

A theoretical analysis of zero-field splitting parameters of Mn²⁺ in zinc lactate trihydrate

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Abstract— The superposition model is used to investigate the crystal field parameters (CFP) of Mn²⁺ ion in single crystal of zinc lactate trihydrate, and then zero-field splitting (ZFS) parameters *D* and *E* are also evaluated by the perturbation formulae. These calculated values of ZFS parameters match well with the experimental values evaluated by electron paramagnetic resonance (EPR) at room temperature. With the help of CFA package and crystal field parameters evaluated by superposition model the energy band positions of optical absorption spectra of Mn²⁺ doped zinc lactate trihydrate are evaluated and compared with the experimental results.

Keywords— A. Organic crystal; C. Crystal structure and symmetry; D. Crystal and ligands fields; D. Spin-orbit effects; E. Electron paramagnetic resonance.

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I. INTRODUCTION

Theoretical analysis predicts zero-field splitting (ZFS) parameters which would provide guidance for experiment. The crystal field theory is widely used in the theoretical study of the spin Hamiltonian parameters of d⁵ (6S) ions [1-5]. Using the formulae derived in these works, ZFS parameters are determined by the electrostatic, the spin-orbit coupling, and the crystal-field parameters of the d⁵ ion in a crystal. To obtain the crystal-field parameters, two models, namely the point-charge model and superposition model were used for some 3dⁿ ions e.g. Cr³⁺; Al₂O₃ [6] and Fe²⁺ in garnets [7] and the results are satisfactory. These two models establish relations between the crystal field (CF) parameters and crystal-structure properties.

Host lattice provides valuable information about structural changes possible when small concentration of paramagnetic impurity is doped. Out of all transition metal of iron group, Mn²⁺ is important because its ground state is 6S_{5/2} [8-12]. The electron spin is affected by high order interaction of crystalline electric field, and in the presence of external magnetic field orientation of spins are free [13]. The spin-lattice relaxation time is large for S state ions, due to this property Mn²⁺ shows fine EPR spectra [12, 14-16] at room temperature.

Theoretical studies based on spin Hamiltonian of d⁵ (6S) ions are very interesting and useful for the studies of orbit lattice interaction [17-22]. Three perturbation procedures can be used for the study of effect of spin Hamiltonian mechanism. According to first and second procedures spin-orbit coupling, the low-symmetry components of the crystal field and the total crystal field, the spin-orbit interaction are used as perturbation terms. And for third procedure spin-orbit coupling, the low-symmetry field, and the off-diagonal part of free-ion Hamiltonian are used as perturbation terms, cubic field and the diagonal part of the free-ion Hamiltonian are used as unperturbed Hamiltonian. This procedure shows good results described by Macfarlane for F-state ions [23].

In this paper, we present the evaluated ZFS parameters for the Mn²⁺ ion in zinc lactate trihydrate (ZLT) under the assumption that this ion occupies the interstitial site. For the calculation of ZFS parameters, Newman superposition model [6, 24] and perturbation expressions are used [25].

II. CRYSTAL STRUCTURE

The crystal structure of zinc lactate trihydrate, Zn (CH₃CHOHCOOH)₂.3H₂O is monoclinic having space group P2₁/c, and the unit cell dimensions are a=9.38Å, b=5.83 Å and c=22.00 Å [26]. There exist six oxygen atoms, two from water molecules and four from two lactate groups are nearest neighbors of Zn and they form a distorted octahedron around the zinc atom. In hydrogen bonding all three water molecules inter, and hydroxyl groups in molecules are also involved. A network of hydrogen bonds plays an important role in stabilization of the structure.

Theoretical investigation

When Mn²⁺ ion is embedded in a crystal, the spin is affected by the crystal field produced by the neighboring ion because the 3d shell of the Mn²⁺ ion is the outer most one. The experimental results for the resonance field of Mn²⁺ ion in ZLT can be analyzed with the spin-Hamiltonian [27]

$$\begin{aligned} \mathcal{H} = & g\mu_B B \cdot S + D\{S_z^2 - \frac{1}{3}S(S+1)\} \\ & + E(S_x^2 - S_y^2) + \left(\frac{a}{6}\right)[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)] \\ & + \frac{F}{180}\{35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2\} \\ & + \frac{K}{4}[\{7S_z^2 - S(S+1) - 5\}(S_+^2 + S_-^2) + (S_+^2 + S_-^2)\{7S_z^2 - S(S+1) - 5\}] + A(S_z I_z) + B(S_x I_x + S_y I_y) \dots (1) \end{aligned}$$

where B is the external magnetic field, g is the spectroscopic splitting factor, μ_B is Bohr magneton, D and E are second order axial and rhombic ZFS parameters, S is effective spin vector. a, F, and K represent the fourth-rank cubic, axial and rhombic ZFS parameters, respectively. The last two terms show the hyperfine interaction. In above equation the effect of F and K terms are small so we can leave out these terms [14, 27, 28]. Isotropic electronic Zeeman interaction approximation used here is generally valid for Mn²⁺ ions [14, 29]. These two approximations in question may slightly affect the fitted value of a [27]. From EPR spectra, the z axis is taken as the direction of the maximum overall splitting, and the direction of the minimum splitting is the x axis [30]. With the help of EPR spectra the laboratory axes (x, y, z) are assigned and these coincide with the crystallographic axes (CA). The Z- axis of the local site symmetry axes, i.e. the symmetry adopted axes (SAA) is along the metal-oxygen bond and the other two axes (X, Y) are perpendicular to Z.

The Hamiltonian for a d5 ion can be expressed as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{cf} + \mathcal{H}_{so} + \mathcal{H}_{ss}, \dots (2)$$

in which, $\mathcal{H}_{cf} = \sum_{kq} B_{kq} C_q^{(k)}$

represent the crystal field Hamiltonian, \mathcal{H}_{so} , \mathcal{H}_{ss} and \mathcal{H}_0 are spin-orbit, spin-spin couplings and free ion Hamiltonian, respectively. Due to spin-spin coupling being very small, spin-orbit interaction called as spin-orbit (SO) mechanism plays important effect in above eqⁿ. The total crystal field with the SO interaction is taken as perturbation term [19, 31] or calculation is performed in the strong-field scheme as done by Macfarlane for F-state ions [32]. In spin Hamiltonian parameters the contribution of spin-spin interaction called as spin-spin (SS) mechanism [33] is much smaller than SO mechanism [34, 35].

In ZLT, oxygen atoms form a distorted octahedron around the zinc atom [26], and there exists nearly orthorhombic symmetry of first kind (OR-I) local symmetry [36]. In case of (OR-I) symmetry, the SO contributions to the ZFS parameters D and E for 3d5 ions are written below [25, 37].

$$\begin{aligned} D^{(4)}(SO) &= \left(\frac{3\xi^2}{70P^2D}\right)[-B_{20}^2 - 21\xi B_{20} + 2B_{22}^2] + \left(\frac{\xi^2}{63P^2G}\right)[-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2] \dots (3), (4) \\ E^{(4)}(SO) &= \left(\frac{\sqrt{6}\xi^2}{70P^2D}\right)[2B_{20} - 21\xi]B_{22} + \left(\frac{\xi^2}{63P^2G}\right)[3\sqrt{10}B_{40} + 2\sqrt{7}B_{44}]B_{42} \end{aligned}$$

where P= 7(B+C), D= 17B+5C and G= 10B+5C. Here the electron-electron repulsion is described by the Racah parameters B and C. In above equation only fourth order term is considered as other perturbation terms are zero/very small [25]. Considering the effect of covalency, the parameter B, C and ξ_d are given in terms of N as $B = N^4 B_0$, $C = N^4 C_0$ and $\xi = N^2 \xi_0$, where N is the average covalency parameter; B₀, C₀ and ξ_0 represent the Racah and spin orbit coupling parameters, respectively for free ion [21, 38]. For free Mn²⁺ ion: B₀ = 960 cm⁻¹, C₀ = 3325 cm⁻¹, ξ_0 = 336 cm⁻¹ are used [14] here.

From optical study [39] we calculated B= 778 cm⁻¹ and C= 3083 cm⁻¹. Further, N is given as [40]

$$N = (\sqrt{B/B_0} + \sqrt{C/C_0})/2 \dots (5)$$

N is determined using above equation. With the help of superposition model the crystal-field parameters B_{kq} for Mn^{2+} in ZLT single crystal are calculated and ZFS parameters are then obtained using Eqs. (3) and (4).

3.1 Superposition model

The superposition model is successfully used to the analyses of the crystal-field splitting. According to this model the crystal field parameters are expressed as [25, 41, 42]

$$B_{kq} = \sum \bar{A}_k(R_j) k_{kq}(\theta_j, \phi_j) \quad (6)$$

where R_j represents the distances between the ligand ion j and paramagnetic ion Mn^{2+} where as R_0 shows the reference distance, normally chosen near a value of the R_j 's and θ_j represents the bond angle in chosen axis system [24, 41]. $K_{kq}(\theta_j, \phi_j)$, called the coordination factor, are the explicit functions of angular position of ligand [24, 25, 42, 43]. $\bar{A}_k(R_j)$, the intrinsic parameter is expressed by the power law [19, 44]

$$\bar{A}_k(R_j) = \bar{A}_k(R_0) \left(\frac{R_0}{R_j} \right)^{t_k} \quad (7)$$

where $\bar{A}_k(R_0)$ is intrinsic parameter for a given ion and symbol t_k is the power law exponent. The crystal-field parameters B_{kq} , given in Appendix A, are calculated with the help of Eq. (6) [45]. For six- fold cubic coordination, $\bar{A}_4(R_0)$ is expressed as $\bar{A}_4(R_0) = (3/4)Dq$ [25] and for $3d^5$ ions the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 8-12$ [7, 17]. Here in our calculation, the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ is taken as 12 (as smaller ratio yields small D and E). Using $Dq = 760 \text{ cm}^{-1}$ [39], we calculated $\bar{A}_4(R_0) = 570 \text{ cm}^{-1}$ and $\bar{A}_2(R_0) = 6840 \text{ cm}^{-1}$. The power law exponents for Mn^{2+} ion are adopted as $t_2 = 3$, $t_4 = 7$ [17].

III. RESULT AND DISCUSSION

ESR and optical study of Mn^{2+} doped ZLT single crystal [39] show that the direction cosines of the distortion axis doesn't match with Zn-O directions, but nearly coincides with the direction cosines of O(9)-O(3) bond indicating that Mn^{2+} ions are expected to occupy an interstitial site in the lattice. In our study we calculate the distances of the ligands, R_j with corresponding angle θ_j (coordination about Mn^{2+} is shown in Fig. 1) as given in Table 1. Our aim is to determine the approximate position of Mn^{2+} ion along the O(9)-O(3) bond. To do this, first of all we check it at mid point of O(9)-O(3) bond. Taking $R_0 = 0.15 \text{ nm}$ [46] the values of D and E come out as $D = 2432 \times 10^{-4} \text{ cm}^{-1}$, $E = 1186 \times 10^{-4} \text{ cm}^{-1}$, $E/D = 0.49$. From EPR study the experimental values are $D = 330 \times 10^{-4} \text{ cm}^{-1}$ and $E = 103 \times 10^{-4} \text{ cm}^{-1}$ [39]. Here we see that our calculated values are very large. Further, by decreasing the value of R_0 we check our results. By doing this we find that D and E are again large. When we take $R_0 = 0.1 \text{ nm}$, which is smaller than the sum of ionic radii of Mn^{2+} and O^{2-} (ionic radii of $Mn^{2+} = 0.08 \text{ nm}$ and $O^{2-} = 0.132 \text{ nm}$ [47]), then we get $D = 288 \times 10^{-4} \text{ cm}^{-1}$, $E = 129 \times 10^{-4} \text{ cm}^{-1}$ and $E/D = 0.46$. Here D and E are near to the experimental values but E/D is not standardized (standardized $E/D < 1/3$ [30]). Now to make our result standardized we use distortion in x, y and z directions as; $x = -0.16$, $y = +0.3$ and $z = -0.09$ and $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 8$, then the values of D and E come out to be $D = 148 \times 10^{-4} \text{ cm}^{-1}$, $E = 49 \times 10^{-4} \text{ cm}^{-1}$ and $E/D = 0.33$. In this case, the value of D and E is smaller than the experimental value. But when we take $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 12$, the standardized results come out to be in reasonable agreement with the experimental values [39], given as $D = 284 \times 10^{-4} \text{ cm}^{-1}$, $E = 95 \times 10^{-4} \text{ cm}^{-1}$, $E/D = 0.33$ and $B_{22}/B_{20} = 0.41$.

With the help of Eqs. (A1) - (A5) B_{kq} parameters are calculated and the values are given as:

$B_{20} = -57420.0 \text{ cm}^{-1}$, $B_{22} = -23413.0 \text{ cm}^{-1}$, $B_{40} = -11581.0 \text{ cm}^{-1}$, $B_{42} = 2557.0 \text{ cm}^{-1}$, $B_{44} = 1109.0 \text{ cm}^{-1}$. These standardized CF parameters are obtained by applying S5 transformation [30]. The calculated ZFS parameters for Mn^{2+} ion in ZLT single crystal by using Eqs. (3), (4) are given in Table 2 together with experimental values and values in other hosts [48-50] for comparison. It is noted that the orthorhombic distortion is stronger in crystals having fluorine ligands as compared to the crystals with oxygen ligands. Optical spectra of Mn^{2+} doped ZLT are theoretically calculated with the help of B_{kq} parameters and CFA program [3, 5, 51]. The CFA program calculates energy levels of the impurity ion by diagonalization of the complete Hamiltonian within the $3d^5$ basis of states in the intermediate CF coupling scheme. The calculated energy values are given in Table 3 together with the experimental ones for the purpose of comparison. A reasonable agreement is obtained between the two.

TABLE 1

LIGAND DISTANCES R_j AND ANGLES θ_j FOR Mn^{2+} ION IN ZINC LACTATE TRIHYDRATE SINGLE CRYSTAL WHEN Mn^{2+} IS LOCATED AT MID POINT OF O (9)-O (3) BOND.

Ligands	Distance R_j (nm)	Angle θ_j (degree) ($\theta_j = \angle LMnZ$)
O(1)	0.2135	46.2
O(3)	0.1312	44.1
O(6)	0.2724	50.8
O(9) w	0.1744	64.0

L = ligand, Mn = metal ion, Z = z-axis.

TABLE 2

COMPARISON OF THE ZFS PARAMETERS CALCULATED FOR Mn^{2+} ION IN ZLT SINGLE CRYSTAL WITH EXPERIMENTAL VALUES TOGETHER WITH VALUES IN OTHER HOSTS.

Host	D ($\times 10^{-4} \text{ cm}^{-1}$)	E ($\times 10^{-4} \text{ cm}^{-1}$)	Ref.
ZLT	284 ³	95 ^a	Present work
	330 ^b	103 ^b	
ZnF ₂	32.8 ^a	120 ^a	[48]
	31.5 ^b	113.5 ^b	
Zn(L-asn) ₂	227 ^a	69 ^a	[49]
	228 ^b	58 ^b	
DGCCT	288 ^a	58 ^a	[50]
	276 ^b	58 ^b	

ZLT = zinc lactate trihydrate, ZnF₂ = zinc fluoride, Zn (L-asn)₂ = bis (L-asparaginato) zinc, DGCCT = diglycine calcium chloride tetrahydrate.

^a = calculated, ^b = experimental.

TABLE 3

EXPERIMENTAL AND THEORETICAL ENERGY VALUES OF DIFFERENT TRANSITIONS IN Mn^{2+} DOPED ZLT.

Transition from ${}^6A_{1g}(S)$	Observed wavenumber (cm^{-1})	Calculated wavenumber (cm^{-1})
${}^4T_{1g}(G)$	18980	14161, 14856, 15385, 17483, 18050, 19600
${}^4T_{2g}(G)$	22969	20737, 20754, 22478, 23835, 23966, 24067
${}^4E_g(G)$	24697	24154, 24216, 24506, 26348
${}^4T_{2g}(D)$	27380	27321, 27347, 27791, 28040, 28903, 30877
${}^4E_g(D)$	29137	31503, 31585, 31606, 33267
${}^4T_{1g}(P)$	32154	33287, 33292, 33306, 33787, 3984, 35117

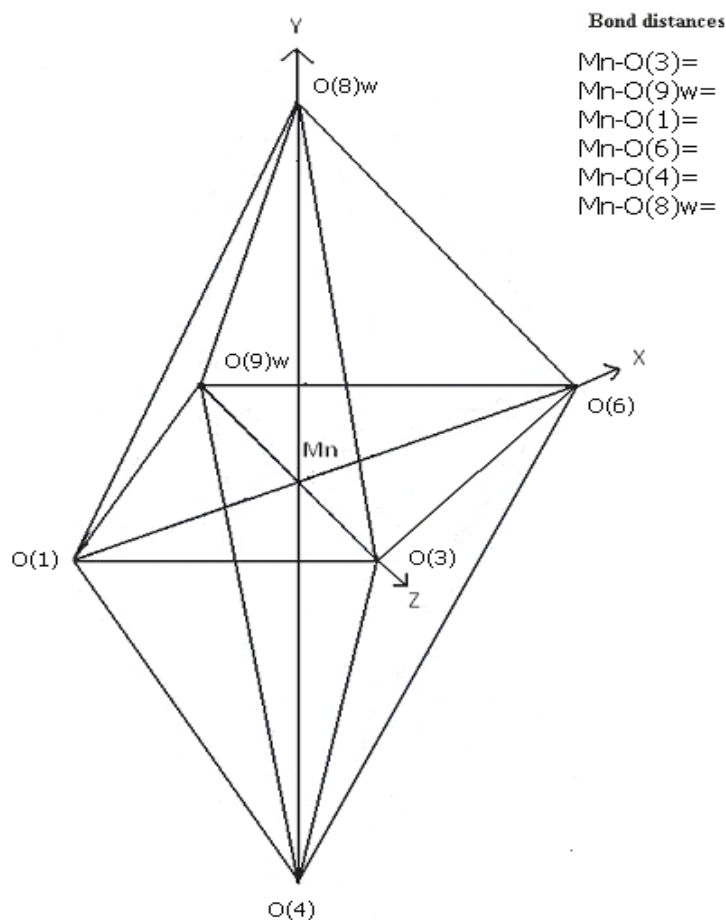


FIG. 1 COORDINATION ABOUT MN²⁺ ION IN ZLT

IV. CONCLUSION

Zero-field splitting parameters have been investigated with the help of superposition model and perturbation formulae. The calculated ZFS parameters for the Mn²⁺ ion at the interstitial site in ZLT single crystal fairly match with the experimental values. The calculated optical energy levels using CFA package are in reasonable agreement with the experimental values. This suggests that the Mn²⁺ ion occupies an interstitial site in ZLT, which is consistent with the experimental result obtained earlier.

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Appendix A

The crystal field parameters B_{kq} for Mn^{2+} at orthorhombic symmetry site using Eq. (6) are:

$$B_{20} = \bar{A}_2 R_0 \left[\left(\frac{R_0}{R_1} \right)^{t_2} (3 \cos^2 \theta_1 - 1) + \left(\frac{R_0}{R_1'} \right)^{t_2} (3 \cos^2 \theta_1' - 1) + \left(\frac{R_0}{R_2} \right)^{t_2} (3 \cos^2 \theta_2 - 1) + \left(\frac{R_0}{R_2'} \right)^{t_2} (3 \cos^2 \theta_2' - 1) \right] \quad A1$$

$$B_{22} = \frac{1}{2} \sqrt{6 \bar{A}_2} R_0 \left[\begin{aligned} & \left(\frac{R_0}{R_1} \right)^{t_2} \sin^2 \theta_1 + \left(\frac{R_0}{R_1'} \right)^{t_2} \sin^2 \theta_1' - \left(\frac{R_0}{R_2} \right)^{t_2} \sin^2 \theta_2 \\ & + \left(\frac{R_0}{R_2'} \right)^{t_2} \sin^2 \theta_2' \end{aligned} \right] \quad A2$$

$$B_{40} = \bar{A}_4 R_0 \left[\begin{aligned} & \left(\frac{R_0}{R_1} \right)^{t_4} (35 \cos^4 \theta_1 - 30 \cos^2 \theta_1 + 3) + \left(\frac{R_0}{R_1'} \right)^{t_4} (35 \cos^4 \theta_1' - 30 \cos^2 \theta_1' + 3) \\ & + \left(\frac{R_0}{R_2} \right)^{t_4} (35 \cos^4 \theta_2 - 30 \cos^2 \theta_2 + 3) + \left(\frac{R_0}{R_2'} \right)^{t_4} (35 \cos^4 \theta_2' - 30 \cos^2 \theta_2' + 3) \end{aligned} \right] \quad A3$$

$$B_{42} = \sqrt{10 \bar{A}_4} R_0 \left[\begin{aligned} & \left(\frac{R_0}{R_1} \right)^{t_4} \sin^2 \theta_1 (7 \cos^2 \theta_1 - 1) + \left(\frac{R_0}{R_1'} \right)^{t_4} \sin^2 \theta_1' (7 \cos^2 \theta_1' - 1) \\ & - \left(\frac{R_0}{R_2} \right)^{t_4} \sin^2 \theta_2 (7 \cos^2 \theta_2 - 1) + \left(\frac{R_0}{R_2'} \right)^{t_4} \sin^2 \theta_2' (7 \cos^2 \theta_2' - 1) \end{aligned} \right] \quad A4$$

$$B_{44} = \frac{1}{2} \sqrt{70 \bar{A}_4} R_0 \left[\begin{aligned} & \left(\frac{R_0}{R_1} \right)^{t_4} \sin^4 \theta_1 + \left(\frac{R_0}{R_1'} \right)^{t_4} \sin^4 \theta_1' \\ & + \left(\frac{R_0}{R_2} \right)^{t_4} \sin^4 \theta_2 + \left(\frac{R_0}{R_2'} \right)^{t_4} \sin^4 \theta_2' \end{aligned} \right] \quad A5$$