

EPR and Optical Absorption Studies of Cu^{2+} Doped Lithium Maleate Dihydrate Single Crystal

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Abstract: Electron paramagnetic resonance (EPR) study of Cu^{2+} doped lithium maleate dihydrate single crystal is done at liquid nitrogen temperature (LNT). Four hyperfine lines are observed in all directions i.e. only single site is observed. The spin Hamiltonian parameters are determined from EPR absorption spectra: $g_x = 2.098 \pm 0.002$, $g_y = 2.150 \pm 0.002$, $g_z = 2.208 \pm 0.002$, $A_x = (55 \pm 5) \times 10^{-4} \text{cm}^{-1}$, $A_y = (52 \pm 5) \times 10^{-4} \text{cm}^{-1}$, $A_z = (50 \pm 5) \times 10^{-4} \text{cm}^{-1}$. The results indicate that the copper ion enters the lattice interstitially. Using the spin Hamiltonian parameters obtained from EPR study the ground state wave function of Cu^{2+} ion in the lattice is determined. The optical absorption study of Cu^{2+} doped lithium maleate dihydrate at room temperature is also performed. With the help of optical absorption study the nature of bonding in the complex is discussed.

Keywords: A. Crystal growth; B. Crystal and ligands field; C. Optical properties; D. Electron paramagnetic resonance.

1. Introduction

The EPR of Cu^{2+} impurities have been widely carried out in variety of single crystals¹⁻⁸. The hyperfine structure of copper ion was first investigated in solid state by the method of EPR. In Cu^{2+} complexes the metal ions have either four or six co-ordination geometry and there are only few exceptions of this. The $3d^9$ configuration of Cu^{2+} is of particular interest because it represents a simple one magnetic hole system. EPR and optical absorption are two supplementary tools to investigate the site symmetry of the impurity, the dynamic behavior of the dopant of the lattice and nature of bonding in crystal. The main objectives of EPR studies of transition metal ions doped in crystals are to find the sites available for the impurity ion and their orientations, the study of phase transition and magnetic properties of unpaired electrons of transition metal ion.

Lithium compounds are used as the standard in the treatment of bipolar disorder. Lithium salts may be helpful for related diagnoses, such as schizoaffective disorder and cyclic major depression⁹. Organolithium reagents are used as strong bases and as reagents for the formation of carbon-carbon bonds. These are also used in polymer synthesis as catalysts or initiators in anionic polymerization of unfunctionalized olefins¹⁰⁻¹². Such compounds are in turn very reactive and are the basis of many synthetic applications¹³. Lithium compounds are used as pyrotechnic colorants and oxidizers in red fireworks and flares¹⁴. Some of these compounds (e.g. lithium niobate) are also used as non-linear optical materials. Due to above, our interest developed in lithium maleate dihydrate.

In the present study, EPR at liquid nitrogen temperature (LNT) and optical absorption at room temperature (RT) of Cu^{2+} doped lithium maleate dihydrate are carried out to find the location of ion in the lattice. The study is also used to obtain the site symmetry of impurity ions as well as to describe the energy level structure and the nature of bonding of Cu^{2+} ion with its various ligands in the crystal.

2. Crystal Structure

Lithium maleate dihydrate, $\text{Li}_2\text{C}_4\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ single crystals are monoclinic, belongs to the space group Cc or $C2/c$ and $Z=8$ ¹⁵. The unit cell dimensions are $a=9.6306$, $b=12.1307$, $c=12.7051 \text{ \AA}$ and $\beta=107.96^\circ$. The projection of the structure along the b -axis is shown in Fig. 1. The main plane of each maleate ion is approximately parallel to (001) . The water molecules are sandwiched between layers of maleate ions and lithium ions lie between the water molecules and the anions. The structure continuously bonded in three dimension by either ionic or hydrogen bonds. Each lithium ion forms bonds to four oxygen atoms and each maleate ion is bounded by its four oxygen atoms to lithium ions and water molecules.

3. Experiments

Single crystals of Cu^{2+} doped lithium maleate dihydrate were prepared by the slow evaporation of an aqueous solution of maleic acid with stoichiometric ratio of lithium hydroxide. For Cu^{2+} doped crystals, an aqueous solution of 0.05 wt% of copper sulphate was added as dopant. Good, transparent and monoclinic prism shaped crystals were grown in about two weeks. The crystals are elongated parallel to a and showing forms (010) , (110) and (001) . The maximum size of the grown crystals is $12\text{mm} \times 1.5\text{mm} \times 0.7 \text{ mm}$. The morphology of the crystal was found to be as

shown in Fig. 2 together with the orientation of the crystal axes.

The EPR spectra of single crystals were recorded at LNT using X-band Varian *E-112* EPR spectrometer with 100 kHz field modulation. The single crystals were mounted at the end of quartz rod using quick-fix and crystal rotations were performed along the three mutually orthogonal axes a , b , c^* at an interval of 10° using goniometer. In the monoclinic system two of the crystal axes are perpendicular to each other, but the third is obliquely inclined. The lithium maleate dihydrate crystal is monoclinic so we choose a , b , c^* experimental axis system for the single crystal studies. In this system a and b are orthogonal crystallographic axes and c^* is orthogonal to both a and b . The optical spectra were recorded on Unicam-5625 spectrophotometer in the wavelength range $195\text{-}1100\text{ nm}$ at room temperature.

4. Results and Discussion

The $3d^9$ system with $S=1/2$ and $I=3/2$ exhibits four hyperfine lines from a single complex. The EPR spectrum of Cu^{2+} doped lithium maleate dihydrate single crystal taken at LNT in ab plane for the magnetic field at angle 0° from a axis (frequency 9.1 GHz) shown in Fig. 3(a). The unit cell of host crystal contains eight molecules per unit cell but only one set of four hyperfine lines is observed. This is explained on the basis of interstitial doping. For a substitutional site of Cu^{2+} in monoclinic crystal with two molecules per unit cell, two sets of four lines should be observed in two planes and only one set of four lines in one plane of rotation¹⁶. In the present study, the number of atoms per unit cell is eight in the monoclinic crystal. Therefore, we should get eight sets of four hyperfine lines in two planes and four sets of four lines in third plane for substitutional site of Cu^{2+} in place of Li^+ . But we have observed only one set of four hyperfine lines in all three ab , bc^* and c^*a planes. This indicates that the Cu^{2+} ion enters interstitially in the host lattice. Also the ionic radius of Li^+ ion (68 pm) is smaller than Cu^{2+} ion (72 pm), which also suggests less possibility of substitution of Cu^{2+} in place of Li^+ . The angular variation of hyperfine lines in all three ab , bc^* and c^*a planes is shown in Fig. 4(a) - (c). The direction of the maximum overall splitting of EPR spectrum is taken as the z -axis and that of the minimum as the x -axis¹⁷. The EPR spectra recorded in ab and c^*a planes showed a large anisotropy in A and g values, however the corresponding variation in bc^* plane is small. The principal values of g and A tensor for lithium maleate dihydrate single crystals were evaluated using Schonland procedure¹⁸, in which all the EPR line positions recorded for the magnetic field in the three planes were fitted to the spin Hamiltonian given by¹⁹

$$(4.1) \quad H = \mu_B (g_x S_x B_x + g_y S_y B_y + g_z S_z B_z) + A_x I_x S_x + A_y I_y S_y + A_z I_z S_z,$$

where $S = 1/2$ and $I = 3/2$ are the electronic and nuclear spins of Cu^{2+} , μ_B is Bohr magneton, g is spectroscopic splitting factor and A is hyperfine structure constant. The spin Hamiltonian parameters g and A together with their direction cosines evaluated using self developed computer program are given in Table 1. The procedure of obtaining principal values of the g -tensor is to rotate the magnetic field about three mutually perpendicular axes fixed in the crystal and to measure the g value variation in the plane perpendicular to each axis, respectively. If the magnetic field has the direction cosines l_1 , l_2 and l_3 with respect to above axes the square of corresponding g -value is given by an expression of the form

$$(4.2) \quad g^2 = \sum_{i,j=1}^3 G_{ij} l_i l_j,$$

where the coefficients G_{ij} depend on the choice of the reference axes. When these coefficients are known for a particular set of axes, the principal g values and principal axes are found by diagonalizing the matrix G . If θ is an angular co-ordinate specifying the direction of the magnetic field in the plane of measurement then the g^2 variation in the plane of measurement must fit to the expression¹⁸

$$(4.3) \quad g^2 = \alpha + \beta \cos 2\theta + \gamma \sin 2\theta,$$

where α , β and γ are functions of the G_{ij} . Fig. 5(a) - (b) shows the angular variation of the g^2 and $g^2 A^2$ in ab , bc^* and c^*a - plane and indicates an approximate rhombic symmetry for copper ion in the lithium maleate dihydrate lattice. The quantities α , β and γ are most accurately determined by obtaining the best fit of equation (4.3) to a large number of g -value measurements at different angles. As this procedure is impracticable the quantities α , β and γ can alternatively be expressed in terms of maximum ($+g$) and minimum ($-g$) g -values in the plane and the angle θ at which the maximum g -value occurs

$$(4.4) \quad \begin{aligned} 2\alpha &= g_+^2 + g_-^2, \\ 2\beta &= (g_+^2 - g_-^2) \cos 2\theta_+, \\ 2\gamma &= (g_+^2 - g_-^2) \sin 2\theta_+. \end{aligned}$$

Since α , β and γ depend on the G_{ij} , their measurement in a single plane

gives rise to three equations satisfied by the G_{ij} . In order to evaluate all G_{ij} , it is necessary to measure the g -value variation in all three ab , bc^* and c^*a planes. This will give nine equations to determine the six independent G_{ij} ; this redundancy is unavoidable and gives a useful check on the internal consistency of the measurements. The G matrix is then diagonalized using the Jacobi method. The principal values of g are obtained as the square roots of the diagonalized G tensor eigen values.

$$(4.5) \quad G_{diag} = R^{-1}GR, \quad g_{xx} = \sqrt{G_{11}}, \quad g_{yy} = \sqrt{G_{22}}, \quad \text{and} \quad g_{zz} = \sqrt{G_{33}},$$

where x , y and z refer to the principal axes of the g -tensor and R is the eigenvector matrix which gives the direction cosines of g_{xx} , g_{yy} and g_{zz} with respect to the rotation axes in the laboratory frame. These can then be transformed into the crystal and hence the molecular framework using the direction cosine of the rotation axes. The principal values of the A -tensor and their direction cosines can also be determined by a similar procedure as for the g -tensor by considering the angular variation of $g^2 - A^2$ in three orthogonal planes.

The values of spin Hamiltonian parameters of Cu^{2+} doped lithium maleate dihydrate obtained here are similar to the results of earlier workers^{5,20-21} shown in Table 2. The direction cosines of different bonds in lithium maleate dihydrate crystal are calculated from X-ray data and compared with those obtained by EPR method. The ionic distances and direction cosines of various bonds are given in Table 3. The direction cosines of $O(1) - O(3)$ bond agree within experimental errors with those obtained for the principal axis of g -tensor of Cu^{2+} ion. This indicates that Cu^{2+} ion takes up interstitial position in the crystal, because for the substitutional doping of Cu^{2+} the direction cosines of one of the metal oxygen bond should coincide with the principal axes of g -tensor²². The simulation of EPR spectrum using EasySpin²³⁻²⁶ and spin Hamiltonian parameters (obtained from the EPR spectra using Schonland procedure) $g_x = 2.098 \pm 0.002$, $g_y = 2.150 \pm 0.002$, $g_z = 2.208 \pm 0.002$, $A_x = (55 \pm 5) \times 10^{-4} \text{ cm}^{-1}$, $A_y = (52 \pm 5) \times 10^{-4} \text{ cm}^{-1}$, $A_z = (50 \pm 5) \times 10^{-4} \text{ cm}^{-1}$ was performed. The simulation was based upon diagonalization of the entire $S = 1/2$, $I = 3/2$ energy matrix. Lorentzian first derivative line shapes were used. The simulated spectrum is in reasonable agreement with the experimental one. The simulated EPR spectrum of lithium maleate dihydrate crystal in ab plane for the magnetic field at angle 0° from a axis (frequency 9.1 GHz) is shown in Fig. 3(b). The parameter errors are determined using statistical method²⁷.

4.1 Optical Spectrum: The optical absorption spectrum of Cu^{2+} doped lithium maleate dihydrate single crystal at room temperature in the wave length range 195-1100 nm is shown in Fig.6 (a)-(b). There are six bands occurring at $\nu_1 = 9090 \text{ cm}^{-1}$, $\nu_2 = 11253 \text{ cm}^{-1}$, $\nu_3 = 12183 \text{ cm}^{-1}$, $\nu_4 = 14239 \text{ cm}^{-1}$, $\nu_5 = 15770 \text{ cm}^{-1}$, $\nu_6 = 19383 \text{ cm}^{-1}$ in visible region and three bands in ultraviolet region at $\nu_7 = 23280 \text{ cm}^{-1}$, $\nu_8 = 31746 \text{ cm}^{-1}$ and $\nu_9 = 42003 \text{ cm}^{-1}$.

From the nature of absorption spectrum in visible region, the band observed at $\nu_2 = 11253 \text{ cm}^{-1}$ can be regarded as the $d-d$ transition band between ground state dxy and the excited state $d_{x^2-y^2}$. The absorption band at $\nu_5 = 15770 \text{ cm}^{-1}$ may be regarded as $d-d$ transition band between dxy and dxz, yz . The third absorption band observed at $\nu_6 = 19383 \text{ cm}^{-1}$ can be assigned as the $d-d$ transition band between ground state dxy and the excited state $d_{3z^2-r^2}$. The bands at 9090 cm^{-1} , 12183 cm^{-1} , and 14188 cm^{-1} may be infrared spectral overtone and/or combination bands²⁸. There are three bands observed in UV region. These bands are probably charge transfer bands, because they arise from the higher-lying energy levels. The observed bands in UV region at 23280 cm^{-1} , 31750 cm^{-1} and 42003 cm^{-1} can be compared with the band for CuCl_4^{2-} complex²⁹. Using the result of CuCl_4^{2-} complex, the transitions $4e \leftrightarrow 5b_2$, $3e \leftrightarrow 5b_2$ and $2a_1 \leftrightarrow 5b_2$ correspond to the observed frequencies 23280 cm^{-1} , 31750 cm^{-1} and 42003 cm^{-1} .

In regular tetrahedral symmetry Td , the ^2D term of the ion splits into a low lying doublet (E) and the higher lying triplet (T_2). The splitting between E and T_2 is equal to

$$(4.1.1) \quad Dt = \frac{20}{27} qF_4(R),$$

where Dt is the tetrahedral cubic splitting, q is the effective charge of ligands in units of elementary charge, F_4 is the fourth-order radial integral of the central field and R is the distance between ligand and central metal ion³⁰. If there is small radial extension of the unpaired electron wave function, the fourth-order radial integral of the central field is equal to

$$(4.1.2) \quad F_4 = \frac{\langle r^4 \rangle}{R^5},$$

where $\langle r^4 \rangle$ is the mean fourth-power radii of $3d$ orbital. Taking

$$\langle r^4 \rangle = 0.19555 \text{ \AA}^4$$

$$(4.1.3) \quad Dt = 16885.488 \frac{q}{R^5},$$

where Dt in cm^{-1} and R in Angstrom. For $2.00 \text{ \AA}$ and $q=5.7e$ the value of Dt is approximately equal to 3000. In our study $R=1.94 \text{ \AA}$ and $q=5.7e$ the value $Dt=3498 \text{ cm}^{-1}$.

The energies of the $3d$ orbitals can be calculated using the matrix element of crystal field perturbation in tetragonal D_{2d} symmetry and solving the secular equation of the second degree³¹. The $3d$ energy levels can be expressed as

$$(4.1.4) \quad E | 3z^2 - r^2 \rangle = 2Ds(3 \cos^2 \beta - 1) + \frac{27}{140} Dt(35 \cos^4 \beta - 30 \cos^2 \beta + 3),$$

$$(4.1.5) \quad E | Xy \rangle = -2Ds(3 \cos^2 \beta - 1) + \frac{9}{140} Dt(35 \cos^4 \beta - 50 \cos^2 \beta + 19),$$

$$(4.1.6) \quad E | Xy \rangle = -2Ds(3 \cos^2 \beta - 1) + \frac{9}{35} Dt(5 \cos^2 \beta - 4),$$

$$(4.1.7) \quad E | 3z^2 - r^2 \rangle = 2Ds(3 \cos^2 \beta - 1) - \frac{9}{70} Dt(35 \cos^4 \beta - 30 \cos^2 \beta + 3),$$

where

$$(4.1.8) \quad Ds = 9539.055 \frac{q}{R^3}$$

is a tetrahedron crystal field parameter in cm^{-1} for R in angstrom and β is deformation angle between the z -axis of the complex and copper-ligand vector. The tetrahedron crystal field parameter Ds is related to Dt as

$$(4.1.9) \quad Ds(\text{cm}^{-1}) = 0.565932 R^2 Dt.$$

In tetrahedral complex Ds exceeds Dt for all known copper ligand separations. For regular tetrahedron, the deformation angle, that is, the angle between the z -axis of the complex and copper-ligand vector, β is 54.74° ; $\beta < 54.74^\circ$ for elongated tetrahedron; $\beta > 54.74^\circ$ for flattened tetrahedron and for a square planer complex $\beta = 90^\circ$ is obtained Hoffmann and Goslar³² have also shown in their study that in compressed tetrahedron angle β between the z axis of complex and copper-ligand vector is $54.75^\circ - 90^\circ$ with

$|xy\rangle$ ground state. When the tetrahedron undergoes elongation, ground state become $|3z^2-r^2\rangle$ and β lies between $0-45^\circ$. When $\beta = 45-54.74^\circ$ the ground state is degenerate $|xz, yz\rangle$. This degeneracy can be removed by spin orbit coupling.

The orbital splitting with respect to ground state is shown in Fig. 7. The angle β cannot be smaller than 30° because of increase in ligand-ligand repulsion. The experimental orbital splitting energies are shown by circles in Fig. 6 and thus β is 80° with $|xy\rangle$ ground state. The experimental and theoretically calculated energies of $d-d$ transition band are shown in Table 4.

4.2 Molecular Orbital Analysis of ESR Data: In a compressed tetrahedron copper complex with dxy ground state, the crystal field can admix $4pz$ state of same symmetry. Similar hybridization effects are found for the dxz , dyz and $4px$, $4py$ states. Because of these effects in complex the wave function can be expressed as³²

$$(4.2.1) \quad \Phi(B_2) = \alpha |Xy\rangle + \eta p_z,$$

$$(4.2.2) \quad \Phi(B_1) = |X^2 - y^2\rangle,$$

$$(4.2.3) \quad \Phi(E) = \gamma |Xz, yz\rangle + \xi p_{x,y},$$

$$(4.2.4) \quad \Phi(A_1) = \delta |3z^2 - r^2\rangle + \delta_1 S.$$

Hence, neglecting second-order terms in η and ξ , the spin Hamiltonian parameters become (assuming axial symmetry approximation, as the difference between the values of g_x , g_y and A_x , A_y is small)

$$(4.2.5) \quad g_{\parallel} = 2.0023 - \frac{8\alpha^2\lambda_d}{E_1},$$

$$(4.2.6) \quad g_{\perp} = 2.0023 - \frac{2}{E_2}(\gamma^2\alpha^2\lambda_d - \alpha\gamma\lambda_p\xi^2),$$

$$(4.2.7) \quad A_{\parallel} = P_d \left[-K\alpha^2 - \frac{4}{7}\alpha^2 + (g_{\parallel} - 2) + \frac{3}{7}(g_{\parallel} - 2) \right] + P_p\eta^2 \left(-K + \frac{4}{5} \right),$$

$$(4.2.8) \quad A_{\perp} = P_d \left[-K\alpha^2 - \frac{2}{7}\alpha^2 + (g_{\perp} - 2) + \frac{11}{14}(g_{\perp} - 2) \right] + P_p\eta^2 \left(-K - \frac{2}{5} \right),$$

where E_1, E_2 are the energy separations between the ground state d_{xy} and the excited states $d_{x^2-y^2}$ and $d_{xz, yz}$, $\lambda_d = -829\text{cm}^{-1}$ and $\lambda_p = 150\text{cm}^{-1}$ are the free ion spin-orbit coupling constants for the 3d and 4d orbital, respectively. P_d and P_p are the Cu^{2+} ion dipolar hyperfine structure parameters of the 3d and 4d orbital. $P_d = 0.0360\text{cm}^{-1}$, $P_p = 0.0402\text{cm}^{-1}$ for Cu^{2+} ion. K is the Fermi contact parameter.

The expression (4.2.5-4.2.8) shows that in our study, four molecular orbital (MO) coefficients $\alpha^2, \eta^2, \gamma^2, \xi^2$ and one Fermi contact parameter K are unknown. The values of MO coefficients α^2, η^2 and Fermi contact parameter K are calculated using expressions for $g_{\parallel}, A_{\parallel}$ and $A_{\perp}$. The rest two MO coefficients γ^2 and ξ^2 are obtained from equation for $g_{\perp}$ by fitting the

MO coefficients using a least-square technique to $M = \left(\frac{g_{\perp, \text{cal}}}{g_{\perp, \text{obs}}} - 1 \right)^2$ with the

condition that the best-fit MO coefficients minimize the value of M . Here obs and cal indicate the observed and calculated value of $g_{\perp}$, respectively. The coefficients γ^2 and ξ^2 are characterized by the value M . The values of $\alpha^2, \eta^2, \gamma^2, \xi^2$ and K are shown in Table 5. The value of M is also shown in Table 5.

The value of α^2 is equal to 1 for completely ionic σ -bonding, but if overlap integral is too small that it can be neglected and $\alpha^2 = 0.5$, the bond will be completely covalent. The smaller value of α^2 , the greater the covalent nature of bonding³³. $\alpha^2 = 0.28$ indicates the σ -bonding is completely covalent. The small value of α^2 also indicates that the nature of bonding with the ligands along the axis is mostly ionic. The value of γ^2 is 0.97, which is

very near to unity. This indicates that the out-of-plane covalent π - bonding is very small. The Fermi contact parameter K is a measure of the polarization produced by uneven distribution of the d- electron density of the inner core s-electrons. It has been found that for 3d transition metal ion K is approximately 0.3³⁴ and in the present study $K=0.38$. The value of η^2 is 0.21, which indicates that the ground state metal orbital contains 21% admixture of 4p state.

5. Conclusion

EPR study of Cu^{2+} doped lithium maleate dihydrate single crystal at LNT and optical absorption study at room temperature have been carried out. Only one site of Cu^{2+} is observed. The principal g and A values are evaluated from the EPR spectra fitted to rhombic symmetry spin Hamiltonian. The Cu^{2+} ion enters the lattice interstitially. The ground state wave function of Cu^{2+} in the lattice is constructed, which contains about 21% admixture of 4p state. The optical absorption has been explained well in terms of D2d symmetry of the oxygen ligands in the Cu^{2+} complex. The MO coefficients calculated for Cu^{2+} doped lithium maleate dihydrate single crystal shows that the σ -bonding is strongly covalent while the bonding between the Cu^{2+} ion and its axial ligands is mostly ionic.

Table 1. Spin Hamiltonian parameters for Cu^{2+} ion site in Lithium Maleate Dihydrate single crystal

Principal values of g- tensor	Direction cosine			Principal values of A-tensor($\times 10^{-4} \text{ cm}^{-1}$)	Direction cosines		
	a	b	c*		a	b	c*
$g_x = 2.098$	-0.2165	-0.3159	0.9238	$A_x = 55$	-0.5281	-0.6139	0.5867
$g_y = 2.150$	-0.5037	0.8467	0.1715	$A_y = 52$	-0.7959	0.5988	0.0898
$g_z = 2.208$	-0.8363	-0.4282	-0.3424	$A_z = 50$	-0.2961	-0.5143	0.8048

Estimated errors for g and A values are ± 0.002 and $\pm 5 \times 10^{-4} \text{ cm}^{-1}$, respectively.

Table2. Spin Hamiltonian parameters for Cu^{2+} ion in different lattices performed by earlier workers

Lattices	g_x	g_y	g_z	A_x	A_y	A_z
	$(\times 10^{-4} \text{ cm}^{-1})$					
$\text{Cs}_2\text{ZnCl}_4:\text{Cu}^{2+}$	2.083 ± 0.004	2.101 ± 0.003	2.446 ± 0.002	51 ± 5	46 ± 5	25 ± 4
$\text{C}_2\text{H}_8\text{N}_2\text{ZnCl}_2:\text{Cu}^{2+}$	2.058 ± 0.002	2.062 ± 0.002	2.297 ± 0.00	9 ± 4	9 ± 4	123 ± 4
$\text{ZnC}_{28}\text{H}_{36}\text{N}_6\text{O}_6:\text{Cu}^{2+}$	2.02 ± 0.002	2.09 ± 0.002	2.163 ± 0.002	30 ± 2	40 ± 2	154 ± 2

Table 3. Distances and direction cosines of various Li-O and O-O vectors in Lithium Maleate Dihydrate single crystal

Bond	Distance (Å)	Direction cosines		
		a	b	c*
Li(1)-O(1)	1.9107	± 0.9827	±0.3016	±0.4904
Li(1)-O(2)	6.0703	±0.9568	±0.1791	± 0.0782
Li(1)-O(3)	2.0151	±0.1115	±0.9813	±0.1946
Li(1)-O(4)	11.0920	±0.1509	±0.2193	±0.9184
Li(1)-O(5)	5.5747	±0.1691	±0.9631	±0.1635
Li(1)-O(6)	8.9286	±0.1619	±0.9843	± 0.0357
Li(2)-O(1)	4.7869	±0.6814	±0.7412	±0.0359
Li(2)-O(2)	5.9449	±0.7441	±0.6828	±0.0487
Li(2)-O(3)	2.0217	±0.7960	±0.4917	±0.1843
Li(2)-O(4)	12.2586	±0.2494	±0.0439	±0.8934
Li(2)-O(5)	4.0475	±0.5749	±0.5923	±0.4142
Li(2)-O(6)	6.7020	±0.4223	±0.8679	±0.1617
O(1)-O(2)	7.5737	±0.9960	±0.0662	±0.0598
O(1)-O(3)	2.9993	±0.5510	±0.8515	±0.1816
O(1)-O(4)	11.4658	±0.0177	±0.2624	±0.9702
O(1)-O(5)	6.2109	±0.1505	±0.9572	±0.2976
O(1)-O(6)	9.4413	±0.0457	±0.9919	± 0.1331
O(2)-O(3)	10.1415	±0.5949	±0.3022	± 0.0081
O(2)-O(4)	16.3904	±0.4565	±0.2147	±0.6505
O(2)-O(5)	11.942	±0.5653	±0.5406	±0.1161

Table 4. Experimental and calculated energies together with D_s and D_t of d-d transfer band

Transition	Band position(cm ⁻¹)		D _s (cm ⁻¹)	D _t (cm ⁻¹)
	Observed	Calculated		
d _{xy} ↔ d _{x²-y²}	11253	7998	1653	4948
d _{xy} ↔ d _{xy,yz}	15770	15815		
d _{xy} ↔ d _{3z2-r2}	19383	19186		

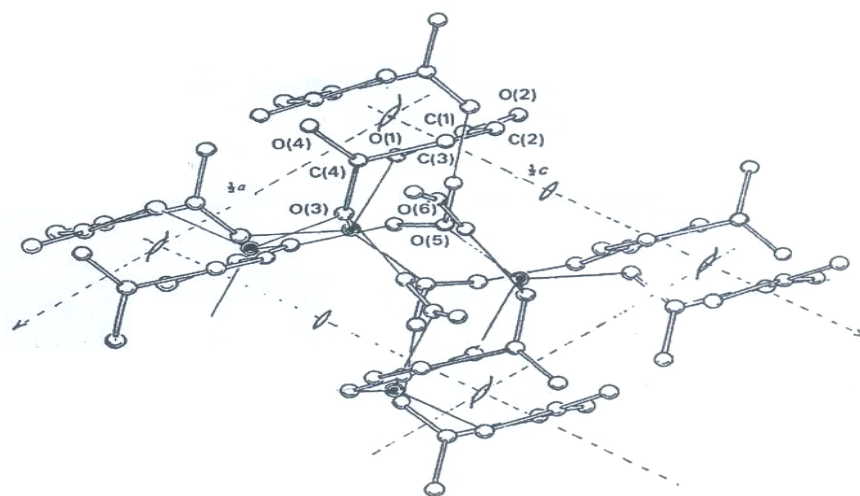


Fig. 1. Projection of crystal structure along b-axis

Table 5. Molecular-orbital coefficients and Fermi contact parameter for Cu^{2+} ion in Lithium Maleate Dihydrate single crystal

α^2	η^2	γ^2	ξ^2	K	$M(\times 10^{-4})$
0.28	0.21	0.97	0.001	0.38	16.047

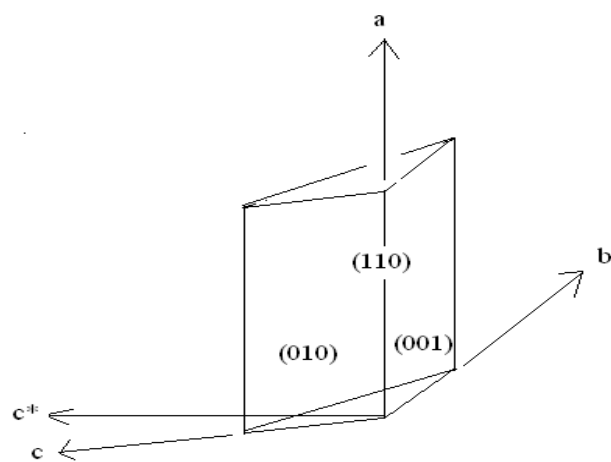


Fig. 2. Morphology and orientation of axes of the crystal

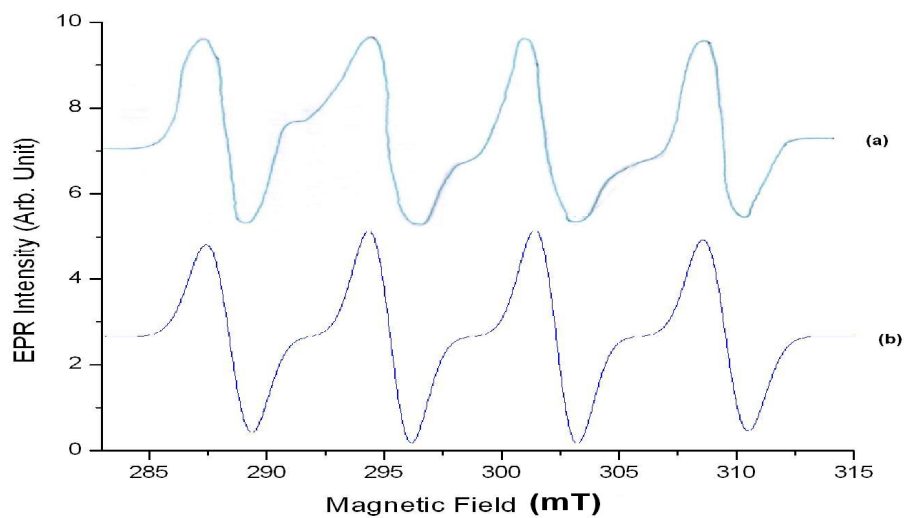


Fig. 3(a). EPR spectrum of Cu^{2+} doped lithium maleate dihydrate crystal in ab- plane for the magnetic field at angle 0° from the a axis (frequency 9.1 GHz)

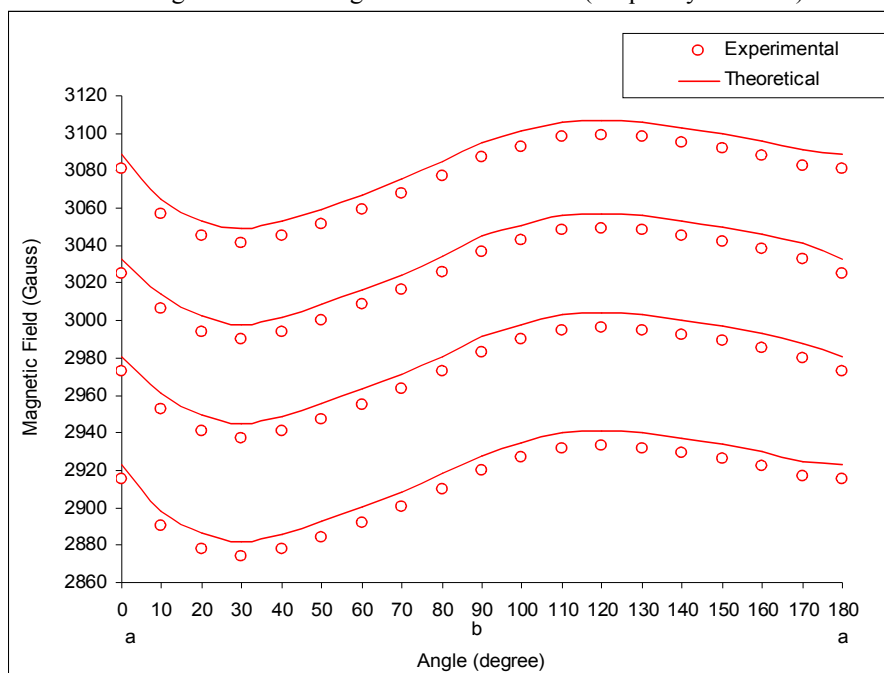


Fig 4(a). Angular variation of EPR line position of Cu^{2+} doped in Lithium Maleate Dihydrate in ab plane

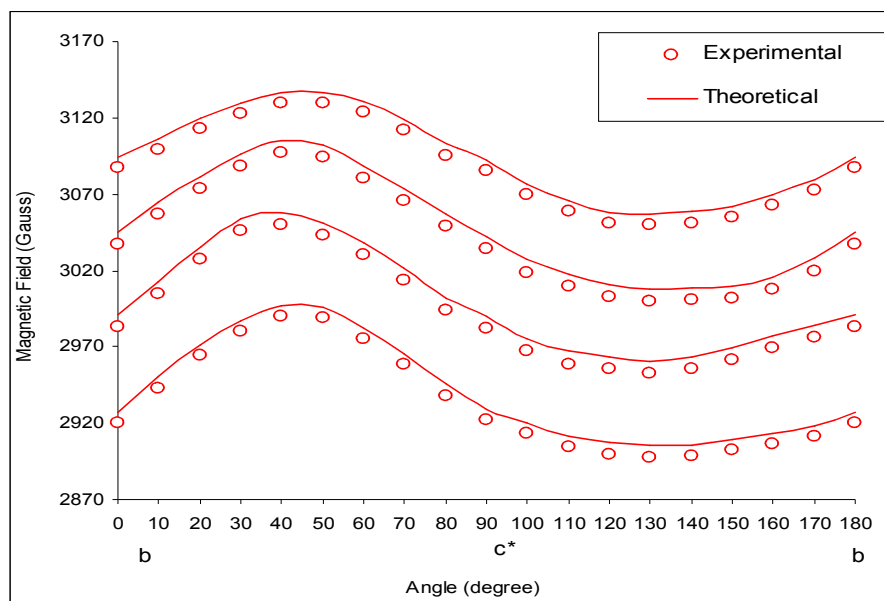


Fig 4(b). Angular variation of EPR line position of Cu^{2+} doped in Lithium Maleate Dihydrate in bc^* plane

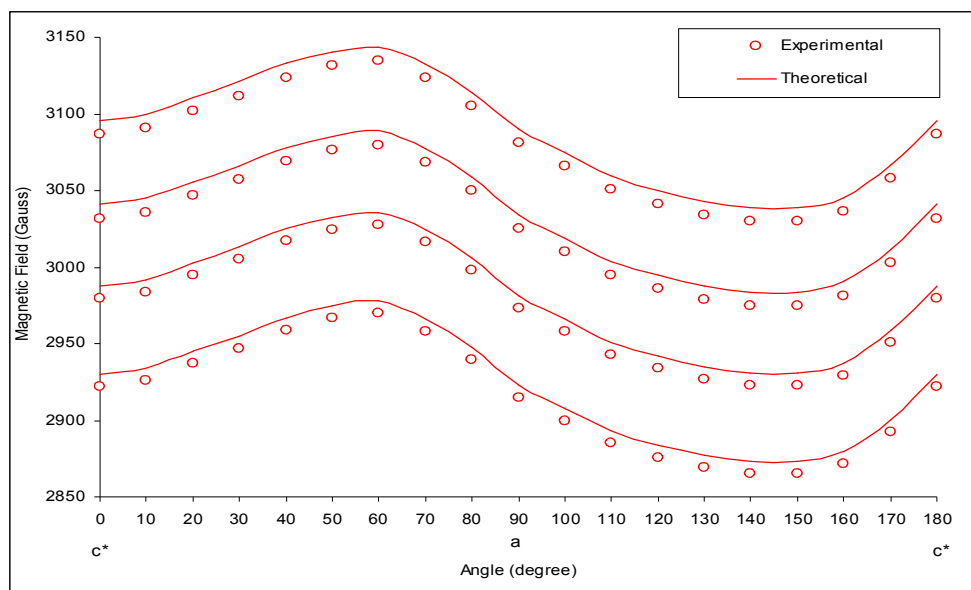


Fig 4(c). Angular variation of EPR line position of Cu^{2+} doped in Lithium Maleate Dihydrate in c^*a plane

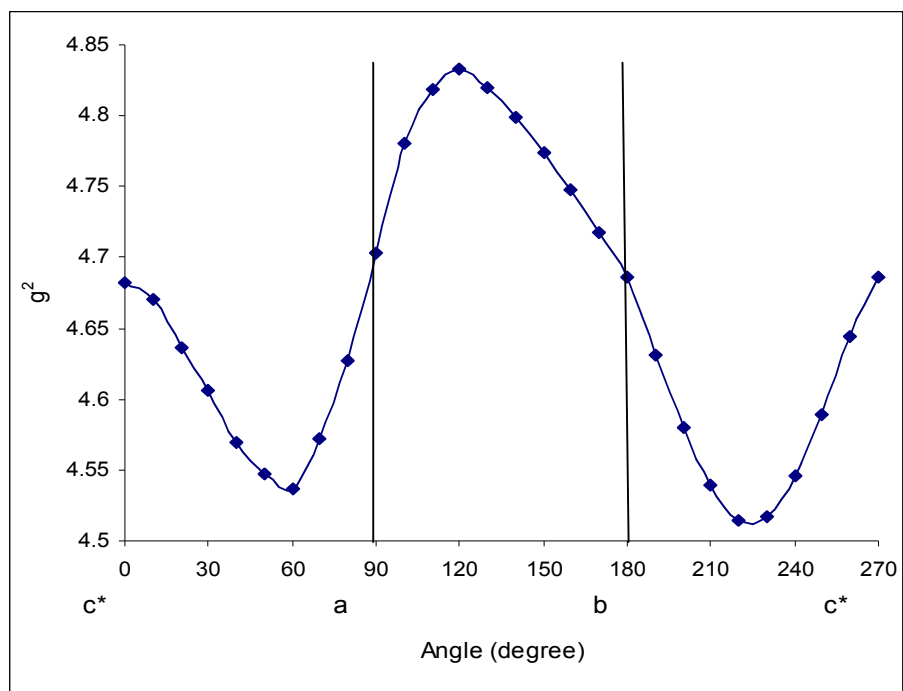


Fig 5(a). Angular variation of g^2 for B in ab, bc* and c*a planes for Cu^{2+} doped in Lithium Maleate Dihydrate

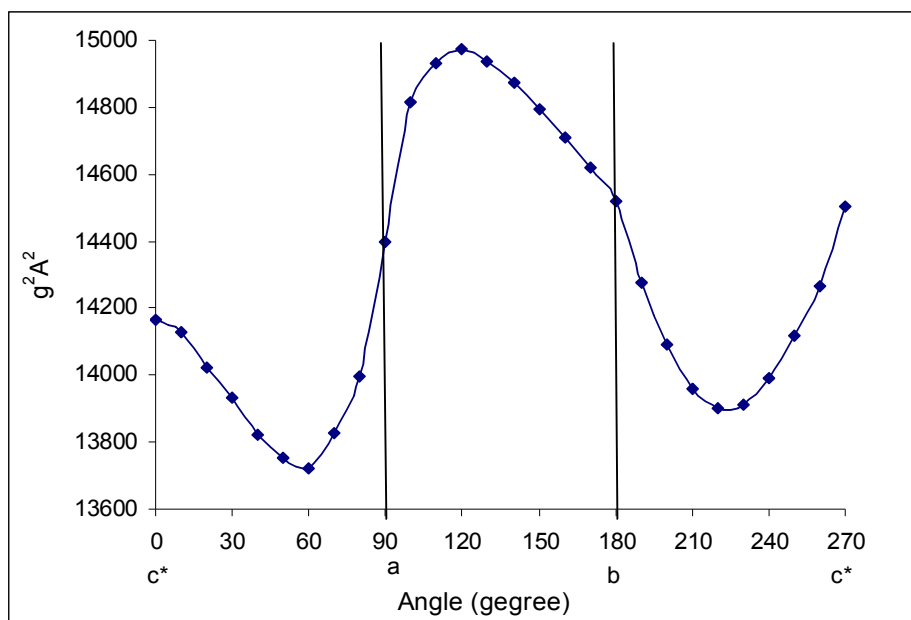


Fig. 5(b). Angular variation of g^2A^2 for B in ab, bc* and c*a planes for Cu^{2+} doped in Lithium Maleate Dihydrate

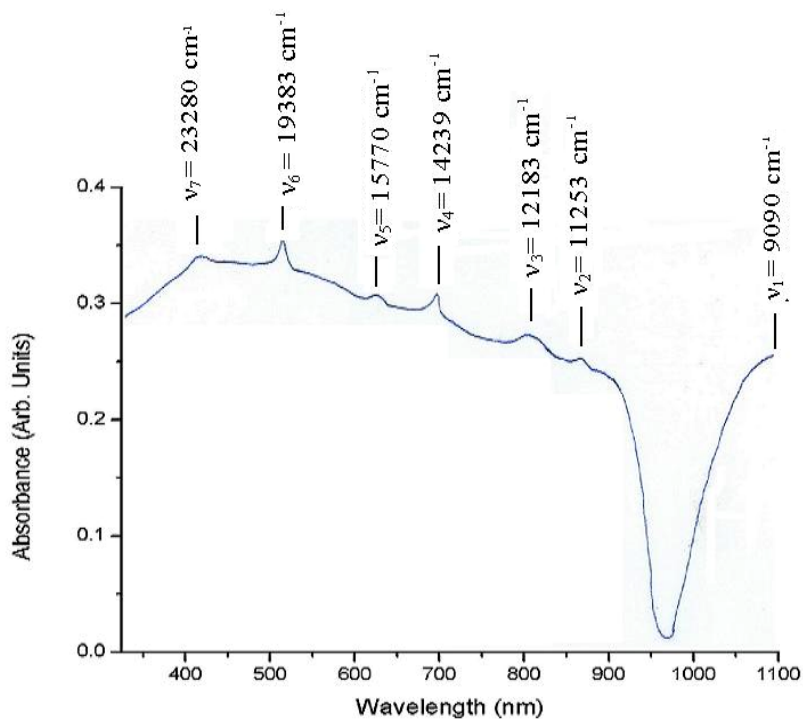


Fig..6(a) Room temperature absorption spectrum in wavelength range 325-1100 nm. The lines indicated by 1-6 correspond to ν_1 to ν_6 , respectively, as cited in text.

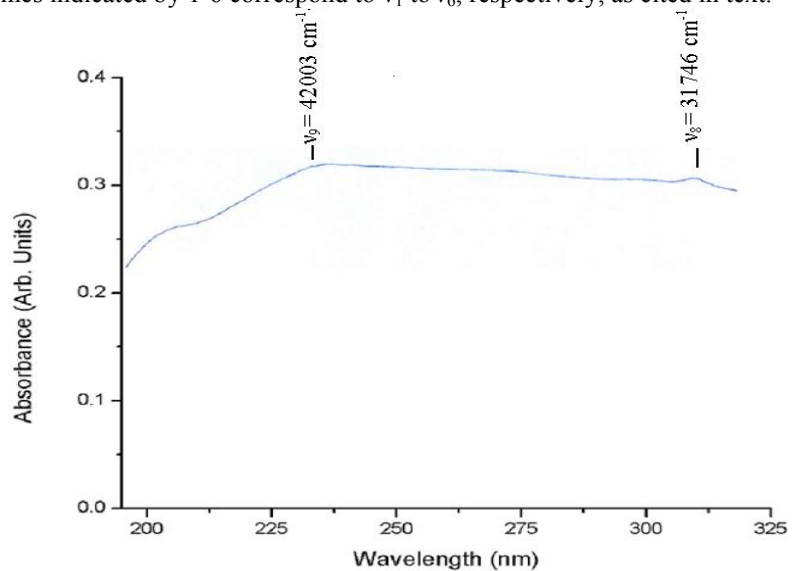


Fig..6(b). Room temperature absorption spectrum in wavelength range 195-325 nm. The lines indicated by 7-9 correspond to ν_7 to ν_9 , respectively, as cited in text.

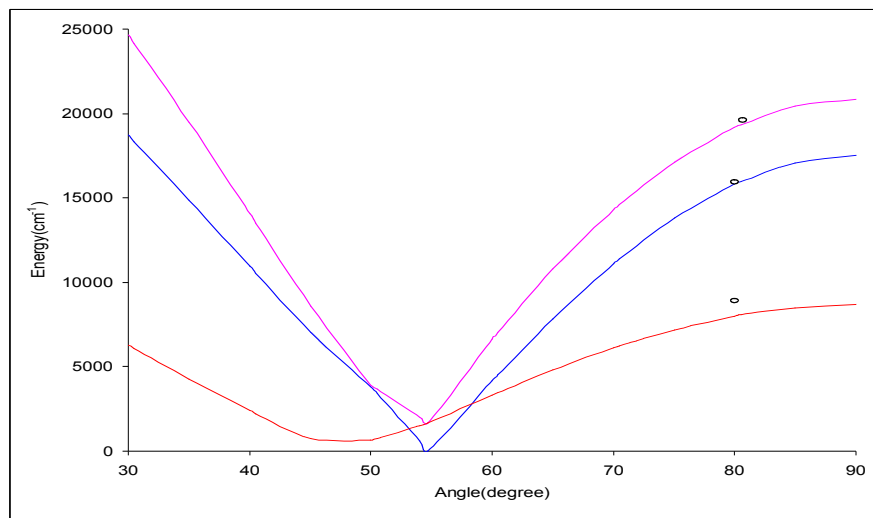


Fig.7. The plot of orbital splitting with respect to ground state (Cu- ligand separation= $1.94\text{\AA}$ and $q=5.7e$ are taken)

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