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# Antisymmetric Exchange in the Trinuclear Clusters of Copper (II)

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The magnetic susceptibility of $Cu_3(C_6H_5N_2O)_3(OH)SO_4 \cdot 10.5\,H_2O$ crystals was measured in the temperature interval 4.2 – 11 K and magnetic field range 0 – 50 kOe. The theoretical analysis of the effects of antisymmetric exchange was performed. An adequate interpretation of the experimental results may be done in terms of an antisymmetric exchange which is about $12\,cm^{-1}$ in the crystals discussed. The rhombic distortions of the trigonal cluster were shown to reduce the antisymmetric exchange.

*Key words:* Exchange interaction – Magnetic susceptibility – Copper (II)

## 1. Introduction

In some cases the energy spectrum of crystals is determined by an exchange interaction between the paramagnetic centers. Besides magnetically concentrated crystals such systems include the impurity crystals in which paramagnetic ions are grouped in pairs, triades etc., donor clusters in semiconductors and the bi- and triradicals. Below, such groups of the paramagnetic exchange coupled centers will be referred to as "exchange clusters". Crystals containing exchange clusters as a unit of regular lattice involve a special class of such objects. Unlike for impurities, structural investigation may be performed for those crystals in such a way that spatial arrangement of paramagnetic ions and their local symmetries are available at sufficiently high accuracy. Experiments on heat capacity [1], magnetic susceptibility [2, 3] and ESR spectra [4, 5] carried out so far reveal restrictions of the traditional Heisenberg-Dirac-Van Vleck (HDVV) model of the isotropic exchange interaction. At the same time a theoretical analysis of the exchange multiplets shows that the symmetry group of the HDVV Hamiltonian is higher than the cluster's point group symmetry; therefore, the exchange multiplets are manyfold degenerate. Investigation of the nature of such "non-physical" degeneracy in the chromium trimeric carboxylate crystals [6–8] exposes two types of a "non-physical" degeneracy. One type of the degeneracies arises from the orbital degeneracies of Heitler-London states corresponding to the HDVV ex-

change multiplets. In general, such degeneracies could be removed by a spin-orbital interaction which is beyond the HDVV model. It may be possible that several Heitler-London orbital multiplets correspond to the same exchange multiplet and that this type of "accidental" degeneracy is completely or partially removed by Coulomb interaction omitted in the HDVV model. In principle the group-theoretical analysis [7] (see also [9, 10]) gives an explanation to the peculiarities of the energy spectrum and $g$-factor anisotropy. It enables us to classify directly the type of non-Heisenberg spin tensor operator which splits the levels and thus to avoid a troublesome choice of the effective spin Hamiltonian.

The present study is concerned with a theoretical analysis of the non-Heisenberg exchange interactions in the trimeric copper(II) clusters. Experiments were performed with such clusters with the aim to determine the antisymmetric exchange parameter.

## 2. Investigation Objects and Experimental Procedure

The $Cu_3(C_6H_5N_2O)_3(OH)SO_4 \cdot 10.5\,H_2O$ crystals were investigated. X-ray analysis [11] has demonstrated that the triades of Cu(II) ions are forming regular triangles. Below 105 K the magnetic susceptibility is essentially lower than the value typical for the Cu(II) ion which indicates the antiferromagnetic interaction between Cu(II) ions with an energy parameter $\sim k \cdot 400°$. Since each Cu(II) ion is affected by the crystal field of the $C_{2v}$ symmetry, the orbital degeneracy of the individual ion's levels is entirely removed. Thus, in terms of the HDVV isotropic exchange model, the Hamiltonian of the cluster can be written as follows:

$$\hat{H}_{ex} = J_0(\hat{s}_1\hat{s}_2 + \hat{s}_2\hat{s}_3 + \hat{s}_1\hat{s}_3)\,, \tag{1}$$

where $s_i = 1/2$, $J_0$ is an exchange integral. The latter, being determined from the high temperature measurement of $\chi(T)$, is about 300 $cm^{-1}$ [11]. Total spin $S$ of the system takes the values 1/2 and 3/2, and we have the equation:

$$E(S) = \frac{J_0}{2}[S(S+1) - 3s(s+1)]\,. \tag{2}$$

The $2D^{(\frac{1}{2})}$ ground state is four-fold degenerated in the intermediate spin $S' = 0.1$. The nature of "non-physical" four-fold degeneracy of the ground state has been studied in [7, 8]. Elucidation of the permutation symmetry of spin functions and comparison with the dual coordinate Young tables corresponding to the Heitler-London states lead to the conclusion that the $2D^{(\frac{1}{2})}$ quadruplet of the HDVV model corresponds to the $^2E$ orbital doublet of the Heitler-London scheme for the trigonal ($D_3$) cluster. Since orbital components of the wave function belong to one irreducible representation, no Coulomb interaction in the system removes this degeneracy. On the other hand the spin-orbital interaction (SOI) which splits it into two Kramers doublets: $^2E \to 2\bar{A} + \bar{E}$, where $2\bar{A}$ and $\bar{E}$ are the two double-valued representations of the $D_3$ group, $2\bar{A} \equiv \bar{A}_1 + \bar{A}_2$, are the complex conjugate representations. The excited state $D^{(\frac{3}{2})} \doteq {}^4A_2$ also splits into two Kramers doublets $2\bar{A} + \bar{E}$. Since for the orbital doublet an antisymmetric square $\{E^2\} = A_2$ the spin-orbital splitting takes place in the first order perturbation

theory while an excited state being orbital singlet is splitted by SOI only in the second order perturbation theory.

In the case of trinuclear $Cu_3$ cluster we note that the first order SOI may be written in the form of an effective antisymmetric (AS) exchange spin operator [12] first derived by Dzialoshinski [13] and Moriya [14] (see also Bates and Jasper [15]). Thus the Heisenberg quadruplet $2D^{(\frac{1}{2})}$ should split by the AS exchange operator in the first order perturbation theory. In the same manner we conclude that the excited state $D^{(\frac{3}{2})} \doteq {}^4A_2$ is splitted by SOI in the second order perturbation theory. The appropriate spin equivalent is an anisotropic exchange. Then we note that according to the group theoretical analysis performed above the splitting effects of spin multiplets under AS exchange take place only in the exchange clusters having the orbitally degenerate levels. If orbital degeneracy of of the individual ion ground state is removed by a local crystal field, orbital degeneracy of the exchange system levels may take place as it is readily seen only in the case of trinuclear clusters and also in symmetric systems with a greater number of ions while it is absent in the binuclear systems. In particular, this idea has been the reason for the choice of trinuclear clusters for investigation.

Moriya [14] has shown that the order of magnitude of the AS exchange parameter is $\frac{\Delta g}{g_e} J_0$ where $g_e = 2$ is the free electron $g$-factor, $\Delta g = g - g_e$ is the change of the $g$-factor of the individual ion in a local crystal field. The latter value is proportional to the SOI constant and hence it is great for Cu(II) ions ($\lambda = -830\,\mathrm{cm}^{-1}$). Since in $Cu(II)_3$ clusters the isotropic exchange is also essential ($J_0 \simeq 300\,\mathrm{cm}^{-1}$ [11]), one should expect to find a sufficiently antisymmetric exchange in such clusters in the region of not too low temperatures. It is favoured also by the sufficiently large energy gap between the $D^{(\frac{1}{2})}$ ground and $D^{(\frac{3}{2})}$ excited states, the latter being practically not populated at the helium temperatures when AS exchange may appear. Therefore Cu(II) clusters are rather suitable objects for the AS exchange investigation and exceed the widely explored trinuclear chromium carboxylates the isotropic exchange of which is an order lower.

The $Cu_3(C_6H_5N_2O)_3(OH)SO_4 \cdot 10.5\,H_2O$ crystals were prepared by the method of [11], the $C_6H_5N_2O$ being a fragment of pyridine-2-aldoxime (pyridine-2-aldoxime was obtained by the procedure of [16] and [17]). Found for the cluster: Cu = 22.83 %, C = 26.68 %, H = 4.23 %, N = 10.80 %; calculated: Cu = 22.90 %, C = 26.90 %, H = 4.68 %, N = 10.82 %. Magnetic susceptibility was measured using pressed cubic samples. Measurements at 4.2–11 K were performed on a vibrational magnetometer designed at the Institute pf Physical Problems of the Academy of Sciences of the USSR [18]. The magnetic field of the superconducting solenoid varied from 0 to 50 kOe. The temperature and field dependence of the molar magnetic susceptibility per copper atom is shown in Fig. 1.

### 3. Magnetic Susceptibility of the Trinuclear Copper (II) Clusters

Let us first consider the temperature and field dependence of $\chi$ in terms of the simple HDVV model (1). Zeeman interaction

$$\hat{H}_Z = g\mu_B \vec{\mathscr{H}} \hat{S} \tag{3}$$

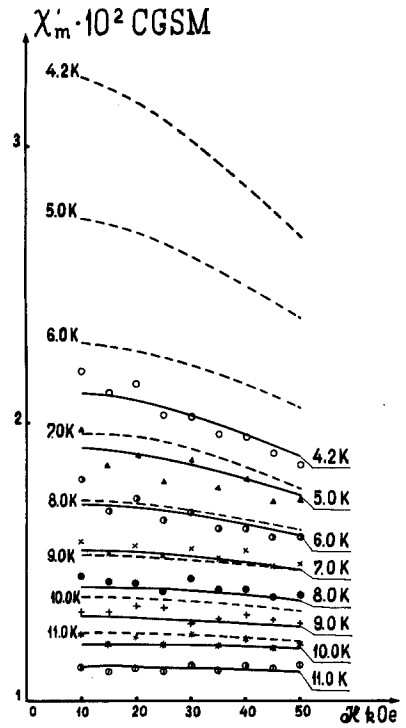


Fig. 1. Temperature and field dependences of magnetic susceptibility of $Cu_3(C_6H_5N_2O)_3(OH)SO_4 \cdot 10.5\,H_2O$ crystals per copper atom. Experimental data: ○ – 4.2 K, ▲ – 5 K, ◑ – 6 K, × – 7 K, ● – 8 K, + – 9 K, * – 10 K, ⓘ – 11 K; - - - - theoretical dependences within the HDVV (5) model, —— theoretical dependences with AS exchange at $G = 12\,\mathrm{cm}^{-1}$ and $g = 2.1$

leads to an isotropic splitting

$$E = g\mu_B \mathcal{H} M_S \tag{4}$$

and the classical equation for magnetic susceptibility [per Cu(II) ion] of the system in the $2D^{(\frac{1}{2})}$ ground state

$$\chi = \frac{1}{3} \frac{g\mu_B}{2\mathcal{H}} \operatorname{th} \frac{g\mu_B \mathcal{H}}{2kT} \tag{5}$$

which differs from the corresponding relation for the monomeric copper(II) cluster with an orbitally non-degenerate ground level only by a factor 1/3. Since the exchange integral $J_0 \simeq 300\,\mathrm{cm}^{-1}$, only the ground state is populated below 11 K. Fig. 1 shows the theoretical curves (5) with $g = 2.1$ typical for Cu(II). We note a significant disagreement between theoretical and experimental results for the field dependence and the absolute values at low temperatures. The Curie-Weiss temperature region of $2kT \gg g\mu_B \mathcal{H}$ is attained at $T = 10$ K. In this region both the theoretical and experimental values of $\chi(T, \mathcal{H})$ are field independent but absolute values differ essentially. This disagreement can not be avoided by a reasonable $g$-factor choice.

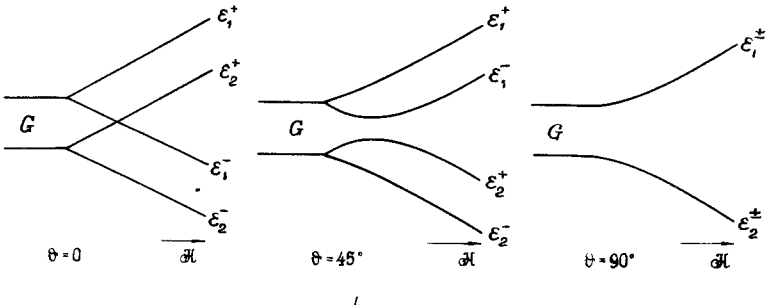


Fig. 2a–c. Zeeman splitting of the ground state of trigonal cluster with spin $s_i = 1/2$: (a) $\mathscr{H} \| C_3 (\vartheta = 0)$, (b) $\vartheta = \frac{\pi}{4}$, (c) $\mathscr{H} \| C_2 \left(\vartheta = \frac{\pi}{2}\right)$

Now let us discuss the effect of AS exchange on the magnetic susceptibility of the trinuclear clusters. The AS Hamiltonian has the form

$$\hat{H}_{\mathrm{AS}} = \sum_{i,j} \vec{G}_{ij} [\hat{\vec{S}}_i \times \hat{\vec{S}}_j]. \tag{6}$$

Using the ground $2D^{(\frac{1}{2})}$ quadruplet spin functions as a basis set and diagonalizing $\hat{H}_{ex} + \hat{H}_{\mathrm{AS}} + \hat{H}_Z$ we find the Zeeman levels of the system as follows

$$\begin{gathered} \varepsilon_{1(2)}^{\pm} = \pm \tfrac{1}{2} [g^2 \mu_B^2 \mathscr{H}^2 + G^2 \pm 2 G g \mu_B \mathscr{H} \cos\vartheta]^{\frac{1}{2}}, \\ G^2 = 3(G_x^2 + G_y^2 + G_z^2), \quad G_\gamma = G_{12\gamma} + G_{23\gamma} + G_{31\gamma}, \quad \gamma = x, y, z, \end{gathered} \tag{7}$$

where $\vartheta$ is an angle between field vector and $C_3$ axis. We see that a two-fold degeneracy of the magnetic sublevels (4) is removed and the spectrum is axial according to the point symmetry of the system under consideration. At $\mathscr{H} \| C_3$ four levels (7) have a linear field dependence and the spectrum has a zero-field splitting unlike the HDVV model. However in a general case (Fig. 2b) field dependence of the levels is essentially non-linear and thus it differs widely from dependence (4) (Fig. 2). We note that the level's scheme of type Fig. 2a may be obtained in the HDVV model as well by assuming a distortion of triangle so that $J_{12} \neq J_{23} = J_{13} \equiv J_0$. Introducing the additional term

$$\hat{H}' = (J_0 - J_{12}) \hat{s}_1 \hat{s}_2 \equiv J' \hat{s}_1 \hat{s}_2 \tag{8}$$

into the Hamiltonian and assuming that $J' \geqq G$ we actually arrive at the level shown in Fig. 2a. However, in this case the spectrum becomes isotropic and the levels' non-linearity (Fig. 2b) is absent in the HDVV model. Moreover it is quite obvious that because of equivalence of the $g$-factors of the two splitted levels in the HDVV model the level splitting under perturbation $\hat{H}'$ does not affect the temperature dependence of magnetic susceptibility. Thus perturbation $\hat{H}'$ restricting the theory within the HDVV model also leads to Eq. (5) and gives no explanation of the experimental results obtained. On the other hand it is clear for physical reasons that the AS exchange reduces the spin magnetic moment of the system due to the non-linearity of levels in the field range $g\mu_B \mathscr{H} \sim G$. Thus the AS exchange may qualitatively explain the disagreement between theory and experiment in Fig. 1.

The magnetic susceptibility tensor

$$\chi_{\alpha\beta} = \frac{kT}{\mathscr{H}_\alpha Z} \cdot \frac{\partial Z}{\partial \mathscr{H}_\beta} \tag{9}$$

($Z$ = partition function) obtained from Eq. (7) contains two independent components $\chi_{\|}$ and $\chi_{\perp}$. Since the polycrystalline samples were measured, the theoretical $\chi(T, \mathscr{H})$ was averaged over the magnetic field orientation using a BESM-4M computer. The best agreement between theory and experiment is attained at $G = 12\ \mathrm{cm}^{-1}$ and $g = 2.1$. It can be seen from Fig. 1 that with an account of AS exchange the theoretical curves coincide practically completely with experimental data in all regions of fields and temperatures investigated.

## 4. The Effect of Static Distortions on the Magnetic Susceptibility

The theory discussed above has been developed for the trinuclear copper(II) clusters for which an exact trigonal symmetry has been established by X-ray analysis. Now extending the approach to a wider class of objects we generalize the theory towards taking into account static distortions (including those from an external field). It was outlined already that in the limiting case of great distortions one observes no AS exchange effect and it is most interesting to consider the case when $|J'|$ and $G$ are of the same order of magnitude. In this case, account should be taken of the static distortions and the AS exchange simultaneously. The states with the given intermediate spin $S' = 0.1$ diagonalize $\hat{H}'$ while operator $\hat{H}_{\mathrm{AS}}$ is non-diagonal. To derive the Zeeman splitting of a distorted system it is convenient to use the basis set which diagonalizes the AS exchange:

$$\Psi_1^{\pm} = c_1^{\pm}\varphi_{\frac{1}{2}}(\tfrac{1}{2}, 1) + c_2^{\pm}\varphi_{\frac{1}{2}}(\tfrac{1}{2}, 0), \quad \Psi_2^{\pm} = c_3^{\pm}\varphi_{-\frac{1}{2}}(\tfrac{1}{2}, 1) + c_4^{\pm}\varphi_{-\frac{1}{2}}(\tfrac{1}{2}, 0),$$
$$c_1^{\pm} = \mp(c_2^{\mp})^* = (c_3^{\pm}) = \pm c_4^{\mp} = \left[-\frac{i}{2}\left(1 \pm \frac{\delta}{\Delta}\right)\right]^{\frac{1}{2}}, \tag{10}$$

where $\delta \equiv |J'|$, $\Delta = \sqrt{\delta^2 + G^2}$, $\varphi_M(S, S')$ are the functions with the given intermediate spin, signs $\pm$ mark the Kramers doublets, and $\Psi_1^{\pm}$ and $\Psi_2^{\pm}$ are basis functions of these doublets. Using this basis set one can obtain the matrix of operator $\hat{H}_{ex} + \hat{H}' + \hat{H}_{\mathrm{AS}} + \hat{H}_Z$ in the following form:

$$\begin{array}{c|cccc|}
 & \Psi_1^+ & \Psi_2^+ & \Psi_1^- & \Psi_2^- \\
\Psi_1^+ & -\varepsilon + \dfrac{\Delta + g\mu_B\mathscr{H}_z}{2} & \dfrac{ig\mu_B\mathscr{H}_-\delta}{\sqrt{2}\Delta} & 0 & \dfrac{ig\mu_B\mathscr{H}_-G}{\sqrt{2}\Delta} \\
\Psi_2^+ & \dfrac{ig\mu_B\mathscr{H}_+\delta}{\sqrt{2}\Delta} & -\varepsilon + \dfrac{\Delta - g\mu_B\mathscr{H}_z}{2} & \dfrac{ig\mu_B\mathscr{H}_+G}{\sqrt{2}\Delta} & 0 \\
\Psi_1^- & 0 & \dfrac{ig\mu_B\mathscr{H}_-G}{\sqrt{2}\Delta} & -\varepsilon - \dfrac{\Delta - g\mu_B\mathscr{H}_z}{2} & -\dfrac{ig\mu_B\mathscr{H}_-\delta}{\sqrt{2}\Delta} \\
\Psi_2^- & \dfrac{ig\mu_B\mathscr{H}_+G}{\sqrt{2}\Delta} & 0 & -\dfrac{ig\mu_B\mathscr{H}_+\delta}{\sqrt{2}\Delta} & -\varepsilon - \dfrac{\Delta + g\mu_B\mathscr{H}_z}{2}
\end{array} = 0, \tag{11}$$

$$\mathscr{H}_{\pm} = \mp\frac{1}{\sqrt{2}}(\mathscr{H}_x \pm i\mathscr{H}_y)$$

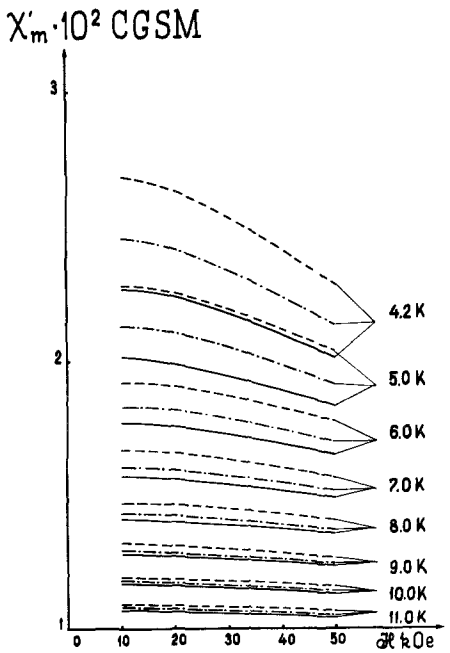


Fig. 3. The effect of static rhombic distortions of trigonal cluster on its magentic susceptibility: —— $\delta = 0$; —·—·— $\delta = 8\ \mathrm{cm}^{-1}$; - - - - $\delta = 16\ \mathrm{cm}^{-1}$; $G = 8\ \mathrm{cm}^{-1}$, $g = 2$

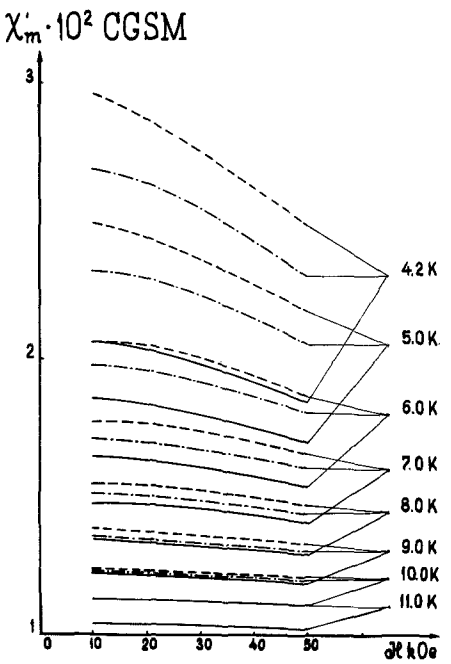


Fig. 4. The effect of AS exchange on magnetic susceptibility of a rhombical distorted trigonal cluster: - - - - $G = 0$; - - - - - $G = 4\ \mathrm{cm}^{-1}$; —— $G = 10\ \mathrm{cm}^{-1}$; $\delta = 2\ \mathrm{cm}^{-1}$, $g = 2$

and one arrives at the following expression for energy levels:

$$\varepsilon_{I(II)}^{\pm} = \pm \tfrac{1}{2}[\delta^2 + G^2 + g^2\mu_B^2\mathscr{H}^2 {}_{(\pm)} 2g\mu_B\mathscr{H}\sqrt{\delta^2 + G^2\cos^2\vartheta}]^{\frac{1}{2}}. \qquad (12)$$

Figure 3 shows the plot $\chi(T, \mathscr{H})$ vs. $\delta$. In the limiting case of great distortions ($\delta \gg G$) the AS exchange is reduced; thus the HDVV model could be used. While $\delta$ increases, the magnetic moment is defrozen and for $\delta \gg G$ the curves $\chi(T, \mathscr{H})$ coincide with the respective HDVV curves [Eq. (5)]. On the other hand, with the inclusion of AS exchange (Fig. 4) the magnetic moment is reduced and, in terms of the magnetic properties, the system being spatially distorted becomes trigonal.

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