



# ESTIMATION OF GROUND STATE WAVE FUNCTIONS AND G-ANISOTROPY IN Cu<sup>2+</sup> DOPED SINGLE CRYSTALS

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## Abstract

In different single crystals doped with Cu<sup>2+</sup> ion, the g-anisotropy has been estimated using spin-Hamiltonian parameters obtained from Electron Paramagnetic Resonance studies. The ground state wave functions of Cu<sup>2+</sup> are also calculated. The some other microscopic parameters were determined from the calculation of ground state wave functions. The calculated g-anisotropies are compared with the experimental results. A good agreement is found between the calculated and experimental g-anisotropies. The ground state is predominantly  $|x^2 - y^2\rangle$  but in some crystals it is found to be  $|3z^2 - r^2\rangle$ . In the present study also, the ground state wave functions of Cu<sup>2+</sup> are predominantly  $|x^2 - y^2\rangle$ , but for some crystals like Laccase, Oxalate and Citrate it is found to be  $|3z^2 - r^2\rangle$ .

**Keywords:** Electron Paramagnetic Resonance (EPR); spin-Hamiltonian parameters; ground state wave function; g-anisotropy; crystal-field symmetry. PACS No. 76.30

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## INTRODUCTION

After the discovery of Electron Paramagnetic Resonance (EPR), this process has been widely studied this process has been widely studied using d<sup>9</sup> ions mainly Cu<sup>2+</sup> as doping host lattice for investigation [1]. EPR is a powerful tool to provide us huge information about the ground state of paramagnetic impurity doped in system like single crystals. In many studies, the local symmetry of d<sup>9</sup> ion is D<sub>4h</sub> or very close to it. The explanation of the experimental spin-Hamiltonian for d<sup>9</sup> ions in D<sub>4h</sub> symmetry was guided by crystal field approximation (CFA) based theories. However for low symmetry ligand field, the magnetic hole system is favored to get detail knowledge about wave functions of electron [2]. The Cu<sup>2+</sup> ion has been used extensively to understand the nature of the crystalline electric field symmetry produced due to the ligands surrounding the central metal ion [3-7] Because of these reasons the studies of transition metal systems for 3d<sup>9</sup> arrangements have been the subject of our interest. If the anisotropy in g and A parameters are exactly known then the exact ground state wave functions are easily calculated. In the present work, the author has estimated the ground state wave functions of Cu<sup>2+</sup> ion in a large number of different lattices [8-13] with the help of spin -Hamiltonian parameters taken from experimental data of earlier research work. The relevant crystal field may be obtained mixing the wave functions. The crystal field theory is applied to find out the anisotropy in g-value. Now a comparison is made between calculated and experimental g-anisotropy. In all the single crystals spin exchange polarization parameter K may be estimated quantitatively with the help of data obtained from experimental work [8-13]. In order to ensure a good agreement between the calculated and experimental results, an attempt was made to obtain g<sub>y</sub>-g<sub>x</sub> values for Cu<sup>2+</sup> ion each system. This paper deals with the calculations of Cu<sup>2+</sup> doped in the different diamagnetic hosts at the room temperature.

## THEORY

The Cu<sup>2+</sup> ion in tetragonal symmetry related to extended octahedron yields the ground state predominantly  $|x^2 - y^2\rangle$  while in the case of the tetragonal symmetry for compressed octahedron it is mostly  $|3z^2 - r^2\rangle$  [14-17]. In lower crystal field symmetry like rhombic and orthorhombic above prediction is entirely different. For these cases  $g_x \neq g_y \neq g_z$  and  $A_x \neq A_y \neq A_z$ , the ground state was predicted as the linear combination [16-17] of

the two orbitals  $|x^2 - y^2\rangle$  and  $|3z^2 - r^2\rangle$ . It will take either the form  $\alpha|x^2 - y^2\rangle + \beta|3z^2 - r^2\rangle$  or  $\alpha|3z^2 - r^2\rangle + \beta|x^2 - y^2\rangle$ . Where  $\alpha$  is very close to one and  $\beta$  is very small in comparison to one ( $\alpha \approx 1$  and  $\beta \ll 1$ ).

In the present work two types of crystals are studied, it is observed that in most of the systems the symmetry for electric field around Cu<sup>2+</sup> ion is rhombic while in few crystals symmetry is orthorhombic. In study it is also seen that in almost all the cases  $g_z \frac{g_x + g_y}{2}$  and in some crystals like Laccase, Oxalate and Citrate it is  $g_z \langle g_x, g_y \rangle$ . In systems for which  $g_z \frac{g_x + g_y}{2}$ , the ground state wave functions is estimated as  $\alpha|x^2 - y^2\rangle + \beta|3z^2 - r^2\rangle$  [14] thereafter this case will be represented by Case A while in crystals Laccase, Oxalate and Citrate (for which  $g_z \langle g_x, g_y \rangle$  expression used as  $\alpha|3z^2 - r^2\rangle + \beta|x^2 - y^2\rangle$ , this is denoted by Case B. Since the value of  $\alpha$  is very near to unity and that of  $\beta$  is much less than unity, the Case A deals with the system having predominantly ground state as  $|x^2 - y^2\rangle$  for Cu<sup>2+</sup> ion and other Case B governs with mostly ground state  $|3z^2 - r^2\rangle$  for same impurity Cu<sup>2+</sup> ion. By applying Bleaney et al. theory [16] so many workers have calculated the ground state wave functions of Cu<sup>2+</sup> ion in different diamagnetic hosts. Sroubek and Zdansky [15] have studied Cadmium and Magnesium tungstates for determination of ground state wave function after doping Cu<sup>2+</sup> ion. In same way Sastry and Sastry [14] also estimated the ground state wave functions of Cu<sup>2+</sup> ion in K<sub>2</sub>CO(SO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O and other Tutton salts. In present study for all the lattices, the ground state wave function is not purely  $|x^2 - y^2\rangle$  or  $|3z^2 - r^2\rangle$  state but an admixture of  $|x^2 - y^2\rangle$  and  $|3z^2 - r^2\rangle$ . As the value of  $\alpha$  is greater than  $\beta$ , the Cu<sup>2+</sup> is found to have a rhombic distorted shape. The ground state wave function and various molecular orbital coefficients have been estimated for Cu<sup>2+</sup> ion by Misra and Kripal [18]. By using the same theory [16] several workers [3, 19-24] have obtained similar type of expressions in different lattices. The expressions used for determination of different parameters in terms spin-Hamiltonian constants contain unknown parameters ( $\alpha, \beta, K$

and P, where K is Fermi contact term/spin-exchange polarization parameter, P is hyperfine interaction parameter and  $\alpha$ ,  $\beta$  are in plane  $\sigma$ -bonding and out-of-plane  $\pi$  bonding coefficients, respectively. These parameters are used for best fit [25-26] to determine  $\delta g$  value by using measured values of spin-Hamiltonian parameters [14]. Now the ground state function, P and K can be easily calculated. The calculated value of  $\delta g_{cal}$  is compared with the experimental value  $\delta g_{exp}$ . The same method has been used in this paper.

### I Expression for Ground State Wave Function:

**Case A:** If  $g_z > \frac{g_x + g_y}{2}$ , then crystal field symmetry will be either rhombic or orthorhombic. In this case the ground state wave function of Cu<sup>2+</sup> ion can be expressed as:

$$\alpha|x^2 - y^2\rangle + \beta|3z^2 - r^2\rangle \quad (1)$$

where  $\alpha \approx 1$  and  $\beta \ll 1$ .

Bleaney [16] predicted the ground state wave function of Cu<sup>2+</sup> ion for crystal field with low symmetry as:

$$\frac{1}{2}(5)^{1/2} f(r)(ax^2 + by^2 + cz^2) \quad (2)$$

Satisfying the following conditions-

$$\begin{aligned} a + b + c &= 0 \\ a^2 + b^2 + c^2 &= 6 \end{aligned} \quad (3)$$

With the help of Equations (1) and (2) and conditions (3) the values of a, b and c can be easily calculated as:

$$\begin{aligned} a &= -(\beta - \sqrt{3}), \\ b &= -(\beta + \sqrt{3}), \\ c &= 2\beta \end{aligned} \quad (4)$$

By applying theory of Bleaney [16] and taking approximation [14], it can be obtained:

$$\begin{aligned} A_x &= p_{fi} \left[ -\alpha^2 K + \Delta g_x + \frac{\Delta g_y}{14} + \frac{2}{7} \alpha^2 - \frac{4\sqrt{3}}{7} \alpha^2 \beta \right], \\ A_y &= p_{fi} \left[ -\alpha^2 K + \Delta g_y + \frac{\Delta g_x}{14} + \frac{2}{7} \alpha^2 + \frac{4\sqrt{3}}{7} \alpha^2 \beta \right], \\ A_z &= p_{fi} \left[ -\alpha^2 K + \Delta g_z - \frac{1}{14} (\Delta g_x + \Delta g_y) - \frac{4}{7} \alpha^2 \right] \end{aligned} \quad (5)$$

The symbols of above Eqns. have their significant meaning [14]. In case of free Cu<sup>2+</sup> the value of  $p_{fi}$  ( $fi$ =free ion) is used as 0.036 cm<sup>-1</sup>. The measured value of  $p_{exp}$  can be estimated by multiplying  $p_{fi}$  by the electrons being found in the <sup>2</sup>D state around the Cu<sup>2+</sup> ion i.e.

$$p_{exp} = \alpha^2 p_{fi} \quad (6)$$

If signs of  $A_i$  are not exactly known then  $A_z$  is assumed to be negative with  $A_x$  and  $A_y$  are chosen in such way to get best fit of theoretical value of  $g_y - g_x$ . The other possible set for sign of  $A_x, A_y$  and  $A_z$  are useless. The various microscopic parameters may be easily calculated by putting the experimental values of  $g_x, g_y, g_z$  and  $A_x, A_y, A_z$  in eqn. (5). The values of these parameters K,  $p_{exp}$  and  $\delta g$  are given in Table 1.

**Case B:** In orthorhombic crystal field symmetry  $g_z < \frac{g_x + g_y}{2}$ , the ground state wave function [15] of Cu<sup>2+</sup> ion can be expressed as:

$$\alpha|3z^2 - r^2\rangle + \beta|x^2 - y^2\rangle \quad (7)$$

where  $\alpha \approx 1$  and  $\beta \ll 1$ .

If we compare Equations (7) and (2) and using conditions (3) then the values of a, b and c is obtained easily as:

$$\begin{aligned} a &= -(1 - \beta\sqrt{3}\beta), \\ b &= -(1 + \sqrt{3}\beta), \\ c &= 2 \end{aligned} \quad (8)$$

$A_x, A_y$  and  $A_z$  are given by-

$$\begin{aligned} A_x &= p_{fi} \left[ -\alpha^2 K + \Delta g_x + \frac{\Delta g_y}{14} - \frac{2}{7} \alpha^2 - \frac{4\sqrt{3}}{7} \alpha^2 \beta \right], \\ A_y &= p_{fi} \left[ -\alpha^2 K + \Delta g_y + \frac{\Delta g_x}{14} - \frac{2}{7} \alpha^2 + \frac{4\sqrt{3}}{7} \alpha^2 \beta \right], \\ A_z &= p_{fi} \left[ -\alpha^2 K + \Delta g_z - \frac{1}{14} (\Delta g_x + \Delta g_y) + \frac{4}{7} \alpha^2 \right] \end{aligned} \quad (9)$$

In present study, for Case B three crystals are available namely, Laccase, Oxalate and Citrate. For such system  $A_z$  is taken to be positive with  $A_x$  and  $A_y$  are taken in such way that to get best fit of theoretical value of  $g_y - g_x$ . The other

combinations of signs for  $A_x$ ,  $A_y$  and  $A_z$  are useless as they gave absurd value of  $\alpha$ ,  $\beta$ ,  $K$ ,  $p_{\text{exp}}$  as in Case A. The estimated values of these microscopic parameters are given in Table 1.

## II Calculation of ( $g_y$ - $g_x$ )

( $g_y - g_x$ ) is the difference between  $g_y$  and  $g_x$ ,

$$\delta g_{\text{exp}} = g_y - g_x,$$

The value of  $\delta g_{\text{exp}}$  is compared with calculated value  $\delta g_{\text{cal}}$ , which is caused by the contributions [15]:

(i)  $\delta g_{\text{cal}}^1$ : this factor is due to mixing of orbital  $|x^2 - y^2\rangle$  with the  $|3z^2 - r^2\rangle$  orbital.

(ii)  $\delta g_{\text{cal}}^2$ : this is due to energy splitting of  $|xz\rangle$  and  $|yz\rangle$  states.

(iii)  $\delta g_{\text{cal}}^3$ : this contribution is because of different covalency of  $|xz\rangle$  and  $|yz\rangle$  states, and

(iv)  $\delta g_{\text{cal}}^4$ : this term is due to mixing of the  $|yz\rangle$  orbital with the  $|xz\rangle$  orbital of the first excited state; it has the same effect as  $\delta g_{\text{cal}}^3$ .

These contributions can play important role in discussion of both the cases viz. Case A of rhombic and orthorhombic crystal field symmetry

( $g_z \langle \frac{g_x + g_y}{2} \rangle$ ) and Case for orthorhombic B

crystal field symmetry ( $g_z \langle g_x, g_y \rangle$ ). It can be shown easily that the orthorhombic (six-fold coordination) crystalline field will be equivalent to the rhombic crystalline field [2].

In rhombic symmetry the crystalline electric field is expressed by:

$$V = Ax^2 + By^2 + Cz^2 + \text{higher terms} \quad (10)$$

In six-fold coordination) crystalline field is given by

$$V = c_2 \left( \frac{2}{a_1^3} - \frac{1}{a_2^3} - \frac{1}{a_3^3} \right) Y_2^0 + \frac{1}{2} (6)^{1/2} \left( \frac{1}{a_2^3} - \frac{1}{a_3^3} \right) (Y_2^2 + Y_2^{-2}) \quad (11)$$

Putting the values of  $Y_2^0$ ,  $Y_2^2$  and  $Y_2^{-2}$  from [27] in Eqn. (11) -

$$V = C_2 \left\{ \left[ A \sqrt{\frac{5}{4\pi}} \sqrt{\frac{1}{4}} (3z^2 - r^2) \right] + B_1 \left[ \sqrt{\frac{5}{4\pi}} \sqrt{\frac{3}{8}} \left\{ \frac{(x+iy)^2}{r^2} + \frac{(x-iy)^2}{r^2} \right\} \right] \right\} + \dots \quad (12)$$

$A_1$  and  $B_1$  are some arbitrary constants

Putting the value of  $C_2$  [28-29] we get:

$$V = bA_1 \sqrt{\frac{5}{4\pi}} \sqrt{\frac{1}{4}} (3z^2 - r^2) + bB_1 \left( \sqrt{\frac{5}{4\pi}} \sqrt{\frac{3}{8}} \right) (x^2 - y^2 + x^2 - y^2) + \text{higher terms} \quad (13)$$

$$V = D(3z^2 - r^2) + C_1(x^2 - y^2) + \text{higher terms}$$

$$= C_1(x^2 - y^2) + 3Dz^2 - D(x^2 + y^2 + z^2) + \text{higher terms}$$

$$= (C_1 - D)x^2 + (-C_1 - D)y^2 + 2Dz^2 + \text{higher terms} \quad (14)$$

$$V = Ax^2 + By^2 + Cz^2 + \text{higher terms} \quad (15)$$

Where  $C_1 - D \equiv A$ ,  $(C_1 + D) \equiv B$  and  $2D \equiv C$

It is clear that both Equations (10) and (15) are similar, therefore by taking into account contributions (ii), (iii) and (iv) the expressions will be same for both the Cases A and B. Therefore it is convenient to discuss contribution due to (i) for both case A and B separately.

**Contribution (i) Case A:** If the splitting of states  $|xz\rangle$  and  $|yz\rangle$  is neglected then the expressions for

$g_x$  and  $g_y$  is expressed as [16]:

$$\begin{aligned} g_x &= 2.0023 + A'(b^2 - c^2) \\ g_y &= 2.0023 + A'(c - a^2) \end{aligned} \quad (16)$$

Where  $A'$  is constant. Using eqn. (4) and substituting the values of a, b and c in above eqn. (16) we get-

$$(\Delta g_x + \Delta g_y) = 6A'$$

$$\delta g_{\text{cal}}^1 = g_y - g_x = -2\sqrt{3}\beta(\Delta g_x + \Delta g_y) \quad (17)$$

If  $\delta g_{\text{exp}}$  is positive  $\beta$  will be negative and  $\beta$  will be positive for negative value of  $\delta g_{\text{exp}}$ .

**Case B:** Using (8) and (16) we get-

$$\delta g_{\text{cal}}^1 = g_y - g_x = -\frac{2}{\sqrt{3}}\beta(\Delta g_x + \Delta g_y) \quad (18)$$

**Contribution (II):** Let us start with Equation (10)

$$V = Ax^2 + By^2 + Cz^2 + \text{higher terms} \quad (10)$$

Neglecting higher order terms and taking integral  $z^2$  to be zero we get-

$$\beta = -\langle x^2 - y^2 | (Ax^2 + By^2) | 3z^2 - r^2 \rangle / E_1 \quad (19)$$

So,

$$E_1 \beta = (-1) \left[ \sqrt{3} A \int_0^n \int_0^{2\pi} \int_0^\pi r^7 \cos^2 \phi (\cos^2 \phi - \sin^2 \phi) \sin^5 \theta (3 \cos^2 \theta - 1) \times dr d\phi d\theta + \sqrt{3} B \int_0^n \int_0^{2\pi} \int_0^\pi r^7 \sin^2 \phi (\cos^2 \phi - \sin^2 \phi) \times \sin^5 \theta (3 \cos^2 \theta - 1) dr d\phi d\theta \right] \quad (21)$$

Therefore  $\beta$  can be written as:

$$\beta = -\frac{2\sqrt{3}}{E_1} N(B-A) \quad (22)$$

Where  $N = \left( \frac{n^8 \cdot 2\pi}{105} \right)$ ,  $E_1$  is energy difference

between states  $|x^2 - y^2\rangle$  and  $|3z^2 - r^2\rangle$ .

$$= 12A \left[ \int_v y^2 x^2 z^2 d\tau - \int_v x^2 x^2 z^2 d\tau \right] + 12B \left[ \int_v y^2 y^2 z^2 d\tau - \int_v y^2 x^2 z^2 d\tau \right] \quad (23)$$

In spherical polar coordinates  $\delta E$  can be written as:

$$\delta E = 12A \left[ \int_0^n \int_0^{2\pi} \int_0^\pi r^7 \sin^2 \phi \cos^2 \phi \sin^5 \theta \cos^2 \theta dr d\phi d\theta - \int_0^n \int_0^{2\pi} \int_0^\pi r^7 \cos^4 \theta \sin^5 \theta \cos^2 \theta dr d\phi d\theta \right] + 12B \left[ \int_0^n \int_0^{2\pi} \int_0^\pi r^7 \sin^4 \phi \sin^5 \theta \cos^2 \theta dr d\phi d\theta - \int_0^n \int_0^{2\pi} \int_0^\pi r^7 \sin^2 \phi \cos^2 \phi \sin^5 \theta \cos^2 \theta dr d\phi d\theta \right] \quad (24)$$

Integrating the above eqn. one can obtain easily-

$$\delta E = 6N(B-A) \quad (25)$$

From eqn. (15) and (25):

$$\delta E = -\sqrt{3}\beta E_1 \quad (26)$$

In g- factor anisotropy [15] can be expressed as:

$$\delta g_{cal}^2 = g_y - g_x = \frac{K}{E_1 - \frac{1}{2}(\delta E)} = \frac{K}{E_1 + \frac{1}{2}(\delta E)}$$

$$\approx \left( \frac{K}{E_1} \right) \left( \frac{\delta E}{E_1} \right) \quad (\text{Here K some arbitrary constant})$$

$$= -\Delta g \sqrt{3}\beta \quad (27)$$

$$E_1 \beta = -\sqrt{3} \int_v (x^2 - y^2) (Ax^2 + By^2) (3z^2 - r^2) d\tau \quad (20)$$

Here  $\sqrt{3} (x^2 - y^2)$  and  $(3z^2 - r^2)$  are the wave functions for  $|x^2 - y^2\rangle$  and  $|3z^2 - r^2\rangle$  states respectively [29]. In spherical polar coordinates (20) will be expressed as (21):

$n = \text{constant}$ ,  $d\tau = \text{elementary volume element}$ .

If  $\delta E$  is energy splitting for states  $|xz\rangle$  and  $|yz\rangle$ , then  $\delta E$  will be:

$$\delta E = \langle yz | (Ax^2 + By^2) | yz \rangle - \langle xz | (Ax^2 + By^2) | xz \rangle$$

$$\delta g_{cal}^2 = -\frac{1}{2} (\Delta g_x + \Delta g_y) \sqrt{3}\beta \quad (28)$$

**Contribution (III):** In this section the contribution because of different covalency of  $|xz\rangle$  and  $|yz\rangle$  states will be discussed qualitatively. For discussion LCAO method will be adopted. This method is mostly used to construct orbitals by linear combination [8, 30-31].

$$\psi = \psi(\Gamma) + \sum_i l_i \psi_i \quad (29)$$

Here  $\psi(\Gamma)$  is a wave function for the central atom transforming in molecular point group as the irreducible representation  $\Gamma$  and  $\sum_i l_i \psi_i$  is linear combination of ligand wave functions transforming like  $\Gamma$ .

Two anti-bonding orbitals can be expressed with the help of LCAO method [8, 30-31].

$$\begin{aligned}\phi_{xz} &= (M_1)^{-1/2}(\psi_{xz} - m_1\chi_{xz}), \\ \phi_{yz} &= (M_2)^{-1/2}(\psi_{yz} - m_2\chi_{yz})\end{aligned}\quad (30)$$

In above eqn.  $\psi_{xz}$  and  $\psi_{yz}$  are dt wave functions for Cu<sup>2+</sup> ion,  $\chi_{xz}$  and  $\chi_{yz}$  are linear combinations of ligand atomic orbitals,  $M_1$  and  $M_2$  are normalization constants. In LCAO approach  $m_i$  and  $1/M_i$  are approximated [32-33] by Equation (30a)

$$m_i = q_{jz}/E_2 \quad (30a)$$

where  $E_2 = E_{dt} - E_{p\pi}$   
( $j = x, y$ )

$E_{dt}$  = energy level of single dt electron for Cu<sup>2+</sup> ion

$E_{p\pi}$  = energy level for  $p\pi$  electron on the attached ligand ion

$q_{jz}$  = resonance integral between dt and  $p\pi$  electrons

$$1/M_i = \frac{1}{1 + q_{jz}/E_2} \approx 1 - \frac{(q_{jz})^2}{E_2} \quad (30b)$$

Now  $\delta E$  can be expressed as-

$$\delta E = \left( \frac{q_{xz}}{E_2} - \frac{q_{yz}}{E_2} \right) \quad (31)$$

Here the sign of  $\delta E$  is opposite to that of eqn. (26) for evaluation of electron energy level.

Using MO method [34-36]  $\delta g$  can be written as-

$$\delta g = \frac{K}{M_1 \left( E_1 - \frac{1}{2} \delta E \right)} - \frac{K}{M_2 \left( E_1 + \frac{1}{2} \delta E \right)} \quad (32)$$

Where  $K$  being a constant. Equations (30a), (30b) and (31) give the value of  $\delta g$

$$\delta g = \Delta g \delta E \left[ \frac{1}{E_1} - \frac{1}{E_2} \right] \quad (33)$$

The first term in the above equation shows the splitting in energy and second term gives the

effect for covalent distortion. By taking energy splitting due to only the covalency effect, the first term is already calculated. The second term will be given by equation (34) or (35).

$$\delta g_{cal}^3 = -\Delta g \frac{\delta E}{E_2} \quad (34)$$

$$\delta g_{cal}^3 = \frac{1}{2} (\Delta g_x + \Delta g_y) \sqrt{3} \beta \left( \frac{E_1}{E_2} \right) \quad (35)$$

**Contribution(IV):** This contribution has same effect as discussed in contribution (III). Therefore the expression has not been estimated.

## RESULTS AND DISCUSSION

In the present study with the help of experimental EPR data g-anisotropy for Cu<sup>2+</sup> in large number of single crystals has been estimated from various microscopic parameters obtained from the evaluation of ground state wave functions. It is observed that there is a good agreement between the calculated and experimental  $\delta g$  values in most of the system studied. In some crystals the value of  $\delta g_{cal}$  is slightly larger than  $\delta g_{exp}$ . Therefore it is clear that in such cases contribution due to point (iii) must be dominated. In 1-10 Phenanthroline there is a poor agreement between  $\delta g_{cal}$  and  $\delta g_{exp}$ . One can find a good agreement between them by adding the contribution [18] II and III above. However, the actual contribution III could not be done as energy  $E_2$  was not exactly known but using expression one can predict approximate value of  $\delta g_{cal}$ . In Acetyl- acetate [8]  $\delta g_{cal}^1$  than  $\delta g_{exp}$  therefore it is clear that contribution III will be important factor. By adding III term this has given a good agreement with  $\delta g_{exp}$ . For Histidine  $\delta g_{cal}$  is very smaller than  $\delta g_{exp}$ . This indicates that after taking contribution II and III one can obtain good agreement with  $\delta g_{exp}$  but best agreement can be obtained at lower temperature probably at LNT (liquid nitrogen temperature). By knowing  $E_1$  and  $E_2$  and evaluating  $\delta g_{cal}^3$  one can have good agreement between  $\delta g_{cal}$  and  $\delta g_{exp}$  in other systems also.

For comparison, the ground state functions and various microscopic parameters of Cu<sup>2+</sup> ion in other lattices are also given Table 2. It can be concluded easily from Table 2 that spin-Hamiltonian parameters and other parameters estimated in the present work are almost very

close to the result of earlier researchers. The best agreement between  $\delta g_{cal}$  and  $\delta g_{exp}$  can be seen at still lower temperature [2]. The low temperature studies of Cu<sup>2+</sup> in systems giving larger difference between  $\delta g_{cal}$  and  $\delta g_{exp}$  value, are in progress and the best fit results will be published later in reputed international journal.

## CONCLUSIONS

In the present theoretical work g-anisotropy for Cu<sup>2+</sup> ion in different lattices are estimated. The ground state wave functions have been also constructed in systems used in study. The various microscopic parameters are also calculated. Using these microscopic parameters and spin-Hamiltonian parameters taken from experimental EPR studies, g-anisotropy has been determined in each system. The hyperfine interaction parameter  $p_{exp}$ , Fermi contact term K,

$\delta g_{cal} (= \sum_i \delta g_{cal}^i; i=1-3)$  and  $\delta g_{exp}$  are also obtained.

The theoretical analysis shows that in most of the crystals ground state wave for Cu<sup>2+</sup> ion is predominantly  $|x^2 - y^2\rangle$ . In Laccase, Oxalate and citrate it is found to be  $|3z^2 - r^2\rangle$ . After comparison of the ground state of Cu<sup>2+</sup> ion in the present work with the lattices studied by earlier researchers [19-22] it is clear that for fourteen crystals of Table 1 the ground state wave function is similar to that of Lithium Potassium Sulphate, Sodium Citrate, Bis (L-asparaginato II), Cadmium (II) formate

dihydrate and complexes I and III of DADT [3], while for Laccase, Oxalate and citrate it is found to be similar with complex II of DADT. The value of K and  $p_{exp}$ , in present paper is almost similar to that of earlier works [3, 19-22]. The g-anisotropy  $\delta g_{cal}$  in each system is calculated and these values are compared with the experimental values  $\delta g_{exp}$ . There is a good agreement between  $\delta g_{cal}$  and  $\delta g_{exp}$  in most of the systems (Table 1). There is huge difference between  $\delta g_{cal}$  and  $\delta g_{exp}$  value for some systems like Histidine, 1-10 Phenanthroline, Oxalate and Phthalocyanine. The best agreement between  $\delta g_{cal}$  and  $\delta g_{exp}$  may be obtained at still lower temperature.

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**Table1.** Ground State wave functions and Microscopic parameters for Cu<sup>2+</sup> ion in different single crystals at RT. (Present Study)

S. No.	Single Crystals	Ground state wave function	K	$p_{exp}$ ( $\times 10^{-4} cm^{-1}$ )	$\delta g_{cal}^1$ x	$\delta g_{cal}^2$ y	$\delta g_{cal}^3$ z	$\delta g_{cal}$ (x+y+z)	$\delta g_{exp}$	Ref.
1.	Acetyl- acetone	$0.913 x^2 - y^2\rangle + (-0.223) 3z^2 - r^2\rangle$	0.384	262.8	+0.156	-	-0.011	+0.1552	+0.140	[8]
2.	Salicylaldehydeimine	$0.866 x^2 - y^2\rangle + (-0.033) 3z^2 - r^2\rangle$	0.391	270.2	+0.011	+0.003	+0.0002	+0.0142	+0.0178	[8]
3.	Phthalocyanine	$0.944 x^2 - y^2\rangle + (-0.333) 3z^2 - r^2\rangle$	0.433	251.2	-0.064	-0.0155	+0.0033	-0.0762	-0.0755	[9]
4.	Phthalocyanine	$0.799 x^2 - y^2\rangle + (-0.411) 3z^2 - r^2\rangle$	0.445	307.2	+0.212	+0.111	-	+0.3242	0.0660	[10]
5.	Laccase	$0.333 x^2 - y^2\rangle + (0.855) 3z^2 - r^2\rangle$	0.268	304.0	+0.101	+0.011	+0.0006	+0.203	+0.1990	[11]
6.	Ceruloplasmin	$0.805 x^2 - y^2\rangle + (0.243) 3z^2 - r^2\rangle$	0.188	283.2	+0.044	+0.011	+0.0022	+0.0572	+0.0541	[11]
7.	Denatured Laccase	$0.886 x^2 - y^2\rangle + (0.103) 3z^2 - r^2\rangle$	0.407	233.0	-0.112	-0.010	-0.0012	-0.1232	-0.1191	[11]
8.	Denatured Ceruloplasmin	$0.905 x^2 - y^2\rangle + (0.363) 3z^2 - r^2\rangle$	0.412	278.0	+0.038	+0.070	+0.001	+0.109	+0.114	[11]
9.	Histidine	$0.805 x^2 - y^2\rangle + (0.233) 3z^2 - r^2\rangle$	0.332	284.5	+0.136	-	-	+0.136	+0.2290	[11]
10.	Imidazole	$0.923 x^2 - y^2\rangle + (-0.037) 3z^2 - r^2\rangle$	0.325	286.9	-0.056	-0.0122	+0.0022	-0.056	-0.059	[11]
11.	2-2' Dipyridyl	$0.877 x^2 - y^2\rangle + (-0.023) 3z^2 - r^2\rangle$	0.382	222.9	-0.117	-0.016	+0.0010	-0.1320	-0.677	[11]

12.	1-10 Phenanthroline	$0.899 x^2 - y^2\rangle + (-0.013) 3z^2 - r^2\rangle$	0.377	296.9	+0.046	+0.005	-	+0.051	+0.175	[11]
13.	Oxalate	$0.293 x^2 - y^2\rangle + (0.789) 3z^2 - r^2\rangle$	0.166	343.2	+0.113	+0.008	+0.0001	+0.1211	+0.033	[11]
14.	EDTA	$0.879 x^2 - y^2\rangle + (0.113) 3z^2 - r^2\rangle$	0.351	340.9	-0.036	-0.008	+0.0006	-0.0434	-0.0399	[11]
15.	Citrate	$0.269 x^2 - y^2\rangle + (0.822) 3z^2 - r^2\rangle$	0.188	277.7	+0.126	+0.005	+0.0001	+0.1311	+0.1122	[11]
16.	Etioporphyrin II	$0.933 x^2 - y^2\rangle + (0.243) 3z^2 - r^2\rangle$	0.338	269.7	-0.044	-0.022	+0.0033	-0.0627	-0.0571	[12]
17.	t-phenylporphin	$0.911 x^2 - y^2\rangle + (0.143) 3z^2 - r^2\rangle$	0.366	279.8	+0.055	+0.004	+0.0003	+0.0593	+0.164	[13]

**Table2.** Ground State wave functions and Microscopic parameters for Cu<sup>2+</sup> ion in some other single crystals at Room Temperature

S. No	Single Crystals		Ground state wave function	K	$P_{exp}$ ( $\times 10^{-4} cm^{-1}$ )	$\delta g_{cal}^1$	$\delta g_{cal}^2$	$\delta g_{cal}$	$\delta g_{exp}$	Ref.	
1.	Lithium Potassium Sulphate	Site I	$0.880 x^2 - y^2\rangle + (0.285) 3z^2 - r^2\rangle$	0.437	270.0	-0.227	-0.056	-0.283	0.049	[19]	
		Site II	$0.885 x^2 - y^2\rangle + (0.289) 3z^2 - r^2\rangle$	0.441	289.0	-0.233	-0.058	-0.292	0.078		
2.	Sodium Citrate		$0.878 x^2 - y^2\rangle + (0.027) 3z^2 - r^2\rangle$	0.262	280.0	-0.021	-0.005	-0.026	0.021	[20]	
3.	Bis (L-asparaginato II)		$0.931 x^2 - y^2\rangle + (0.018) 3z^2 - r^2\rangle$	0.168	310.0	-0.006	-0.001	-0.007	0.031	[21]	
4.	Cadmium(II) formate dihydrate	Site I	$0.973 x^2 - y^2\rangle + (-0.443) 3z^2 - r^2\rangle$	0.417	340.0	0.313	0.078	0.391	0.025	[22]	
		Site II	$0.998 x^2 - y^2\rangle + (-0.419) 3z^2 - r^2\rangle$	0.405	360.0	0.267	0.067	0.334	0.020		
5.	DADT	Complex I	Site I	$0.873 x^2 - y^2\rangle + (0.073) 3z^2 - r^2\rangle$	0.310	299.0	0.050	0.008	0.058	0.035	
			Site II	$0.799 x^2 - y^2\rangle + (0.022) 3z^2 - r^2\rangle$	0.316	311.0	0.034	0.011	0.045	0.020	
		Complex II	Site I	$0.303 x^2 - y^2\rangle + (0.716) 3z^2 - r^2\rangle$	0.372	353.0	0.052	0.008	0.060	0.058	[3]
			Site II	$0.297 x^2 - y^2\rangle + (0.723) 3z^2 - r^2\rangle$	0.385	372.0	0.051	0.005	0.056	0.054	
		Complex III	Site I	$0.845 x^2 - y^2\rangle + (0.081) 3z^2 - r^2\rangle$	0.470	285.0	0.039	0.003	0.042	0.032	
			Site II	$0.894 x^2 - y^2\rangle + (0.119) 3z^2 - r^2\rangle$	0.366	274.0	0.049	0.008	0.057	0.050	

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