

## ANOMALOUS MAGNETIC BEHAVIOUR OF COPPER ACETATE MONOHYDRATE

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Recent attempts (Mookherji *et al* 1963, Guha 1965, 1966, Mathur 1965) to explain the observed anisotropy in paramagnetic susceptibility of copper acetate monohydrate by postulating temperature dependent values of  $g$ -tensor and/or the exchange interaction co-efficient have been based on the assumption of  $C_{4v}$  symmetry. It is known from electron spin resonance spectroscopy (Bleaney *et al* 1952, Abe *et al.* 1957) the symmetry is lower and we assume  $C_{2v}$  symmetry (Kokoszka *et al* 1965) to explain the phenomenon more successfully.

The ground state for each half unit of the system can then be written as

$$|a\rangle = \mu\phi_{xz} + \nu\phi_{-y^2xz} \quad \dots (1)$$

where  $\phi_{xz}$  and  $\phi_{-y^2xz}$  are the respective  $d$ -orbitals modified by suitable combination of ligands  $s$  and  $p$  orbitals. The mixing co-efficient  $\mu$  and  $\nu$  will be functions of ligand field parameters. The other higher lying states will be

$$|c\rangle = \phi_{xy}, \quad |d\rangle = \phi_{xz}, \quad |e\rangle = \phi_{yz} \quad \dots (2)$$

and

$$|b\rangle = \nu\phi_{xz} - \mu\phi_{-y^2xz}$$

The different valence bond configurations will be  $a_1a_2, a_1b_2, a_1b_2, a_2b_1$  etc where the subscripts 1' and 2' refer to the two centres. By operating on the ground

configuration  $a_1a_2$  with  $-Z_{off} \left( \frac{1}{r_{1B}} + \frac{1}{r_{2A}} \right) \cdot \frac{Z_{off}}{R} + \frac{1}{r_{12}}$  it can be shown that  $J$

will be a function of one and two electron integrals involving  $\phi_{xz}, \phi_{-y^2xz}$  and the mixing coefficients  $\mu$  and  $\nu$ . Expressing the sum of spin-orbit and magnetic perturbation in the form of spin-Hamiltonian it can be shown that the spectroscopic splitting factors and the principal ionic susceptibilities are given by

$$g_x = 2 \left\{ 1 - \frac{2(\mu\sqrt{3} + \nu)^2 R_x k_x' \zeta_d}{E_{ad} - E_{aa}} \right\}$$

$$g_y = 2 \left\{ 1 - \frac{2(\mu\sqrt{3} - \nu)^2 R_y k_y' \zeta_d}{E_{ac} - E_{aa}} \right\}$$

$$g_z = 2 \left\{ 1 - \frac{8\nu^2 R_z k_z' \zeta_d}{E_{ac} - E_{aa}} \right\}$$

$$K_x = N \frac{1/D g_x^2 \beta^2 e^{-J'/kT} (1 - e^{-D/kT}) - 3\alpha_x e^{-J'/kT} (2e^{-D/kT} + 1) - 1\alpha_x}{1 + e^{-J'/kT} + 2e^{-J'+D/kT}}$$

$$K_y = N \frac{1/D g_y^2 \beta^2 e^{-J'/kT} (1 - e^{-D/kT}) - 3\alpha_y e^{-J'/kT} (2e^{-D/kT} + 1) - 1\alpha_y}{1 + e^{-J'/kT} + 2e^{-J'+D/kT}}$$

$$K_z = N \frac{\frac{g_z^2 \beta^2}{kT^2} e^{-J'+D/kT} - 3\alpha_z e^{-J'/kT} (1 + 2e^{-D/kT}) - 1\alpha_z}{1 + e^{-J'/kT} + 2e^{-J'+D/kT}}$$

and

$$J' = J + D_x + D_y \quad \dots (3)$$

where  $R_i$ 's and  $k_i$ 's ( $i = x, y, z$ ) are the spin-orbit and the orbital reduction factors respectively,  $\alpha$ 's denote the high frequency terms (the superscripts '1' and '3' indicate whether they originate from the singlet or the triplet levels);  $\zeta_d$  is the  $S=0$  coupling coefficient for the dimer;  $D_i$ 's are the spin Hamiltonian parameters

$$\text{and } D = D_z - \frac{D_x + D_y}{2}.$$

By adjusting the ligand field parameters, the mean susceptibility and the anisotropy data (remeasured by us) in the temperature range 90°K–300°K as also the  $g$ -values and the optical absorption bands at 11000  $\text{cm}^{-1}$  (Garddon, 1961) 14500  $\text{cm}^{-1}$  and 28000  $\text{cm}^{-1}$  (Tonnet *et al* 1964) can all be fitted within an outside limit of 2%. In doing so  $\mu$  and  $\nu$  come out to be 0.124 and 0.984 respectively. Using these values of  $\mu$  and  $\nu$  and the table of integrals calculated by Ross and Yates (1959) one obtains  $J = -138 \text{ cm}^{-1}$ .

It is concluded that :

(1) Mookherji and Mathurs' (1953) magnetic anisotropy data, which is very close to ours, can be made to correspond to the observed e.s.r. data if the effect of orbital reduction is considered in the high frequency term.

(2)  $J$ , calculated theoretically is of the right order of magnitude and sign, considering the rather severe approximations namely, that the integrals involving only the  $d$ -orbitals have been considered through the ligand orbitals may contribute appreciably to  $J$ , that the integrals involving products of  $d_{x^2-y^2}$  and  $d_{z^2}$  have not been considered and that the effect of superexchange interaction, transmitted through the  $\pi$  orbitals of the carbon atoms have not been taken in to account.

(3) The larger value of  $J$  in copper thioacetate is due to the additional orthorhombicity introduced due to the replacement of two of the four oxygen ligands in each half unit by sulphur atoms.

(4) The bonding is neither a pure  $\sigma$ -type or  $\delta$ -type but a mixture of the two.

(5) The band at  $28000\text{ cm}^{-1}$  is of Laporte forbidden type arising from  ${}^3ab_u \rightarrow {}^3aa_u$  and  ${}^3ab_g \rightarrow {}^3aa_g$  transitions (both the levels Span  $A_1$  representation). The large separation may be attributed to a strongly anisotropic ligand field.

The details will be communicated within a very short period.

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