

ORTHORHOMBIC LIGAND FIELD THEORY OF THE MAGNETIC BEHAVIOURS OF $\text{Cu}(\text{NH}_4\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$

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ABSTRACT. The e.p.r. measurements on $\text{Cu}(\text{NH}_4\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ clearly indicate an orthorhombic distortion of the ligand field acting on the hexa-coordinated Cu^{2+} ion. Assuming an orthorhombic ligand field of both second and fourth order, the expression for the principal orthorhombic g -values and magnetic susceptibilities have been derived with due consideration of the presence of covalency overlap of the d -orbitals of the central metal atom with the electronic charge clouds of the ligand atoms. For reasons of completeness, the calculation has been extended upto the 3rd order correction terms in the perturbation procedure adopting Pryce's spin-Hamiltonian formalism, although these third order terms have been neglected while fitting the theory with the experiments. Attempts have been made to fit the theory with the experiments of optical absorption, principal g -tensors and magnetic anisotropies and mean susceptibility as best as possible by evaluating the values of certain parameters appearing in the theoretical expressions. Important inferences have been drawn regarding the remarkable variation of the anisotropic component of the ligand field with temperature and the anisotropic reduction of the orbital moment and S.O. coupling coefficient from their respective free ion values due to the covalency effect.

INTRODUCTION

Recent e.p.r. measurements at room temperature in four copper Tutton salts (Bose *et al* 1964; Ghosh *et al*, 1965) have shown that the symmetry of the ligand field acting on the central Cu^{2+} ion in these crystals is perceptibly orthorhombic. This is in general consistent with the findings of Bleaney *et al* (1949) and Bagguley and Griffiths (1952) though for the want of a convenient and accurate method of determining orthorhombic g -values and their orientations at that time, their e.p.r. data had to be often given in terms of g_{\parallel} and g_{\perp} , apparently indicating only an approximately uniaxial symmetry of the ligand field. The experiment of Bagguley and Griffiths on some dilute Cu^{2+} Tutton salts showed large changes in relative magnitudes of g_i 's between 300°K and 90°K.

Using a recent convenient method (Bose *et al*, 1964) for determining accurately the magnitudes and orientations of orthorhombic g_i 's in crystals, we have carried out e.p.r. measurements on $\text{Cu}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ at both liquid oxygen ($\sim 90^\circ\text{K}$) and room temperature ($\sim 300^\circ\text{K}$). In this salt and a few others unlike $\text{Cu}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, magnetic measurements (Bose *et al*, 1957) show very small changes with

temperature in the orientation of crystalline χ_1 and χ_2 axes in the (010) plane, but with a tetragonal approximation the ionic anisotropy deviates from Curie law and the ionic orientations appear to change to some extent as the temperature varies. It would be interesting then with the powerful e.p.r. method at our disposal to probe into the actual nature of these ionic deviations and changes which have so little outward manifestations in the crystalline behaviours.

Polder's theory (1942) of the susceptibility of Cu^{2+} ion assumed a purely electrostatic dipolar model of the octahedron which was considered to possess only a tetragonal distortion and could not properly assign the energy levels of the ligand field (Bose *et al*, 1957) primarily, owing to the inapplicability of the above model and the approximate nature of calculation from the available data on crystal structure, dipole moment and the radius of 3d orbit. Bleaney, Bowers and Pryce (1955) extended Abragam and Pryce's theory (1951) to the octahedrally co-ordinated Cu^{2+} ion under the second order orthorhombic field to interpret the results of e.p.r. measurements.

In the present work we have derived the theoretical expressions for the principal g -values and the susceptibilities for the octahedrally co-ordinated Cu^{2+} ion by assuming an orthorhombic field of both second and fourth order with due consideration of the presence of overlap between the central ion 3d-orbitals with the s - and p -orbitals of the neighbouring ligand atoms, resulting in the formation of molecular orbitals of the magnetic electrons in such complexes (Van Vleck, 1935, Stevens, 1953; Owen 1955). These theoretical expressions involve certain parameters, connected with the ligand co-efficients and the overlap effect and attempts are then made to fit the theory uniquely with the experimental data by evaluating the reasonable values of these parameters, consistent with the other independent observation from optical absorption. This procedure of interpreting the experimental data leads to important inferences regarding the remarkable variation of the anisotropic part of the ligand field with temperature, and the anisotropic reduction of the S.O coefficient and the orbital moment from their respective free ion values due to the effect of convalency overlap.

FINE STRUCTURE ENERGY LEVELS OF THE LIGAND FIELD

In a cubic field of O_h symmetry, the free ion ground state 2D of Cu^{2+} ion splits into an upper orbital triplet T_{2g} and a lower orbital doublet E_g . The superposed orthorhombic component of the ligand field lifts all the orbital degeneracies of both T_2 and E_g , but S.O interaction has no effect on the lower cubic doublet E_g in the first order. Hence in our perturbation procedure, we first apply the total ligand field inclusive of the anisotropic part on the free ion ground state and then adopt Pryce's (1950) Spin Hamiltonian formalism for the calculation of g -values and magnetic susceptibilities.

Electronic configuration of Cu^{2+} ion being $3d^9$, the system can be conveniently described in terms of a single hole in the completed $3d$ sub-shell. This hole is subjected to an orthorhombic potential given by

$$V = D'(x^4 + y^4 + z^4 - \frac{2}{3} r^4) + Ax^2 + By^2 - (A+B)z^2 + ax^4 + by^4 \\ - (a+b)z^4 + 6ay^2z^2 + 6bx^2z^2 - 6(a+b)x^2y^2 \quad \dots \quad (1)$$

In case of tetragonal symmetry about z axis,

$$A = B \text{ and } a = b,$$

and the expression for V reduces to that given by Abragam and Pryce (1951) for tetragonal potential.

Putting,

$$\frac{A+B}{2} = -\sigma', \quad \frac{A-B}{2} = \delta'$$

$$\frac{a+b}{2} = -\gamma', \quad a-b = \epsilon'$$

We get a convenient expression for V as follows :

$$V = D'(x^4 + y^4 + z^4 - \frac{2}{3} r^4) + \sigma'(3z^2 - r^2) + \delta'(x^2 - y^2) \\ + \gamma'(2z^4 - x^4 - y^4 + 12x^2y^2 - 6y^2z^2 - 6x^2z^2) \\ + \epsilon'(x^4 - y^4 + 6y^2z^2 - 6x^2z^2) \quad (3)$$

In (1) and (3) first the term represents the cubic component of the potential and remaining terms arise from the orthorhombicity of the ligand field. The ligand field interaction for the d -hole is

$$H_v = +eV$$

To find the eigen values of H_v and the corresponding eigen functions, we need to evaluate the matrix elements of H_v between the orbitally five-fold degenerate free ion states of the d -hole which are denoted by $d_0, d_{\pm 1}, d_{\pm 2}$ the suffixes indicating the possible l_z values. Matrix elements of the first four terms (i.e. with $D', \gamma', \sigma', \delta'$) in (3) can be easily calculated using Stevens's equivalent operator technique (Stevens, 1952) and noting that

$$2z^4 - x^4 - y^4 + 12x^2y^2 - 6y^2z^2 - 6x^2z^2 \\ = 5(x^4 + y^4 + z^4 - \frac{2}{3}r^4) - 3(x^4 - 6x^2y^2 + y^4)$$

For the remaining term (i.e. with ϵ') in (3), we note that

$$\epsilon'(x^4 - 6x^2z^2 + 6y^2z^2 - y^4) = -\epsilon' \frac{8\sqrt{\pi}}{3\sqrt{10}} r^2 (Y^2_4 + Y^{-2}_4)$$

Matrix element for this term can be easily calculated with the help of Wigner co-efficient formula (Stevens, 1952). Thus operating H_v on $d_0, d_{\pm 1}$ and $d_{\pm 2}$, and solving the relevant secular equation we get the following eigen values

$$\left. \begin{aligned} E_1 &= 6D - [36(\sigma + 3\gamma)^2 + 3(2\delta - \epsilon)^2]^{\frac{1}{2}} \\ E_2 &= 6D + [36(\sigma + 3\gamma)^2 + 3(2\delta - \epsilon)^2]^{\frac{1}{2}} \\ E_3 &= -4D + 6\sigma - 24\gamma \\ E_4 &= -4D - 3\sigma + 12\gamma - (3\delta + 2\epsilon) \\ E_5 &= -4D - 3\sigma + 12\gamma + (3\delta + 2\epsilon) \end{aligned} \right\} \dots (4)$$

and the corresponding eigen functions are

$$\left. \begin{aligned} \psi_1 &= a_1 d_0 + b_1 \frac{1}{\sqrt{2}} (d_2 + d_{-2}) \\ \psi_2 &= b_1 d_0 - a_1 \frac{1}{\sqrt{2}} (d_2 + d_{-2}) \\ \psi_3 &= \frac{1}{\sqrt{2}} (d_2 - d_{-2}) \\ \psi_4 &= \frac{1}{\sqrt{2}} (d_1 - d_{-1}) \\ \psi_5 &= \frac{1}{\sqrt{2}} (d_1 + d_{-1}) \end{aligned} \right\} \dots (5)$$

where

$$\left. \begin{aligned} D &= \frac{3}{5} eD' \beta \bar{r}^4 \\ \sigma &= e\sigma' \alpha r^2 \\ \delta &= e\delta' \alpha r^2 \\ \gamma &= e\gamma' \beta \bar{r}^4 \\ \epsilon &= \frac{8}{3} \sqrt{\pi e \rho e' r^4} \end{aligned} \right\} \alpha = -\frac{2}{21}, \quad \beta = +\frac{2}{63}$$

corresponding to the configuration $3d^1$, since the system has been described in terms of hole.

in which α and β are the numerical factors appearing in Stevens' equivalent operators and ρ is the numerical factor appearing in Wigner coefficient formula for the matrices of the type

$$\langle L = 2, M | r^4 [Y_4^2 + Y_4^{-2}] | L = 2, M = \pm 2 \rangle$$

and

$$\frac{b_1}{a_1} = \frac{6(\sigma + 3\gamma) - [36(\sigma + 3\gamma)^2 + 3(2\delta - \epsilon)^2]^{\frac{1}{2}}}{\sqrt{3}(2\delta - \epsilon)}$$

$$a_1^2 + b_1^2 = 1$$

For octahedral co-ordination the cubic field parameter D is negative (D' being negative and β positive). Moreover under cubic field alone ($\sigma = \delta = \gamma = \epsilon = 0$), it is evident from (4) that the original five fold degenerate free ion states of the d -hole split up into lower orbital doublet E_g of energy $6D$ and an upper orbital triplet T_{2g} of energy $-4D$, the overall cubic field separation being $10D$. In the superposed orthorhombic field the cubic orbital doublet and triplet levels split up into two and three levels respectively, the orbital degeneracy being thus completely removed. Further it will be seen from (4) that in the orthorhombic field, mean centre of the three split components (ψ_3, ψ_4, ψ_5) of the cubic triplet T_{2g} lies at $-4D$ which is also the energy value of the cubic triplet T_{2g} and that of the two split components (ψ_1, ψ_2) of the cubic doublet E_g lies at $6D$, the energy value of the cubic doublet E_g . This has resulted from the particular choice of the form of expression for the orthorhombic potential V . Thus the separation of the mean centres mentioned above, is $10D$ which is also the cubic field splitting and this fact will be taken into consideration while evaluating the parameter D from optical absorption spectrum.

Assuming the orthorhombic distortion of the octahedron to be small, ψ_1 with energy E_1 is evidently the lowest level, ψ_2 lies next and the relative order of ψ_3, ψ_4, ψ_5 depends on the sign and magnitudes of the parameters $D, \sigma, \delta, \gamma$ and ϵ . The fitting of experimental data, shown later also justifies our assumption regarding the relative order of the ligand field levels

Calculation of g-values

The ligand field energy states (5) can be expressed in term of real d -orbitals which can replace the combination of d function in (5) as follows :

$$\frac{1}{\sqrt{2}} (d_2 + d_{-2}) \equiv d_{x^2-y^2}$$

$$d_0 = d_{3z^2-r^2}$$

$$\frac{1}{\sqrt{2}} (d_2 - d_{-2}) = d_{xy}$$

$$\frac{1}{\sqrt{2}} (d_1 + d_{-1}) = d_{yz}$$

$$\frac{1}{\sqrt{2}} (d_1 - d_{-1}) = d_{xz}$$

The suffixes (x^2-y^2) etc. on the R.H.S. represent the angular parts of the real d -orbitals. Now, the orbitals in the complex are not pure atomic d -orbitals, they are considerably modified by appropriate combination of ligand σ and π orbitals. These modifications are now taken into consideration while calculating the g -values and magnetic susceptibility.

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Denoting a molecular orbital by a ϕ -function with the suffix same as that for the original real d -orbital, the fine structure energy states (5) is now written as

$$\begin{aligned}\Psi_1 &= a_1\phi_{3z^2-r^2} + b_1\phi_{x^2-y^2} \\ \Psi_2 &= b_1\phi_{3z^2-r^2} - a_1\phi_{x^2-y^2} \\ \Psi_3 &= \phi_{xy} \\ \Psi_4 &= \phi_{yz} \\ \Psi_5 &= \phi_{zx}\end{aligned}\quad \dots (6)$$

The S.O. interaction has no effect in the first order on the lowest orbital singlet Ψ_1 and hence for the calculation of g -value and magnetic susceptibility we adopt Pryce's Spin Hamiltonian formalism (Pryce, 1950). The Spin Hamiltonian is given by

$$\begin{aligned}H_s &= \langle \Psi_1 | H' | \Psi_1 \rangle - \sum_{n \neq 1} \frac{\langle \Psi_1 | H' | \Psi_n \rangle \langle \Psi_n | H' | \Psi_1 \rangle}{E_n - E_1} \\ &+ \sum_{n \neq 1} \sum_{m \neq 1} \frac{\langle \Psi_1 | H' | \Psi_m \rangle \langle \Psi_m | H' | \Psi_n \rangle \langle \Psi_n | H' | \Psi_1 \rangle}{(E_n - E_1)(E_m - E_1)} \\ &- \sum_{n \neq 1} \frac{\langle \Psi_1 | H' | \Psi_n \rangle \langle \Psi_n | H' | \Psi_1 \rangle \langle \Psi_1 | H' | \Psi_1 \rangle}{(E_n - E_1)^2}\end{aligned}\quad \dots (7)$$

where H' stands for the perturbation $\zeta \vec{L} \cdot \vec{S} + \beta \vec{H}(\vec{L} + 2\vec{S})$ in which ζ is the S.O. coupling coefficient for the free ion, and the various matrix elements of the type $\langle \Psi_j | H' | \Psi_k \rangle$ occurring in (7) imply that states Ψ 's are acted on only by the orbital operators appearing in the expression for the perturbation H' . While evaluation various matrices of the type $\langle \Psi_j | \vec{L} | \Psi_k \rangle$, the relationship between two types of matrices of the operators \vec{L} and $\zeta \vec{L}$, one calculated between the atomic d -orbitals and the other between the corresponding molecular orbitals, are given as follows (Low, 1960) :

$$\begin{aligned}\langle \phi(\rho) | L_i | \phi(\rho) \rangle &= \langle d(\rho) | L_i | d(\rho) \rangle = 0 \\ \langle \phi(\tau) | L_i | \phi(\tau) \rangle &= k_i \langle d(\tau) | L_i | d(\tau) \rangle \\ \langle \phi(\rho) | L_i | \phi(\tau) \rangle &= k_i' \langle d(\rho) | L_i | d(\tau) \rangle \\ \langle \phi(\rho) | \zeta L_i | \phi(\rho) \rangle &= 0 \\ \langle \phi(\tau) | \zeta L_i | \phi(\tau) \rangle &= R_i \langle d(\tau) | \zeta L_i | d(\tau) \rangle \\ \langle \phi(\rho) | \zeta L_i | \phi(\tau) \rangle &= R_i' \langle d(\rho) | \zeta L_i | d(\tau) \rangle\end{aligned}$$

where $i = x, y, z$; $\phi(\tau)$ and $\phi(\rho)$ represent the molecular orbitals ($\phi_{xy}, \phi_{yz}, \phi_{zx}$) and ($\phi_{3z^2-r^2}, \phi_{x^2-y^2}$) resulting from the modification of the corresponding atomic

orbitals $d(\tau)(d_{xy}, d_{yz}, d_{zx})$ and $d(\rho)(d_{3z^2-r^2}, d_{x^2-y^2})$ respectively. The k_i 's and R_i 's, are known as the orbital reduction and S.O. coupling reduction factors respectively arising from the covalency effect, and these are considered to partake of the symmetry of the ligand field. Evaluating the matrices in (7) we finally get the expression for the Spin Hamiltonian expressed as a polynomial in spin variables only and this will operate on the spin states $|S_z = \frac{1}{2}\rangle$ and $|S_z = -\frac{1}{2}\rangle$. Thus the Spin Hamiltonian for $H||z$ becomes

$$H_s(z) = 2\beta H[S_z(1-u_3R'_z k'_z + \lambda_1 R'_y R'_z k'_z - \lambda_2 R'_x R'_y k'_z + \lambda_3 R'_y R'_x k'_z) + 2i(\lambda_4 R'_x{}^2 S_x S_y - \lambda_5 R'_y{}^2 S_y S_x)] - \nu_x \beta^2 H^2 \quad \dots (8)$$

For $H||x$

$$H_s(x) = 2\beta H[S_x(1-u_1 R'_x k'_x - \lambda_1 R'_y R'_z k'_x - \lambda_2 R'_y R'_z k'_x - \lambda_3 R'_y R'_z k'_x) + 2i(\lambda_5 R'_y{}^2 S_y S_z - \lambda_6 R'_z{}^2 S_x S_z)] - \nu_x \beta^2 H^2 \quad \dots (9)$$

and for $H||y$

$$H_s(y) = 2\beta H[S_y(1-u_2 R'_y k'_y + \lambda_1 R'_x R'_z k'_y + \lambda_2 R'_x R'_z k'_y - \lambda_3 R'_z R'_x k'_y) + 2i(\lambda_6 R'_z{}^2 S_z S_x - \lambda_4 R'_x{}^2 S_x S_z)] - \nu_y \beta^2 H^2 \quad \dots (10)$$

$$\text{where } u_1 = \frac{(a_1\sqrt{3}+b_1)^2\zeta}{E_3-E_1}, \quad u_2 = \frac{(a_1\sqrt{3}-b_1)^2\zeta}{E_5-E_1}, \quad u_3 = \frac{(a_1\sqrt{3}-b_1)^2\zeta}{E_4-E_1},$$

$$\lambda_1 = \frac{b_1(a_1\sqrt{3}-b_1)\zeta^2}{(E_3-E_1)(E_4-E_1)}, \quad \lambda_2 = \frac{b_1(a_1\sqrt{3}+b_1)\zeta^2}{(E_3-E_1)(E_5-E_1)}, \quad \lambda_3 = \frac{(3a_1^2-b_1^2)\zeta^2}{2(E_5-E_1)(E_4-E_1)}$$

$$\lambda_4 = \frac{(a_1\sqrt{3}+b_1)^2\zeta^2}{2(E_5-E_1)^2}, \quad \lambda_5 = \frac{(a_1\sqrt{3}-b_1)^2\zeta^2}{2(E_4-E_1)^2}, \quad \lambda_6 = \frac{b_1^2\zeta^2}{(E_3-E_1)^2}$$

$$\nu_x = \frac{(a_1\sqrt{3}+b_1)^2 k_x'^2}{E_5-E_1}, \quad \nu_y = \frac{(a_1\sqrt{3}-b_1)^2 k_y'^2}{E_4-E_1}, \quad \nu_z = \frac{4b_1^2 k_z'^2}{E_3-E_1}$$

In equations (8), (9) and (10), terms independent of H have been omitted since they do not produce any zero field splitting of the Kramers degenerate spin states of $S_z = \pm 1/2$. The last term in each of the above equations also does not produce any splitting of the degenerate components and is not important in the calculation of g -values, but this being dependent on H^2 assumes much importance in the calculation of susceptibility constituting the temperature independent paramagnetism and hence is retained.

Operating on the spin states $|\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ with the Hamiltonian $H_s(x)$ we get a secular matrix which on diagonalization gives the following energy values for $H||x$.

$$W_{\pm}(x) = -\nu_x \beta^2 H^2 \pm [1 - u_1 R'_x k'_x - \lambda_1 R'_y R'_z k'_x - \lambda_2 R'_y R'_z k'_x - \lambda_3 R'_y R'_z k'_x - \lambda_5 R'_y{}^2 - \lambda_6 R'_z{}^2] \beta H$$

Thus g_x is given by

$$g_x = \frac{W_+(x) - W_-(x)}{\beta H} = 2[1 - u_2 R'_x k'_x - \lambda_1 R'_y R'_z k'_x - \lambda_2 R'_y R'_z k'_z - \lambda_3 R'_y R'_z k'_x - \lambda_5 R'_y{}^2 - \lambda_6 R'_z{}^2] \quad \dots (11)$$

The expression for energy values $W_{\pm}(x)$ are now suitably written as

$$W_{\pm}(x) = -v_x \beta^2 H^2 \pm \frac{1}{2} g_x \beta H \quad \dots (12)$$

Similar calculation for $H||y$ gives

$$W_{\pm}(y) = -v_y \beta^2 H^2 \pm \frac{1}{2} g_y \beta H \quad \dots (13)$$

$$g_y = 2[1 - u_2 R'_y k'_y + \lambda_1 R'_x R'_z k'_y + \lambda_2 R'_x R'_z k'_y - \lambda_3 R'_x R'_z k'_y - \lambda_4 R'_x{}^2 - \lambda_6 R'_z{}^2] \quad (14)$$

and for $H||z$

$$W_{\pm}(z) = -v_z \beta^2 H^2 \pm \frac{1}{2} g_z \beta H \quad \dots (15)$$

$$g_z = 2[1 - u_3 R'_z k'_z + \lambda_1 R'_y R'_x k'_z - \lambda_2 R'_y R'_x k'_z + \lambda_3 R'_y R'_x k'_z - \lambda_4 R'_x{}^2 - \lambda_5 R'_y{}^2] \quad \dots (16)$$

Calculation of susceptibility

The general expression for g_m -ionic susceptibility is given by

$$K_i = \left[-\frac{N}{H} \frac{\sum \frac{\partial W(i)}{\partial H} \exp\left(-\frac{W(i)}{kT}\right)}{\sum \exp\left(-\frac{W(i)}{kT}\right)} \right] \quad \dots (17)$$

Lt
 $H \rightarrow 0$
 $(i = x, y, \text{ or } z)$

The limit can be easily evaluated using L' Hospital's rule in our case since the expression reduces to the indeterminate form $\frac{0}{0}$ if we put $H = 0$. Thus the expression for susceptibility along the three directions x, y and z reduces to

$$K_i = \frac{N\beta^2}{KT} \cdot \frac{g_i^2}{4} + 2N\beta^3 v_i \quad (i = x, y \text{ or } z) \quad \dots (18)$$

The mean susceptibility is then given by

$$\bar{\chi} = \bar{K} = 1/3(K_x + K_y + K_z) \quad \dots (19)$$

RESULTS AND DISCUSSIONS

$\text{Cu}(\text{NH}_4\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ belongs to the monoclinic system (space group $P2_1/a$) and contains two magnetically inequivalent ions in the unit cell as known from c.p.r. experiments and also from the recent X-ray structure analysis of the isomorphous nickel, Tutton salts (Morosin and Lingafelter, 1964). Orientation of one

ion (the paramagnetic complex) can be derived from the other by reflection in the (010) plane. The mean magnetic susceptibility $\bar{\chi}$ and principal crystalline anisotropies ($\chi_1 - \chi_2$) and ($\chi_1 - \chi_3$) have been accurately determined between 300°K and 90°K in our laboratory (Bose *et al*, 1957 Ghosh- to be published). Further, the principal g -tensors and their orientations have been determined here by the accurate e.p.r. technique (described elsewhere, Bose *et al*, 1964) both at room temperature and 90°K (Table I). The calculated values of crystalline anisotropies and mean susceptibility in Table II have been obtained by using equations (18), (19) and the following relation :

$$\chi_j = \sum_{i=x,y,z} K_i \mu_{ij}^2 \quad (j = 1, 2, 3)$$

where μ_{ij} is the direction cosine of K_i with χ_j . The values of μ_{ij} at room temperature and 90°K are furnished by our e.p.r. measurements at the two temperatures, presuming of course that the direction of K_i 's are coincident with those of g_i 's. The overall changes of μ_{ij} 's are found to be not very large. Therefore, at intermediate temperatures they have been assumed to have intermediate values between those at 90°K and 300°K, obtained by linear interpolation, consistent with the orthogonality relations between them.

TABLE I

The principal g -tensors and their orientations in $\text{Cu}(\text{NH}_4\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystals from e.p.r. measurements (a, b , are the principal crystallographic axes).

a. Temperature 300°K

Principal g -tensors	angles with respect to			
	χ_1	χ_2	$\chi_3 \equiv b$	a
$g_x = G_2 = 2.12_3$	64° . 9	40° . 6	119° . 3	36° . 6
$g_y = G_1 = 2.05_2$	63° . 1	130° . 1	128° . 0	92° . 2
$g_z = G_3 = 2.39_6$	38° . 3	85° . 9	51° . 9	53° . 5

b. Temperature 90°K

Principal g -tensors	angles with respect to			
	χ_1	χ_2	$\chi_3 \equiv b$	a
$g_x = G_2 = 2.12_0$	60°	62° . 4	137°	47° 2
$g_y = G_1 = 2.06_8$	71° 4	157° 1	110° 3	107° 6
$g_z = G_3 = 2.40_0$	36° 3	85° 4	53°	48°

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The x , y and z axes of the ion have been chosen in such a way that it gives the closest fit of the theory with the experimental results (Table II). The z and y axes are thus found to correspond to the directions of the highest and lowest g -tensors respectively. This is quite consistent with the previously observed fact that under tetragonal approximation $g_{||}(=g_z)$ is greater than $g_{\perp}(\approx \sqrt{\frac{1}{2}(g_x^2 + g_y^2)})$ (Bleaney *et al.*, 1949; Bose *et al.* 1957).

It has been found on actual calculation that the third order terms in g -values are very small contributing less than 0.5 per cent of the total and hence those are neglected. Then the number of parameters appearing in the theoretical expressions for g -values, magnetic susceptibilities and ligand field energy levels reduces to eleven viz, D , σ , δ , γ , ϵ , k'_x , k'_y , k'_z , R'_x , R'_y and R'_z . The relative values of k_1 's and those of R_1 's ($i = x, y, z$) are, of course, dependent on the lower symmetric field parameters σ , δ , γ and ϵ although they may not be explicitly expressible in terms of the latter. The cubic field parameter D is readily furnished by the optical absorption experiment on aqueous solution of some cupric salts (Dreisch and Trommer, 1937; Mookerjee *et al.*, 1959) in which the Cu^{2+} ion is also co-ordinated by six water molecules as in copper Tutton salts. The experiments show a broad peak at $12,300 \text{ cm}^{-1}$ which does not vary much from salt to salt and with temperature and may be considered to correspond approximately to a transition from the mean centre of the split components of E_g to that of the split component of T_{2g} in the orthorhombic field, the separation between the mean centres being $10D$. The few other peaks occurring at much higher frequencies such as 17000 cm^{-1} , $35,000 \text{ cm}^{-1}$ etc. are supposed to arise from charge transfer processes and not from transitions between ligand field levels. Having thus found the parameter D , the remaining ten parameters are then adjusted by trial so as to fit the experiments of susceptibility, anisotropy and g -values as best as possible, taking the values at 90°K to be the standard and making the deviations between calculated and observed values at other temperatures as small as possible. The flexibility of the choice of covalency parameters k_i 's and R_i 's is limited by the condition that they lie between 0.5 and 1. Extensive trial and error computations have shown that it is possible to fit the theory exactly with the experiments only at one temperature and not at all temperatures. The reason for the particular choice of the temperature 90°K at which the theory has been made to fit the experiments almost exactly is that at this temperature the experimental results are very accurate; the signal to noise ratio and the sharpness of resonance signal as well as the percentage accuracy of the anisotropy and susceptibility measurements are very high. In this procedure of evaluation of the parameters, we assume them to be constant with temperature. However, some of them, especially the anisotropic field parameters σ , δ , γ and ϵ may change by a large amount as the temperature varies but for the moment we consider them to remain the same, as otherwise the solution of the parameters from the given experimental data become non-unique.

TABLE II

Values of the parameters showing the closest fit between the calculated and observed results for $\text{Cu}(\text{NH}_4\text{ScO}_4)_2 \cdot 6\text{H}_2\text{O}$

$$D = -1230 \text{ cm}^{-1}, \quad \sigma = -98 \text{ cm}^{-1}, \quad \gamma = -5 \text{ cm}^{-1}, \quad \delta = 14 \text{ cm}^{-1}, \quad \epsilon = 54 \text{ cm}^{-1}$$

$$k'_x = 0.86, \quad k'_y = 0.85, \quad k'_z = 0.84, \quad R'_x = 0.91, \quad R'_y = 0.80, \quad R'_z = 0.84$$

$$\zeta = -829 \text{ cm}^{-1} \text{ (free ion value)}$$

a. Spectroscopic splitting factors

	Theoretical (Best fitting at 90°K)	Experimental	
		at 300°K	at 90°K
g_x	2.113	2.12 ₃	2.12 ₀
g_y	2.073	2.05 ₂	2.06 ₈
g_z	2.400	2.39 ₆	2.40 ₀

b. Susceptibilities

Temperature	$(\chi_1 - \chi_2) \times 10^6$		$(\chi_1 - \chi_3) \times 10^6$		$\bar{\chi} \times 10^6$	
	Theo	Experi*	Theo	Experi*	Theo	Experi*
90°K	1053	1054	443	445.5	5103	5101
140°K	685	692.1	270	276.5	3285	3281
200°K	475	486.6	197	182.1	2330	2326
240°K	397	405.3	154	146	1949	1943
300°K	317	322	128	112	1574	1566

*Experimental results for crystalline anisotropies are taken from the measurements of Bose *et al* (1957)

† Experimental values of mean susceptibilities are taken from the magnetic measurements (unpublished) of P.K. Ghosh.

The parameters best suited to fit the theory with the experimental results are shown in table II. The results indicate an appreciable anisotropic covalency overlap of the ligand charges with the charge cloud of the central metal atom as indicated by the values $k'_x = 0.86$, $k'_y = 0.85$, $k'_z = 0.84$ for the orbital reduction as also $R'_x = 0.91$, $R'_y = 0.80$, $R'_z = 0.84$ for the S.O. reduction factors. Due to the covalency effect, the orbital moment is reduced by 14, 15 and 16 per cent and S.O. coupling coefficient by 9, 20 and 16 per cent along x , y and z directions respectively, from the free ion values. It is to be noted that while the calculated values of mean susceptibility at different temperatures agree to within 0.6 per cent of the experimental results, those of magnetic anisotropy systematically deviate by an amount changing from zero at 90°K up to a maximum of about 12.5 per cent

at 300°K from the experimental values. The agreement between theoretical and experimental values has been made closest at 90°K in our investigation for reasons mentioned earlier. But there still exist systematically increasing discrepancies for both the mean as well as the anisotropy as the temperature rises and these must be attributed to the fact that the lower symmetric field parameters σ , δ , γ and ϵ which have been considered so far as temperature independent must be appreciably varying with temperature. This is also corroborated by the earlier findings of Bose *et al* (1957) on copper Tutton salts. As a matter of fact, the variation of anisotropic field parameters with temperature is quite evident from our measurement of g -values at the two temperatures 90°K and 300°K. The paramagnetic resonance experiment which offers a direct probe into the paramagnetic complex clearly shows the variation although small of the principal g -values and hence the variation of anisotropic ligand field splittings with temperature. Moreover, the e.p.r. measurement shows that the paramagnetic complex changes its orientations with temperature very perceptibly at least in the xy -plane. With orientational changes, the packing in the lattice must be changing and hence the anisotropic part of the ligand field (Van Vleck, 1939 Bose *et al* 1957). The effect may be vice versa in the sense that the change of the ligand field may also cause orientational changes.

In the absence of sufficient data at different temperatures from other independent sources it is not possible to fit uniquely the experimental magnetic data alone assuming the anisotropic field parameters to vary with temperature. It is, however, enough for the present purpose in spite of several simplifying approximations to indicate the systematic change in the anisotropic component of the ligand field with temperature. It may be mentioned in closing that the ionic anisotropy vs. inverse temperature curve theoretically follows a straight line but experimentally deviates from linearity. The neglect of the 3rd order terms in g_i mentioned earlier will cause a constant but small difference in the values of g_i at all temperatures and hence only a slight change in the inclination of the above theoretical curve without introducing any curvature. Thus, the neglect of third order terms in no way can explain the systematically increasing deviation from the expected Curie law. Moreover resonance line-width experiments (Bleaney *et al*, 1949) show that exchange interaction in these dilute Cu^{2+} salts is too small ($<0.1\text{K}$) to explain the deviation.

A C K N O W L E D G M E N T

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