found at concentrations of Co $x > 2\%$, where it becomes observable due to the development of the antiferromagnetic order [6].

It is worth to note that the experimental data in Figs. 1, 3, 4 suggest a selected character of b-axis. Indeed, for $\mathbf{B}_\omega \parallel \mathbf{b}$ the resonance A is completely damped ($\mathbf{B} \parallel \mathbf{a}$) or its magnitude is reduced ($\mathbf{B} \parallel \mathbf{c}$) and in the case of $\mathbf{B} \parallel \mathbf{b}$, a more complicated resonant absorption mode develops.

The scenario of the collective resonant mode of spin chains with the staggered field along the **b** direction has been discussed previously [11]. However, independent of the physical nature of the anisotropy in $CuGeO_3$:Co, a general semiclassical description of magnetic resonant oscillations can be given. It is shown schematically in Fig. 5. The magnetization in the 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 [10]. As long as magnetic resonance probes normal modes of magnetization, oscillations described by vector **m** for excitation of a mode vector $\mathbf{B}_\omega$ should have a nonzero projection on any **m** component [10], i.e., the

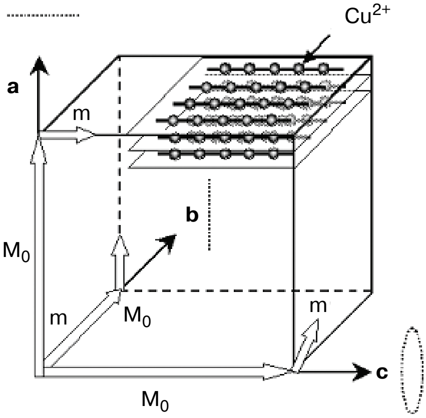

Fig. 5. Scheme of possible magnetic oscillations of the mode A in the semiclassical approximation in three cases ($\mathbf{B} \parallel \mathbf{M}_0 \parallel \mathbf{a}$, $\mathbf{B} \parallel \mathbf{M}_0 \parallel \mathbf{b}$, and $\mathbf{B} \parallel \mathbf{M}_0 \parallel \mathbf{c}$). Oscillating contribution **m** is assumed to vary harmonically with time in cases $\mathbf{M}_0 \parallel \mathbf{a}$ and $\mathbf{M}_0 \parallel \mathbf{b}$. For $\mathbf{M}_0 \parallel \mathbf{a}$ vector **m** rotates around *c*-axis. Dotted lines mark trajectories of the vector $\mathbf{M} = \mathbf{M}_0 + \mathbf{m}$ end.

condition $(\mathbf{B}_\omega, \mathbf{m}) \neq 0$ for the scalar product should be held. For the geometry $\mathbf{B} \parallel \mathbf{a}$ and the normal mode, where precession of magnetization around the field direction takes place, $\mathbf{m} = (0, m_b, m_c)$ and both projections of $\boldsymbol{m}$ on *b*- and *c*-axes are nonzero. Therefore, any alignment of the vector $\mathbf{B}_\omega$ in the **b**-**c** plane will excite precession. The weak dependence of the resonance amplitude on $\mathbf{B}_\omega$ alignment corresponds to the condition $m_b \approx m_c$. Thus, for the mode B and $\mathbf{B} \parallel \mathbf{a}$ the trajectory of the vector end is a circle lying in the **b**-**c** plane (a similar consideration is apparently applicable to the mode B in geometries $\mathbf{B} \parallel \mathbf{b}$ and $\mathbf{B} \parallel \mathbf{c}$).

The same analysis can be applied for the resonance A. Data in Fig. 1 suggest that in the geometry $\mathbf{B} \parallel \mathbf{a}$ the oscillating contribution to magnetization should acquire the form $\mathbf{m} = (0, 0, m_c)$ leading to the "active" polarization $\mathbf{B}_\omega \parallel \mathbf{c}$ and the "nonactive" polarization $\mathbf{B}_\omega \parallel \mathbf{b}$ (Fig. 1). Therefore, in this case the end of the vector **M** should move along the line parallel to the *c*-axis. Analogously, $\mathbf{m} = (m_a, 0, 0)$ for $\mathbf{B} \parallel \mathbf{b}$ and linear oscillation will happen along the *a*-axis. For $\mathbf{B} \parallel \mathbf{a}$, 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 $\mathbf{B}_\omega \parallel \mathbf{c}$ suggests that the trajectory of the vector **M** will be an ellipse in the **a**-**b** plane elongated in the **a** direction.

To the best of our knowledge, 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, antiferromagnetic and ferromagnetic resonances) essentially exploits semiclassical magnetization precession in the external field, and hence leaves no space to this 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 with a strong dependence on microwave polarization. This resonance coexists with the EPR on Cu^{2+} chains and is likely caused by strong magnetic anisotropy in this compound.

Acknowledgments

The support from the Russian Fund for Basic Research grant nr. 04-02-16574 and Russian Academy of Sciences Program "Strongly correlated electrons" is acknowledged.

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