Anisotropic exchange interaction in CuTe$_2$O$_5$

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We presented detailed ESR linewidth investigations on CuTe$_2$O$_5$ single crystals. The anisotropic exchange interaction within the Cu alternating chain was successfully applied to describe its angular dependence. Hence from an ESR point of view, CuTe$_2$O$_5$ turns out to be alternating chain Cu(1)-Cu(2)-Cu'(1) and magnetic inequivalent Cu(3)-Cu(4)-Cu'(3) chain. Based on previous results on magnetic susceptibility in [3] and angular dependence ESR linewidth analyses, we believe that strongest isotropic exchange interaction is in 4 pair [Cu(2)-Cu'(1) or Cu(4)-Cu(3)] and equal J$_{1a}$=93.3K and the second strongest value of exchange interaction in structural dimer (1 pair) is J$_{1b}$=40.7K.

1. Introduction

The discovery of a spin-Peierls transition in the one dimensional (1D) Heisenberg antiferromagnet CuGeO$_3$ [1] in 1993 entailed an intensive search for other inorganic spin-Peierls systems. This renewed the investigations of transition-metal oxides with spin S=1/2 ions such as Cu^{2+}. Transition-metal compounds based on Cu^{2+} ions with a 3d^9 configuration exhibit an enormously rich variety of magnetic structures depending on the effective magnetic dimensionality. Introducing lone-pair cations like Se^{4+} or Te^{4+} into the magnetic system was suggested as a fruitful path to tailor the magnetic dimensionality and to create new magnetic structures.

The compound investigated in this study is the related system CuTe$_2$O$_5$ which exhibits a monoclinic structure with space group P2$_{1/c}$ and lattice parameters a=6.871 Å, b=9.322 Å, c=7.602 Å, and β =109.08° [2]. The lattice consists of pairs of strongly distorted and edge-sharing CuO$_6$ octahedra with a Cu-Cu distance of 3.18 Å. The lattice unit includes four Cu positions. These structural dimer units Cu(1)-Cu(2) or Cu(3)-Cu(4) are separated by Te-O bridging ligands and a Cu-Cu distance of 5.28 Å. The copper ions in position Cu(1)[x,y,z]-Cu(2)[$\bar{x}$+1;$\bar{y}$+1;$\bar{z}$+1]-Cu'(1)[x;y;z+1], where x=0.34117; y=0.48715; z=0.29408 [2] and $\bar{y}$+1 = 0.51285 ≈ y form the alternating chain along c axis. The chain Cu(1)-Cu(2)-Cu'(1) lies practically in (ac) plane. The copper ions Cu(3)[$\bar{x}$+1; y + 0.5;$\bar{z}$+ 0.5 +1]-Cu(4)[x; $\bar{y}$+ 0.5+1; z + 0.5]-Cu'(3)[$\bar{x}$+1; y + 0.5;$\bar{z}$+ 0.5] form a second chain like structure running approximately along crystallographic *c* axis. The chains are arranged along the approximate crystallographic *b* axis. Two structural Cu(1)-Cu(2)-Cu'(1) and Cu(3)-Cu(4)-Cu'(3) are magnetically inequivalent.

The magnetic susceptibility of CuTe$_2$O$_5$ shows a maximum at Tmax=56.6 K and a strong decrease for lower temperatures, which can be roughly modeled by isolated magnetic dimers. The high-temperature susceptibility corresponds to a Curie-Weiss law with a Curie-Weiss temperature of θ =-41 K. The spin susceptibility in CuTe$_2$O$_5$ was studied in [3]. They cannot unambiguously determine the magnetic structure by fitting the susceptibility. But the alternating spin-chain and the modified Bleaney-Bowers approach well described experimental dates. For this reason, authors [3] and [4] investigated in detail the possible exchange paths between adjacent Cu ions. In the spin dimer analysis based on EHTB calculations, the strength of an antiferromagnetic interaction between two spin sites is estimated by considering the antiferromagnetic spin exchange parameter $J = -(\Delta e)^2 / U_{eff}$ [5], where U$_{eff}$ is the effective on site repulsion, Δe – energy split. The strongest interaction is J_6 (see Table 1). The first-principles NMTO-down folding study [4] reveals that the strongest Cu-Cu interaction is given by the Cu pairs (№4) belonging to different structural dimer units, and connected to two O-Te-O bridges. The results of examination by EHTB [3] and NMTO [4] methods are listed in Table 1.

Table 1. The relative strengths of the spin exchange interactions compared to the strongest interaction J_i/J_6 [3] and Cu-Cu hopping parameters t_i^2/t_4^2 [4] in CuTe$_2$O$_5$.

№	R Cu-Cu (Å)	J_i/J_6 [3]	$(t_i/t_4)^2$ [4]
1	3.187	0.59	0.12
2	5.282	0.05	-
3	5.322	0.14	0.01
4	5.585	0.11	1
5	5.831	0.01	0.015
6	6.202	1	0.28
7	6.437	0.05	0.002
8	6.489	0.09	-
9	6.871	0.26	-

The results [4] is contrary to resent study by [3], which represented the CuTe$_2$O$_5$ system as alternating spin chain system with strong intra and inter dimmer coupling. For solved this problem here we present a detailed investigation of the angular and temperature dependence of the ESR line width in CuTe$_2$O$_5$. We will show that the anisotropy of the line width can be well described by symmetric anisotropic exchange interaction between nearest neighbor spins in alternating chain.

2. Experimental details

Large single crystals of CuTe$_2$O$_5$ was in the form of platelets with a maximum size of $0.2\times1\times1$ mm^3. ESR measurements were performed in a Bruker ELEXSYS E500 cw spectrometer at 9.4 GHz in the temperature range $5 < T < 300$ K. ESR detects the power P absorbed by the sample from the transverse magnetic microwave field as a function of the static magnetic field H. The ESR signal of CuTe$_2$O$_5$ consists of a single exchange narrowed resonance line with nearly temperature independent g tensors, except for the temperatures (T<25K), where a splitting of the ESR line occurs due to the formation of clusters. The line width shows a pronounced anisotropy with the largest values for the magnetic field applied along the b axis. Figure 1 presents the detailed angular dependence of the ESR line width at 60K, 200K and room temperature.

3. Theoretical background

The theory of the ESR line width is well-developed for conventional exchange-coupled spin systems. It has been shown that in the case of sufficiently strong exchange interaction the ESR spectrum is narrowed into a single Lorentz line with a line width ΔH (half width at half maximum) determined by second M_2 and forth M_4 moments [6]:

$$\Delta H = \frac{\pi}{\sqrt{3}}\left(\frac{M_2^3}{M_4}\right)^{1/2} \qquad (1)$$

We consider a system of exchange-coupled spins S_{1i} with an effective spin Hamiltonian given by:

$$H = J_{1a}(S_1 S_a) + \sum_{\alpha,\beta=x,y,z} J_{1a}^{\alpha\beta} S_1^\alpha S_a^\beta + J_{1b}(S_1 S_b) +$$
$$+ \sum_{\alpha,\beta=x,y,z} J_{1b}^{\alpha\beta} S_1^\alpha S_b^\beta + J_{1c}(S_1 S_c) + \sum_{\substack{\alpha,\beta=x,y,z \\ \gamma=1,3}} g_\gamma^{\alpha\beta} \mu_B H_\gamma^\alpha H_\gamma^\beta \qquad (2)$$

where the scalar J_{1a} denotes the strongest isotropic exchange between two spins 1 and a, J_{1b} denotes the second value isotropic exchange between two spins 1 and b, J_{1c} is the minimum isotropic exchange between two spins 1 and c. The last term described the Zeeman splitting of the spin states in an external magnetic field H_γ^α with gyromagnetic tensor $g_\gamma^{\alpha\beta}$ and Bohr magneton μ_B. If $J_{1c} << J_{1a}$ and $J_{1c} << J_{1b}$, in coordinates x, y, z, where the z axis is defined by the direction of the applied magnetic field H, the second and forth moments due to anisotropic exchange is given by:

$$M_2(J) = \frac{2S(S+1)}{3}\left(B(J_{1a}) + B(J_{1b})\right) \qquad (3)$$

$$M_4 = \frac{a(6a-7)}{30}\left(J_{1a}^2 B(J_{1a}) + J_{1b}^2 B(J_{1b})\right) + \frac{a^2}{9}\left(J_{1b}^2 B(J_{1a}) + J_{1a}^2 B(J_{1b})\right) + \qquad (4)$$
$$+ \frac{a^2 J_{1a} J_{1b}}{9}\begin{pmatrix} (2J_{1a}^{zz} - J_{1a}^{xx} - J_{1a}^{yy})(2J_{1b}^{zz} - J_{1b}^{xx} - J_{1b}^{yy}) + \\ + (J_{1a}^{xx} - J_{1a}^{yy})(J_{1b}^{xx} - J_{1b}^{yy}) + \\ + 10J_{1a}^{xz}J_{1b}^{xz} + 10J_{1a}^{yz}J_{1b}^{yz} + 4J_{1a}^{xy}J_{1b}^{xy} \end{pmatrix},$$

where $a = S(S+1)$

and

$$B(J_{1a}) = (2J_{1a}^{zz} - J_{1a}^{xx} - J_{1a}^{yy})^2 + (J_{1a}^{xx} - J_{1a}^{yy})^2 + 10(J_{1a}^{xz})^2 + 10(J_{1a}^{yz})^2 + 4(J_{1a}^{xy})^2.$$

The value $J_{1\gamma}^{\alpha\beta}$, where $\alpha,\beta = x,y,z$, $\gamma = a,b$, are exchange-tensor components in the coordinates with $z \| H$. They can be expressed via the intrinsic exchange parameters [7].

4. Determinatin of the exchange parameters

Now we focus our attention on the angular dependence of the ESR line width, which we investigated in detail for the three crystallographic planes at 60K, 200K and room temperature. Typical data are shown in Fig.1.

We will describe the angular dependence of the ESR line width using anisotropic exchange interaction between neighboring spins. The symmetric anisotropic exchange interaction between two neighboring spins S_i and S_j can be written in local coordinates as $H^{(i,j)} = J_{x'x'}S_i^{x'}S_j^{x'} + J_{y'y'}S_i^{y'}S_j^{y'} + J_{z'z'}S_i^{z'}S_j^{z'}$, where $J_{x'x'} + J_{y'y'} + J_{z'z'} = 0$. The local coordinates for inequivalent pairs are different. It is necessary for the estimation of the anisotropic exchange constants to find $\sim\left[\frac{(g-2)}{g}\right]^2 J$. In this case the largest anisotropic exchange interaction is for strongest isotropic exchange value. The strongest interaction has number 6 pair in. EHTB model [3] (see table 1). In this case the maximum of ESR line width must shift on 37 degrees from b axis in

(bc) plane. But experimental curve hasn't such behavior. For this reason we believe that the strongest interaction in the fourth pair (see table 1) [4] is between two Cu^{2+} ions, which are situated at different structural dimer (Cu(2)-Cu'(1) or Cu(4)-Cu'(3)). The second strongest interaction is between two Cu^{2+} ions situated within the same structural dimer unit (first pair of table1). In Fig. 2 we show alternating chain model in the (bc) plane. The angular dependence of the ESR line width was approximated by Eqs (1), is illustrated in Fig. 1. For the all temperatures the results of the fit procedure are plotted in Table 2. According to the magnetic susceptibility fit [3] for alternating chain, the strongest interaction is J_{1a}=93.3K for 4 pair. The second strongest value is J_{1b}=40.7K for 1 pair. The g-tensor was founded before from angular dependencies resonance field and anisotropic effect Zeeman [8].
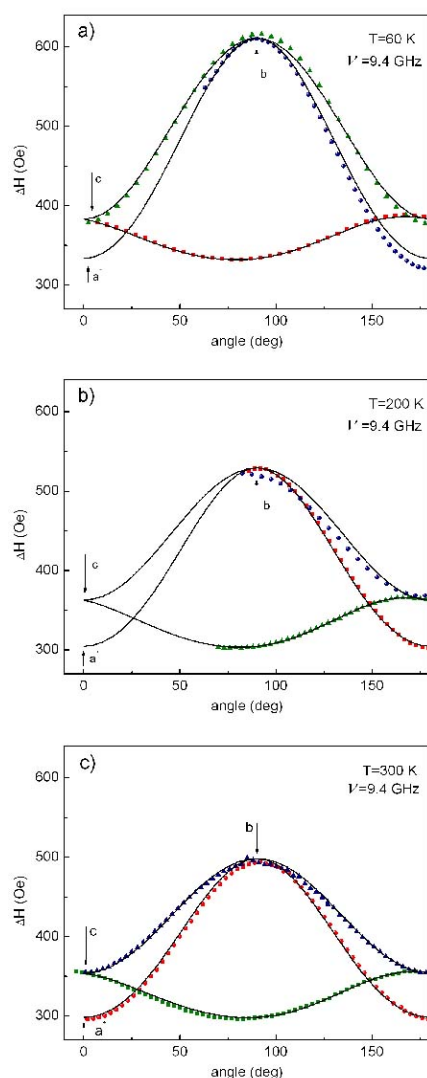
Table 2. The parameters of anisotropic exchange interaction at different temperatures.

T(K)	$J_{1a}^{x"x"}$ (K)	$J_{1a}^{z"z"}$ (K)	$J_{1b}^{x'x'}$ (K)	$J_{1b}^{z'z'}$ (K)
60	-1	2.19	0.55	-0.33
200	-0.82	1.98	0.65	-0.42
300	-0.82	1.92	0.64	-0.42

The directions of anisotropic exchange interaction local axis in a*bc coordinate system for two inequivalent copper ions pairs were given matrixes. For 1 pairs:

$$\begin{pmatrix} -0.71 & 0.2773 & 0.6473 \\ -0.3025 & -0.9502 & 0.0752 \\ 0.6359 & -0.1424 & 0.7585 \end{pmatrix} \text{ and}$$

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for 4 pairs:

$$\begin{pmatrix} 0.929 & -0.0158 & -0.3696 \\ 0 & 0.999 & -0.0429 \\ 0.3699 & 0.0399 & 0.9283 \end{pmatrix} \text{ and}$$

$$\begin{pmatrix} 0.929 & 0.0158 & -0.3696 \\ 0 & 0.999 & 0.0429 \\ 0.3699 & -0.0399 & 0.9283 \end{pmatrix}.$$
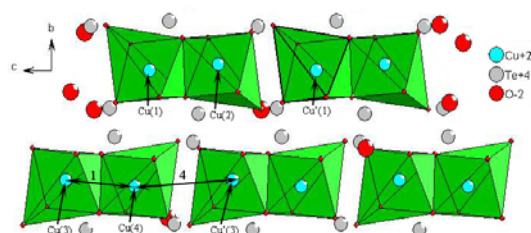

*Fig. 1. Angular dependence of the resonance linewidth for three planes (a*b), (bc), (a*c). The solid lines have been obtained from the fit as described in the text.*

Fig. 2. The model of alternating spin-chain Cu(1)-Cu(2)-Cu'(1) and Cu(3)-Cu(4)-Cu'(3) in (bc) plane.

5. Conclusions

To summarize, we presented detailed ESR line width investigations on CuTe$_2$O$_5$ single crystals. The anisotropic exchange interaction within the Cu alternating chain was successfully applied to describe its angular dependence. Hence from an ESR point of view, CuTe$_2$O$_5$ turns out to be alternating chain Cu(1)-Cu(2)-Cu'(1) and magnetic inequivalent Cu(3)-Cu(4)-Cu'(3) chain. Based on previous results on magnetic susceptibility in [3] and angular dependence ESR line width analyses, we believe that strongest isotropic exchange interaction is in 4 pair [Cu(2)-Cu'(1) or Cu(4)-Cu(3)] and equal J_{1a}=93.3K and the

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