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Exchange Interactions in Cu_2AlBO_5 and Cu_2GaBO_5

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Abstract. Single crystals of ludwigite Cu2MeBO5 (Me=Al, Ga) were synthesized by flux growth technique. The calculations of the exchange integrals in frameworks of indirect coupling model revealed that monoclinic distortions strongly affect exchange interactions. We have performed electron spin resonance (ESR) measurements for untwined single crystals of Cu2MeBO5 (Me=Al, Ga). The observed anisotropy of the ESR linewidth result from the one-dimensional chain like structure of Cu2MeBO5 (Me=Al, Ga) and the anisotropic exchange interactions between Cu ions, respectively.

INTRODUCTION

Different quantum effects become apparent in low-dimensional magnetic compounds at relatively high temperatures. When two magnetic subsystems are present, the pattern of exchange interactions and charge ordering becomes considerably more complex. The magnetic structure of such objects can therefore manifest itself in the form of spin ladders, ribbons, or zigzag walls. Oxyborates with ludwigite structure are a fine example of such systems. Their general formula is $M1_2^{2+}M2^{3+}BO_5$, where M1 and M2 are ions of the iron group. The results from detailed studies of the magnetic properties of $Co_{2-x}Fe_xBO_5$ single crystals with low iron concentrations were presented in [1]. It was shown that the ordering temperature grows considerably at iron concentration x = 0.10, but the magnetic behavior and direction of the easy magnetization axis typical of Co_3BO_5 are retained. It is safe to say that ludwigites feature a fairly complex pattern of exchange interactions between heterovalent ions. Data on the magnetic properties of ludwigites with one nonmagnetic metal ion would be of use in analyzing the dynamics of variation in magnetic properties. The unit cell of the investigated ludwigites contains Z = 4 formula units, so the unit cell can contain up to twelve divalent cations (Cu^{2+}, $3d^9$) with spin S = 1/2. Each magnetic Cu^{2+} ion is surrounded by six oxygen ions forming a strongly distorted octahedron. We can identify four types of structurally nonequivalent oxygen octahedral, which correspond to four atomic sites of copper ions. Four types of oxygen octahedral form chains which are presented in Fig. 1. Interatomic distances between cations and anions are given in [2, 3].

The temperature dependences of the molar heat capacity and magnetic susceptibility of Cu_2AlBO_5 and Cu_2GaBO_5 were investigated in [4]. It was obtained that the antiferromagnetic ordering transition occurs in Cu_2AlBO_5 and Cu_2GaBO_5 single crystals at T_N = 2.4 and 4.1 K, respectively. The complex nature of exchange interactions is corroborated by the results from estimating superexchange interactions with the indirect exchange model developed in [5]. The structure of ludwigite with space group P21/c is characterized in the indirect exchange theory by 16 possible integrals of the indirect exchange coupling of Cu–O–Cu interactions. The formulas for calculating these exchange interaction integrals and their values were determined in [5] by assuming that copper ions can occupy any of the four metallic crystallographic sites. Cu_2GaBO_5 and Cu_2AlBO_5 single crystals were synthesized via solution–melt crystallization. Lattice parameters and synthesis process are described in [4]. The crystal structure is presented in Fig. 1. One site in Cu_2AlBO_5 and Cu_2GaBO_5 is occupied by a nonmagnetic ion, and six exchange interaction integrals remain. Here we present the investigations of magnetic properties of Cu_2GaBO_5 and Cu_2AlBO_5 ludwigites, which contain only one magnetic ion Cu^{2+}.

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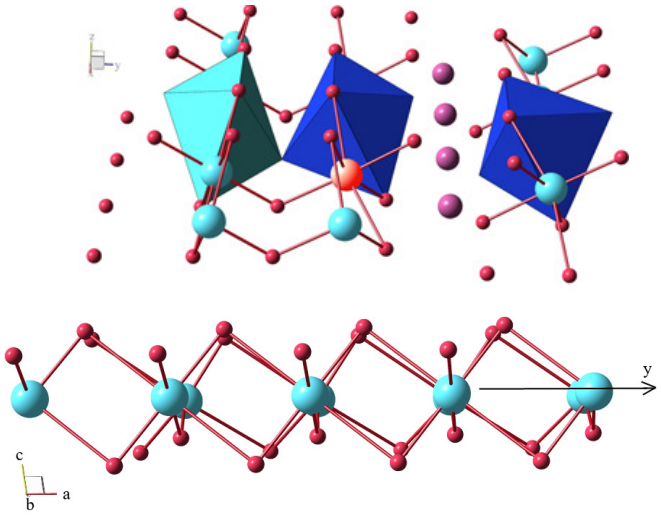

FIGURE 1. Crystal structure of Cu_2MBO_5 (M = Ga, Al) ludwigites. Dark magenta and light magenta octahedrons surround Cu1/M and Cu2/M positions, dark blue and light blue octahedrons surround Cu3/M and Cu4/M positions, respectively.

INDIRECT COUPLING MODEL

To analyze the magnetic structures and estimate the superexchange interactions in Cu_2MeBO_5 (Me=Ga, Al) crystal, we used a simple indirect coupling model [6] based on the theory of the super-exchange interaction of Anderson [7] and Zavadskii [8] and Eremin [9]. Within the indirect coupling model, the structure of the crystals can be characterized by the following integrals of the indirect exchange coupling with regard to occupations of individual cation orbitals and symmetries of the lattice of indirect couplings J_{ij} $(\alpha\beta)$, where i and j are the numbers of nonequivalent crystallographic positions for magnetic ions and α,β are the angles of the indirect coupling between magnetic ions. The calculated exchange integrals for Cu_2GaBO_5 are presented in the TABLE 1.

As can be seen from the table, the antiferromagnetic structures along a axis are energetically more favorable. The exchange interactions are shown in the FIG. 2.

TABLE 1. The calculated value of super exchange integrals

	N_i	N_j	α	β	J, K	Distance (Å)
J_1	3	1	119,4°		-0,7	3,35
J_2	1	1	89,5°	89,5°	7,9	3,11
J_3	3	3	87,4°	88,9°	7,9	3,11
J_4	4	4	86,1°	103,2°	0,7	3,11
J_5	2	2	96,5°	96,5°	1,3	3,11
J_6	4	3	97,2°	99,5°	0,1	3,4
J_7	4	1	86,6°	98,9°	2,4	3,04
J_8	4	3	97,0°	99,2°	2,4	2,97
J_9	4	1	99,4°	95,6°	4,7	2,96
J_{10}	3	2	97,8°	98,0°	6,2	2,99
J_{11}	3	2	90,0°	97,4°	3,2	3,11
J_{12}	4	2	92,8°	82,0°	0,9	2,99
J_{13}	4	2	165,4		0,0	4,71
J_{14}	4	2	159,0°		-1,7	3,87
J_{15}	4	3	118,6°		1,3	3,41
J_{16}	4	3	114,2°		0,2	3,23

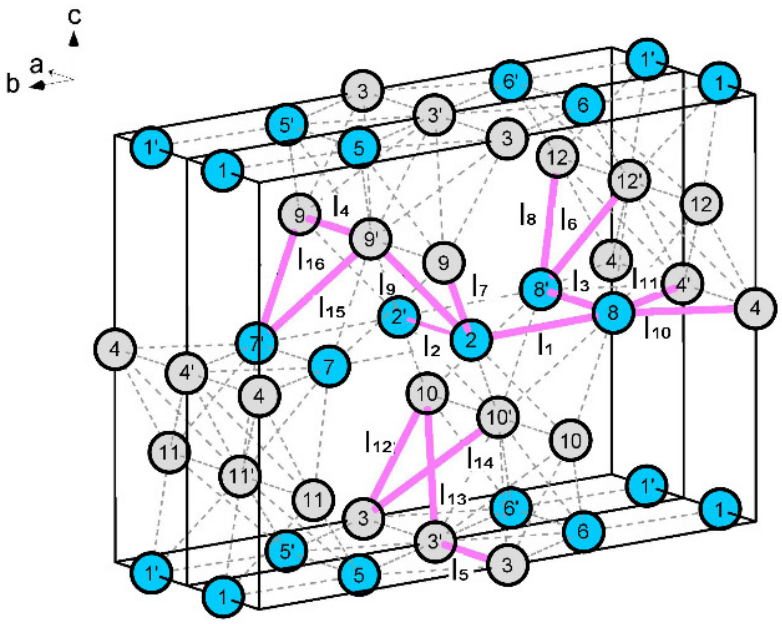

FIGURE 2. The exchange interactions in Cu_2MeBO_5 (Me=Ga, Al).

EXPERIMENT

The electron spin resonance (ESR) spectra of compounds were measured on an ER 200 SRC (EMX/plus) spectrometer (Bruker) at the frequency of 9.4 GHz (X-band) and 34GHz (Q-band) in the temperature range from 5 to 250 K at the magnetic field $B \leq 1.8$ T. Spectrometer was equipped with a flow helium cryostat (Oxford Instruments) operating in the temperature range $T = 5 – 300$ K. To make conclusions about the spin dynamic of Cu_2GaBO_5 and to get the evolution of the corresponding ESR parameters with temperature we analyzed the ESR line shape. The typical ESR spectra for monocrystal Cu_2GaBO_5 and Cu_2AlBO_5 in X- and Q-bands are shown in Fig.3. All spectra consist of a broad exchange-narrowed resonance line i.e., any line splitting or inhomogeneous broadening is averaged out by the isotropic exchange interaction. The ESR lines are related to the copper exchange coupled system.

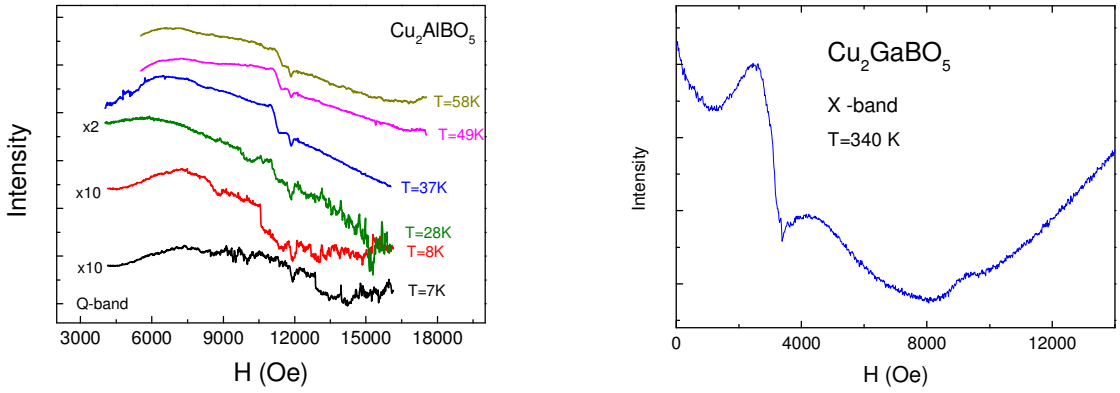

FIGURE 3. ESR spectra in Cu_2AlBO_5 and Cu_2GaBO_5 monocrystals.

The g value of Cu_2AlBO_5 and Cu_2GaBO_5 are found between 2.05 and 2.27 dependent on the orientation of the single crystal within the external magnetic field. These results are typical for Cu^{2+} ions.

At high temperature the linewidth of Cu_2AlBO_5 and Cu_2GaBO_5 exhibits values between 7500 Oe and 10000 Oe, In general, the ESR linewidth in the case of sufficiently strong exchange interaction can be analyzed in terms of the high-temperature approach ($k_BT \gg J$) [10]:

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

where the second and forth moments M_2 are defined by:

$$\begin{aligned} M_2 &= \frac{\left\langle \left[H_{\text{an}}, S^+ \right] \left[S^-, H_{\text{an}} \right] \right\rangle}{\hbar^2 \left\langle S^+ S^- \right\rangle}, \\ M_4 &= \frac{\left\langle \left[H_{\text{ex}}, [H_{\text{an}}, S^+] \right] \left[[S^-, H_{\text{an}}], H_{\text{ex}} \right] \right\rangle}{\hbar^4 \left\langle S^+ S^- \right\rangle}. \end{aligned} \tag{2}$$

Here g is effective g value, ħ is the Planck constant, and μ_B is the Bohr magneton. The second moment M_2 and the exchange frequency ω_{ex} can be expressed via microscopic Hamiltonian parameters *Hint*. The second moment shows an orientation dependence with respect to the external magnetic field. The second moment is defined by anisotropic interactions of relativistic nature. Counting that in the Cu_2AlBO_5 and Cu_2GaBO_5 the usually dominating single ion anisotropy is absent as $S = 1/2$, the relativistic interactions of neighbor spins are taken into consideration. The relevant pair interaction was described as anisotropic exchange interaction previously. Note, that taking into account the anisotropic exchange interactions was fruitful for explanation of magnetic properties of several spin $S = 1/2$ chain compounds, e.g., $LiCuVO_4$ [11] and $CuGeO_3$ [12] as well as $CuTe_2O_5$ [13,14]. The results of our ESR experiments will be discussed in the frame of the following model Hamiltonian:

$$H = J_{1l} \mathbf{S}_1 \mathbf{S}_l + \sum_{\alpha,\beta=x,y,z} J_{1l}^{\alpha\beta} S_1^\alpha S_l^\beta + J_{1r} \mathbf{S}_1 \mathbf{S}_r + \sum_{\alpha,\beta=x,y,z} J_{1r}^{\alpha\beta} S_1^\alpha S_r^\beta . \tag{3}$$

Here J_{1l}, $J_{1l}^{\alpha\beta}$ are the parameters of the isotropic and anisotropic exchange interactions with the left (l) nearest neighbour spins of magnetic ion, and J_{1r}, $J_{1r}^{\alpha\beta}$ are the parameters of the isotropic and anisotropic exchange interactions with the right (r) nearest neighbor spins of magnetic ions, respectively. It is assumed that $Jxx+Jyy+Jzz = 0$. For brevity, the summation over the spins of the chain is not indicated.

$$H_Z = \sum_{\alpha,\beta=x,y,z} g_{\alpha\beta} \mu_B H_\alpha S_\beta . \tag{4}$$

Here H_Z denotes the interaction of spins with an external magnetic field, the summation over the all spins of the chain is not indicated. One of the axes (x; y; z) is directed along the exchange bond for anisotropic exchange interaction. The directions of two other axes are defined by symmetry of local environment. The details of second moment calculations for anisotropic exchange interaction are presented in Ref.[15]. To estimate the expected strength of the two anisotropic exchange contributions in *H*int, one has to consider the respective bond geometries. The intra-chain anisotropic contribution $\mathbf{J_1}$ is of identical configuration in another compound LiCuVO4, so we have considered the same so called ring-exchange geometry of the Cu-O2 ribbons yielding $Jcc1 = -2$K [11]. We substitute the values of the anisotropic exchange interaction between the spins of copper ions in the chain (ring exchange) and the calculated

value of the isotropic exchange interaction 2K in the formula (1-4) and ration from [15] we obtain that the ESR linewidth is about 7000, which is observed in the experiment.

SUMMARY

Calculation of the exchange interactions has shown that in the system there is a competition of exchange interactions, and some exchange interactions are close to zero. In our proposed structure there are magnetic frustrating interactions that can lead to the decomposition into subsystems. The presence of almost zero interactions can lead to the fact that one of the sublattices or subsystems will be weakly related to the rest ones, or not fully ordered. From the symmetric anisotropic exchange components *Jzz* and calculated isotropic symmetric exchange interaction in single crystalline Cu_2AlBO_5 and Cu_2GaBO_5 we were also able to estimate the ESR line width that coincides with experimental data.

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