

Theoretical Zero Field Splitting Parameters of Mn^{2+} doped BCCD Single Crystal

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Abstract -The superposition model (SPM) has been used to find crystal field (CF) parameters of Mn^{2+} doped betaine calcium chloride dihydrate (BCCD) single crystals. The zero field splitting (ZFS) parameters D and E are then estimated using perturbation theory. These parameters show good matching with the experimental values indicating thereby that the Mn^{2+} ion substitutes at Ca^{2+} site in BCCD single crystal. The CF energy levels of the Mn^{2+} ion determined by diagonalizing the complete Hamiltonian are in reasonable agreement with the experimental ones. The process used may be applied for the modeling of other ion-host systems to explore the applications of crystals in technology and industry.

Keywords: A. Inorganic compounds; A. Single Crystal; C. Crystal structure and symmetry; D. Crystal and ligand fields; D. Optical properties; E. Electron paramagnetic resonance.

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I. INTRODUCTION

A review of the superposition model (SPM) has been presented [1] with reference to its applications in electron paramagnetic resonance (EPR) spectroscopy of transition ions in crystals. SPM provides semi-empirical modeling of the zero field splitting (ZFS) parameters and crystal field (CF) parameters used in EPR spectroscopy [2–7] and optical spectroscopy [8–12], respectively. The origin of the physical CF Hamiltonian, H_{CF} , and the effective spin Hamiltonians (SH), H_{SH} , including ZFS Hamiltonian, H_{ZFS} together with their areas of applicability have been described [13-19].

SPM and point-charge model are generally used to calculate the crystal field (CF) parameters [13, 20]. Moreover, the exchange charge model (ECM) is also a powerful and reliable tool for analysis and interpretation of the crystal field effects in rare-earth and transition metal ion doped crystals [21]. In the present study, we have calculated the ZFS parameters and CF parameters B_{kq} using SPM. Newman [22] proposed superposition model for CF based on the following assumptions: (1) The CF at a paramagnetic ion can be expressed as an algebraic sum of contributions from other ions in the crystal. (2) When the paramagnetic ion is at origin of a chosen coordinates frame, all the major CF contributions from every ion in the crystal are axially symmetric with respect to its position vector. (3) Only neighboring or coordinated ions need to be considered for their CF contributions. (4) CF contributions from single ion (ligand) are transferable across different host crystals. The first assumption implies the validity of the superposition principle in describing the CF while the axial symmetry assumption (2) allows to freely transform one coordinate frame to another. However, a more restrictive form of assumption (3) is often adopted in which only the nearest neighbour ions are considered. The last assumption (4) on ligand transferability means that the CF contributions from a single ligand depend only on the ligand type and its distance from the paramagnetic ion. In order to carry out a SPM analysis of the CF splitting, an almost pre-requisite condition is to have a reliable set of polar coordinates (R_L , θ_L , Φ_L) for all the ligands concerned as obtained from the X-ray data of the host crystal. If transition metal ions are doped as impurities, they will probably induce certain amount of local distortion or lattice relaxation due to the mismatch in the ionic charge, ionic size and / or inter-ionic bonding. If there is sufficient number of CF parameters, a linear or non-linear least-square fit may be applied to those CF parameters to obtain the fitted values of the SPM intrinsic parameters and the power-law exponents. Newman & Siegel [23] made a critical analysis of the experimental spin-Hamiltonian parameters for Mn^{2+} and Fe^{3+} in CaO and MgO crystals verifying that the CF for 3d ions satisfies the superposition principle and provides explicit values of the SPM parameters for the EPR data. Yeung & Newman [24] developed a rigorous lattice relaxation model to calculate the locally distorted ligand positions for the Eu^{2+} at the orthorhombic sites in various alkali halides. Yeung [25] applied the similar

approach to a reliable set of ligand distances as calculated for the alkaline earth oxides to obtain sets of SPM intrinsic parameters ($R_0 = 2.0 \text{ \AA}$) for Mn^{2+} and Fe^{3+} doped MgO, CaO and SrO: $\overline{b_2} = (-1552 \pm 48) \times 10^{-4} \text{ cm}^{-1}$ (for Fe^{3+}) and $(-6440 \pm 113) \times 10^{-4} \text{ cm}^{-1}$ (for Mn^{2+}) with fixed $t_2 = 16$ for both ions. $\overline{b_4} = (9.9 \pm 0.8) \times 10^{-4} \text{ cm}^{-1}$ (for Fe^{3+} and Mn^{2+}) with fixed $t_4 = (16 \pm 4)$ for both ions. For separate fitting of t_2 , the fitted values were 17.7 and 14.4 for Mn^{2+} and Fe^{3+} , respectively.

Betaine is a methyl group donor that functions in the normal metabolic cycle of methionine. It is a naturally occurring choline derivative commonly ingested through diet, having a role in regulating cellular hydration and maintaining cell function [26, 27]. Homocystinuria is an inherited disorder that leads to the accumulation of homocysteine in plasma and urine. Betaine reduces plasma homocysteine levels in patients with homocystinuria [28]. Although it is present in many food products, the levels found there are insufficient to treat this condition. Calcium Chloride Dihydrate is an excellent water soluble crystalline Calcium source for uses compatible with chlorides. Chloride compounds can conduct electricity when fused or dissolved water. Chloride materials can be decomposed by electrolysis to chlorine gas and the metal. They are formed through several chlorination processes whereby at least one chlorine anion (Cl^-) is bonded to the relevant metal or cation. The chloride ion controls fluid equilibrium and pH levels in metabolic systems. They can form either inorganic or organic compounds. Ultra high purity and high purity compositions improve both optical quality and usefulness as scientific standards [29]. Thus the betaine calcium chloride dihydrate will also have various applications. Betaine calcium chloride dehydrate show various structural transitions associated with ferroelectric, ferroelastic, antiferroelectric, commensurate and incommensurate phases [30].

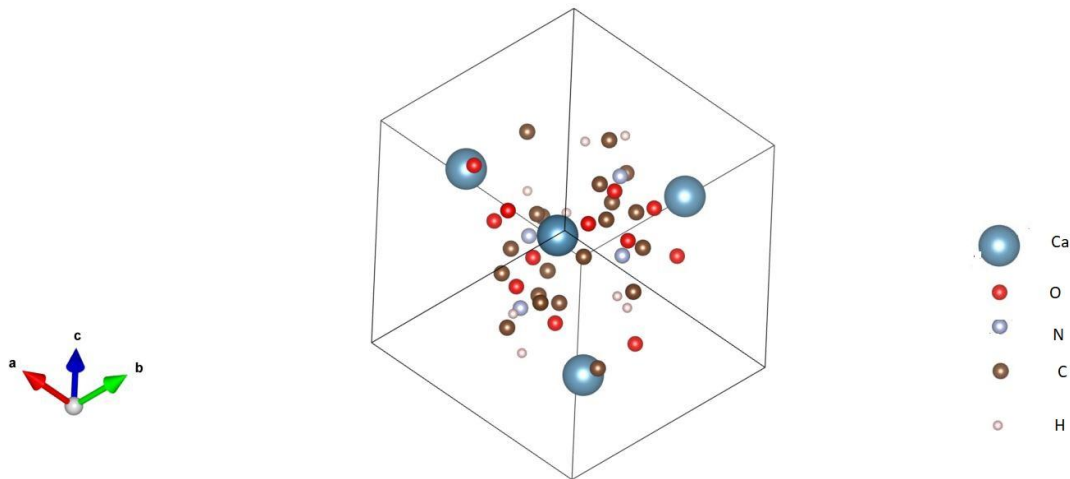
At lower temperatures the system undergoes a sequence of structural phase transitions to different structures modulated along c [30]. Between 164 K and 127 K the modulation is incommensurate with the wave vector reducing continuously from 0.320 to 0.285. Below this temperature down to 125 K the modulation remains commensurate. For $125 > T > 116$ K a second incommensurate phase occurs in which the wave vector reduces continuously from 0.285 to 0.25. At lower temperatures three commensurate phases are observed in the temperature ranges 116 to 73 K, 73 to 47 K and $T < 47$ K, respectively the behaviour being described as an incomplete devil's staircase [31].

EPR study of Mn^{2+} doped betaine calcium chloride dihydrate (BCCD) has been reported [32]. Mn^{2+} ions substitute Ca^{2+} in the crystal lattice. The spin Hamiltonian parameters have been determined at 300 K. Synthesis, density functional theory and spectroscopic studies of Arginine derivatives have been done [33]. Non-linear optical properties in $\text{Cr}(\text{CO})_3\text{L}$ complexes are also reported [34]. Theoretical study of octreotide derivatives as anti-cancer drugs has been done [35]. Quantum chemical simulation of hydrocarbon compounds with high enthalpy has also been performed [36]. The above studies have motivated us to perform a theoretical study of Mn^{2+} doped BCCD. In the present investigation, the ZFS parameters D and E for the Mn^{2+} ion at substitutional Ca^{2+} site in BCCD are determined using CF parameters and perturbation formulae [37]. The theoretical values of D and E are in reasonable agreement with the experimental ones [32].

CRYSTAL STRUCTURE

The crystal structure of BCCD at 300 K (high temperature reference phase) is orthorhombic with space group Pnma . The lattice parameters $a = 1.097 \text{ nm}$, $b = 1.015 \text{ nm}$, $c = 1.082 \text{ nm}$ and $Z = 4$ [38]. The coordination about the Ca atoms is shown in Fig. 1 together with symmetry adapted axes system (SAAS) (the diagram is made using VESTA software [39]).

Fig. 1: Coordination around Mn^{2+} in BCCD single crystal.



The site symmetry around Mn²⁺ ions substituting for Ca²⁺ is orthorhombic, as suggested by EPR study [32].

THEORETICAL INVESTIGATION

The following spin Hamiltonian [13, 40] can be used to obtain the resonance magnetic fields

$$\mathcal{H} = g\mu_B\mathbf{B}\cdot\mathbf{S} + D\left\{S_z^2 - \frac{1}{3}S(S+1)\right\} + E(S_x^2 - S_y^2) + \left(\frac{a}{6}\right)[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)] + \mathcal{A}S_zI_z + \mathcal{B}(S_xI_x + S_yI_y) \quad (1)$$

where g , μ_B , \mathbf{B} are the isotropic spectroscopic splitting factor, Bohr magneton, and external magnetic field. D and E are the second-rank axial and rhombic ZFS parameters, while a is the fourth-rank cubic one. \mathcal{A} and \mathcal{B} in Eq. (1) give the hyperfine ($I = 5/2$) interaction constants. The electronic Zeeman interaction is assumed to be isotropic for 3d⁵ ions [7, 40-43]. The maximum overall splitting direction of EPR spectrum is taken as the z axis and that of the minimum as the x axis [44, 45]. The laboratory axes (x, y, z) obtained from EPR spectra coincide with the crystallographic axes (CAS), a, b, c. The z-axis of the local site symmetry axes (the symmetry adapted axes (SAA)) is along the Mn-O2 bond and the other two axes (x, y) are normal to the z-axis.

Calcium ion in BCCD exists within a distorted octahedron of oxygen and chlorine ions [32, 38] and the local symmetry is assumed as orthorhombic of first kind (OR-I) [46]. In an OR-I symmetry, the ZFS parameters D and E of 3d⁵ ions are found [37, 47] as:

$$D = (3\xi^2/70P^2D)(-B_{20}^2 - 21\xi B_{20} + 2B_{22}^2) + (\xi^2/63P^2G)(-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2) \quad (2)$$

$$E = (\sqrt{6}\xi^2/70P^2D)(2B_{20} - 21\xi)B_{22} + (\xi^2/63P^2G)(3\sqrt{10}B_{40} + 2\sqrt{7}B_{44})B_{42} \quad (3)$$

where $P = 7B + 7C$, $G = 10B + 5C$, and $D = 17B + 5C$; B and C being the Racah parameters.

In terms of the average covalency parameter N , the parameters B , C and ξ are given by [48-50]

$$B = N^4B_0, C = N^4C_0; \xi_d = N^2\xi_d^0 \quad (4)$$

where B_0 , C_0 , and ξ_d^0 are the free ion Racah and spin-orbit coupling parameters, respectively [42-43]. $B_0 = 960$ cm⁻¹, $C_0 = 3325$ cm⁻¹ and $\xi_d^0 = 336$ cm⁻¹ for free Mn²⁺ ion are used [40].

As we could not find the optical study of the present system, using optical absorption of Mn²⁺ doped crystal with oxygen ligands [51]: B = 917cm⁻¹ and C = 2254 cm⁻¹ were taken. The average value [49, 50] of N = $(\sqrt{B/B_0} + \sqrt{C/C_0})/2 = 0.911$ is used to obtain D and E from Eqs. (2) and (3).

The SPM is used to find the CF parameters, B_{kq} for Mn²⁺ ion in BCCD single crystal and ZFS parameters are then estimated using these B_{kq}.

The crystal-field splitting of rare-earth ions [50] and also of transition ions [53-55] have been explained previously by SPM. This model yields the CF parameters as [37, 52]

$$B_{kq} = \sum \bar{A}_k(R_j) K_{kq}(\theta_j, \phi_j) \quad (5)$$

where R_j are the distances between the Mn²⁺ ion and the ligand ion j, R₀ is the reference distance, near a value of the R_j's. θ_j are the bond angles in a chosen axis system (SAAS) [22, 56]. The summation is taken over all the nearest neighbour ligands while the coordination factor K_{kq}(θ_j, φ_j) are the explicit functions of angular position of ligand [22, 37, 57-59]. The intrinsic parameter $\bar{A}_k(R_j)$ is determined by the power law [46] as:

$$\bar{A}_k(R_j) = \bar{A}_k(R_0) (R_0/R_j)^{t_k} \quad (6)$$

where $\bar{A}_k(R_0)$ is intrinsic parameter for a given ion host system. The symbol t_k is called power law exponent. The CF parameters, B_{kq} are determined from Eq. (5) [60].

For 3d⁵ ions, $\bar{A}_2(R_0) / \bar{A}_4(R_0)$ lies in the range 8 -12 [50]. In the present study, we have taken $\bar{A}_2(R_0) / \bar{A}_4(R_0) = 12$. For 3d⁵ ions in the 6-fold cubic coordination $\bar{A}_4(R_0)$ can be found from the relation: $\bar{A}_4(R_0) = (3/4) Dq$ [43]. Since $\bar{A}_4(R_0)$ is independent of the coordination [61], the above relation is used to find $\bar{A}_4(R_0)$ taking Dq = 756 cm⁻¹ [51].

II. RESULT AND DISCUSSION

The ionic radius of the Mn²⁺ ion (0.080 nm) is smaller than the Ca²⁺ (0.099 nm) ion, a small distortion may take place [62] when Mn²⁺ substitutes at Ca²⁺ site. The bond distances of different ligands, R_j along with the angles θ_j and φ_j are calculated from the crystal structure data of BCCD and are shown in Table 1.

Table 1. Coordinates of ligands, Mn-ligand bond distances R_j and coordination

angles θ_j and φ_j for Mn²⁺ ion doped BCCD single crystals.

Ligands	x (Å)	y (Å)	z (Å)	R(nm) (ND)	R(nm) (WD)	θ ^o	φ ^o
Cl	0.3046	0.4459	0.0877	0.5705 R ₁	0.3485 R ₁ +ΔR ₁	89.12 θ ₁	86.94 φ ₁
O3	0.0909	0.4050	0.3504	0.5680 R ₂	0.5740 R ₂ +ΔR ₂	86.46 θ ₂	89.08 φ ₂
O1	0.5374	0.2500	0.4114	0.7811R ₃	0.7911 R ₃ +ΔR ₃	86.98 θ ₃	86.05 φ ₃
O2	0.3417	0.2500	0.3675	0.6025 R ₄	0.6525 R ₄ +ΔR ₄	86.50 θ ₄	86.74 φ ₄
Cl'	0.3046	0.0541	0.0877	0.3517 R ₅	0.4416 R ₅ +ΔR ₅	88.57 θ ₅	85.03 φ ₅
O3'	0.0909	0.0949	0.3504	0.4037 R ₆	0.2067 R ₆ +ΔR ₆	85.02 θ ₆	88.70 φ ₆

Position of Mn²⁺: Ca (0.1951, 0.25, 0.2239), ND = No distortion, WD = With distortion.

Taking R_0 as slightly smaller than the sum of ionic radii of Mn²⁺ (0.80 nm) and O²⁻ (0.140 nm) [63] i.e. $R_0 = 0.186$ nm, $\overline{A_2}(R_0) / \overline{A_4}(R_0) = 12$, $t_2 = 4.5$, $t_4 = 1.4$; no distortion, we obtain B_{kq} and then $|D|$ and $|E|$ being different than the experimental values as shown in Table 2. Taking other parameters as above and $t_2 = 3$ $t_4 = 7$ [22], the values of $|D|$ and $|E|$ are inconsistent with the experimental ones and also the ratio $|E|/|D|$ comes out to be larger than 0.33 and therefore $t_2 = 4.5$, $t_4 = 1.4$ were taken for calculation. Because $|D|$ and $|E|$ estimated with no distortion were inconsistent with the experimental values, the distortion was included into calculation. The bond distances of different ligands R_j and the angles θ_j and ϕ_j calculated for this case are also presented in Table 1. The calculated CF parameters, B_{kq} from Eq. (5) and transformation S5 for standardization [44, 45] as well as ZFS parameters $|D|$ and $|E|$ using other parameters as above are given in Table 2. From Table 2, $|D|$ and $|E|$ show reasonable match with the experimental values when distortion is included into calculation. Such type of model calculations have been reported in case of Mn²⁺ and Fe³⁺ doped anatase TiO₂ crystal [64]. The interstitial sites for Mn²⁺ ions in BCCD were also investigated but ZFS parameters found were much different from the experimental values and so have not been shown here to save the space.

Table 2. CF parameters and ZFS parameters calculated by the SPM for Mn²⁺ ion doped BCCD single crystal with experimental values.

Site	R ₀ (nm)	B ₂₀ (cm ⁻¹)	B ₂₂ (cm ⁻¹)	B ₄₀ (cm ⁻¹)	B ₄₂ (cm ⁻¹)	B ₄₄ (cm ⁻¹)	D (×10 ⁻⁴ cm ⁻¹)	E (×10 ⁻⁴ cm ⁻¹)	E / D
Site I ND	0.186	-722.619	-882.19	2459.474	2591.011	5351.201	438.5	103.5	0.24
Site I WD	0.186	-5323.75	-4186.95	3405.313	3601.746	6768.494	892.3 892.5 ^e	301.1 25.0 ^e	0.33 0.03 ^e

ND = No distortion, WD = With distortion, ^e = experimental.

Using calculated CF parameters [65] and CFA program the optical absorption spectra of Mn²⁺ doped BCCD single crystals are evaluated. The CF energy levels of the Mn²⁺ ion are determined by diagonalizing the complete Hamiltonian in the intermediate crystal field coupling scheme. The calculated energy values are shown in Table 3 together with the experimental ones for comparison. It is noted from Table 3 that there is a reasonable agreement between the two. Therefore, the result found using SPM with distortion supports the experimental finding that Mn²⁺ ions substitute at Ca²⁺ sites in BCCD single crystal [32].

Table 3. Experimental and calculated (CFA program) energy band positions of Mn²⁺ doped BCCD single crystal.

Transition from	Observed wave number (cm ⁻¹)	Calculated wave number (cm ⁻¹)
⁶ A _{1g} (S)		
⁴ T _{1g} (G)	16044	
⁴ T _{2g} (G)	20433	21905, 21935, 21943, 21954, 21959, 21967
⁴ E _g (G)	24108	21976, 21991, 22438, 22450
⁴ A _{1g} (G)	24242	24501, 24566
⁴ T _{2g} (D)	26724	26224, 26764, 26809, 26922, 26966, 27153
⁴ E _g (D)	30451	29835, 30201, 30555, 30756
⁴ T _{1g} (P)	33956	32028, 33233, 33562, 33911, 33990, 34586
⁴ A _{2g} (F)	36846	36859, 36889
⁴ T _{1g} (F)	38521	37886, 38337, 38343, 38514, 38789, 38927

III. CONCLUSIONS

The zero field splitting (ZFS) parameters have been estimated using the superposition model and perturbation theory. The calculated ZFS parameters for Mn²⁺ ion in BCCD single crystal at the substitutional Ca²⁺ site are in reasonable match with the experimental ones. The CF energy levels of the Mn²⁺ ion obtained

using CF parameters and CFA program are in reasonable agreement with the experimental values. We conclude that the Mn²⁺ ion substitutes at Ca²⁺ site in BCCD single crystal. Thus the theoretical results support the experimental finding. The procedure used in the present investigation may be applied for the modeling of other ion-host systems to explore the applications of crystals in technology and industry.

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Declarations

Ethical Approval:

This research did not contain any studies involving animal or human participants, nor did it take place on any private or protected areas. No specific permissions were required for corresponding locations.

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Maroj Bharati and Vikram Singh- performed calculations, wrote the manuscript and prepared the figure.

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