Theoretical Study of Zero Field Splitting Parameters of Mn^{2+} doped Ammonium Catena - Di-μ-Chromatodiammine Cadmium (II) Crystal at Orthorhombic Symmetry Site

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Abstract— The crystal field parameters (CFPs) of Mn^{2+} doped Ammonium Catena - Di-μ-Chromatodiammine Cadmium (II) (ACD) single crystal are determined using superposition model (SPM). The zero field splitting parameters (ZFSPs) D and E are then found with the help of perturbation and microscopic spin Hamiltonian (SH) theory. The evaluated D and E show reasonable agreement with the experimental values from electron paramagnetic resonance. The results indicate that the Mn^{2+} ion enters the lattice substitutionally at Cd^{2+} site in ACD crystal. The procedure used here may be applied for the modeling of other ion-host systems.

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

I. INTRODUCTION

The Electron Paramagnetic Resonance (EPR) of Mn^{2+} has been largely employed to probe site symmetry [1-3], phase transition [4-5] and host spin-lattice relaxation [6-7]. Mn^{2+} with high spin d^5 configuration is selected as EPR probe due to its long spin-lattice relaxation time and also because of the fact that the zero-field splitting is highly sensitive to the strength and symmetry of the crystal field [8-11].

Superposition model (SPM) is used to get physical and geometrical information contained in crystal field parameters of various ion-host systems [12, 13]. Because the positions of ligands are essential to apply this model, the theories of local distortion in crystals are very important. The above model gave quite reasonable results for Fe^{3+} and Mn^{2+} spin Hamiltonian parameters as shown by earlier workers [14, 15].

Different mechanisms have been suggested for the ground state splitting of the magnetic ions doped in crystals [16-19]. In majority of the systems, cubic field and the diagonal part of free-ion Hamiltonian are considered to be unperturbed terms while the spin-orbit coupling, the low-symmetry field, and the off-diagonal part of free-ion Hamiltonian are taken as the perturbation terms [20].

The crystal of Ammonium Catena - Di-μ-Chromatodiammine Cadmium (II), [(NH$_4$)$_2$[Cd(NH$_3$)$_2$(CrO$_4$)$_2$] (ACD) was selected for study because of the fact that the Cd^{2+} in this is present in tetragonally compressed geometry [21] and when doped

with Mn^{2+} its EPR gave the unusually high second-rank axial zero field splitting parameter D and the forbidden hyperfine transitions. EPR of Mn^{2+} doped ACD at X-band showed highly complicated spectra and hence, EPR study of Mn^{2+} doped ACD was done at Q-band frequency [22]. The spectra were analyzed and various spin Hamiltonian parameters determined.

Two possibilities, namely, substitutional and interstitial, for Mn^{2+} ion location in the ACD crystal may be considered. It was concluded [22] that Mn^{2+} ion enters the lattice of ACD substitutionally at Cd^{2+} site. In this work, the zero-field splitting parameters (ZFSPs) D and E are evaluated for the Mn^{2+} ion at substitutional Cd^{2+} site in ACD crystal; using crystal field parameters (CFPs) obtained from SPM and perturbation equations [23]. The values of D and E determined with the help of this model give reasonable agreement with the experimental ones [22].

This section was dedicated to the introduction of Hamiltonians and SPM methodology in brief. The remaining part of the paper is organized as follows. Section II presents the related work associated with the SPM analysis. Section III provides the methods adopted for calculation of CFPs and ZFSPs. Section IV contains the results and its discussion on the basis of analysis. In section V, conclusions of the study and future scope are presented.

II. RELATED WORK

The SPM analysis has been done for different ion-host systems [14-20]. The crystal structure of ACD has been reported to show phase transition [21]. At and above 300 K, it is monoclinic with space group C2/m and cell dimensions, a = 12.8380(1), b = 6.0308(6), c = 7.5890(6) Å, β = 110.15(14)° and Z = 2. The central Cd^{2+} is surrounded by four oxygen atoms at the corners of a square from four different CrO_4 polyhedra. Two nitrogens of ammonia molecule occupy the axial positions along the c-axis. The geometry around Cd^{2+} is axially compressed octahedron as shown in Fig. 1.   The site symmetry around Mn^{2+}ions may be taken as approximately orthorhombic, as indicated by EPR study of Mn^{2+}: ACD [22].
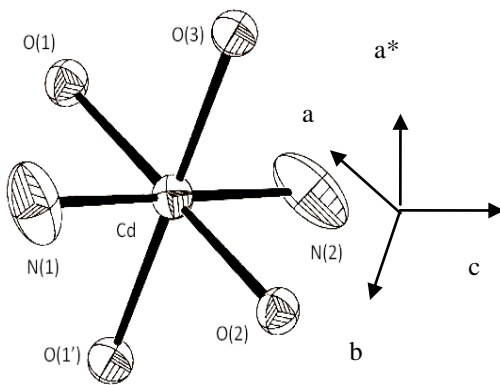

Figure 1. Coordination around Mn^{2+} in ACD single crystal.

III. MATERIALS AND METHODS

The resonance magnetic fields may be obtained employing the spin Hamiltonian [24, 25]

$$\mathcal{H} = g\mu_B \boldsymbol{B}.\boldsymbol{S} + D\{S_z^2 - \frac{1}{3}S(S+1)\} + E(S_x^2 - S_y^2) +$$

$$(\frac{a}{6})[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)]$$

$$+ \frac{F}{180}\{35 S_z^4 - 30 S(S+1)S_z^2 + 25S_z^2 -$$

$$6S(S+1) + 3S^2(S+1)^2\} + \frac{K}{4}[\{7S_z^2 - S(S+1) - 5\}$$

$$(S_+^2 + S_-^2) + (S_+^2 + S_-^2)\{7S_z^2 - S(S+1) - 5\}] + \mathcal{A}S_z I_z + \mathcal{B}(S_x I_x + S_y I_y) \tag{1}$$

where g is the isotropic spectroscopic splitting factor, μ_B is the Bohr magneton, $\boldsymbol{B}$ is the external magnetic field. D and E are the second-rank axial and rhombic ZFSPs, while a, F, and K are the fourth-rank cubic, axial and rhombic ones, respectively. The last two terms in Eq. (1) give the hyperfine (I = 5/2) interaction. The F and K terms are deleted as their effect is very small [24, 26, 27]. The isotropic assumption for the electronic Zeeman interaction

is generally valid for $3d^5$ ions [24, 28]. These two assumptions may slightly affect the value of a [29]. The maximum overall splitting direction of EPR spectrum is taken as the z axis and that of the minimum as the x axis [30]. As the crystallographic axis system (CAS), (a, b, c), is not Cartesian [21], the modified crystallographic axis system CAS* (a*, b, c) is considered as shown in Fig. 1 (the axis a* is perpendicular to c and b). The z-axis of the local site symmetry axes, i.e. the symmetry adapted axes (SAA) is along the metal nitrogen bond and the other two axes (x, y) are normal to the z-axis. A common axis system (a*//x, b//y, c//z) is taken to simplify the calculations. There are two sites for Mn^{2+} in ACD, the distortion axis for one site is considered to be along the Cd-N bond and for the other site, it is taken to be normal to this direction.

In ACD, cadmium ion is located within a distorted octahedron of oxygen and nitrogen ions [22] and the local symmetry is taken approximately as orthorhombic of first kind (OR-I) [31]. In an OR-I symmetry, the ZFSPs D and E of $3d^5$ ions are found [23, 32] as:

$$D = (3\xi^2/70P^2D)(-B_{20}^2 - 21\xi B_{20} + 2B_{22}^2)$$

$$+(\xi^2/63P^2G)(-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2) \tag{2}$$

$$E = (\sqrt{6}\xi^2/70P^2D)(2B_{20} - 21\xi)B_{22}$$

$$+(\xi^2/63P^2G)(3\sqrt{10}B_{40} + 2\sqrt{7}B_{44})B_{42} \tag{3}$$

where P = 7B+7C, G = 10B+5C, and D = 17B+5C; B and C are the Racah parameters. Eqs. (2) and (3) are quite good for weak-field cases, and are also valid for the low-symmetry components [23].

\Taking the covalency effect into account, the parameters B, C and ξ are given in terms of the average covalency parameter N as [33-34]

$$B = N^4 B_0, C = N^4 C_0; \xi_d = N^2 \xi_d^0 \tag{4}$$

Here B_0, C_0, and ξ_d^0 are the free ion Racah and spin-orbit coupling parameters, respectively [33-34]. B_0 = 960 cm⁻¹, C_0 = 3325 cm⁻¹, ξ_d^0 = 336 cm⁻¹ for free Mn^{2+} ion [24].

From optical absorption of Mn^{2+} doped crystal with oxygen and nitrogen ligands [35]: B = 770 cm⁻¹ and C = 2322 cm⁻¹ were determined. The average value [34] of N = $(\sqrt{B/B_0} + \sqrt{C/C_0})/2$ = 0.917 is used to get the ZFSPs D and E from Eqs. (2) and (3).

The SPM is employed to calculate the CFPs, B_{kq} for Mn^{2+} ion in ACD single crystal and ZFSPs are then evaluated using these CFPs.

The SPM has quite well explained the crystal-field splitting of $4f^n$ ions [36] and also of some $3d^n$ ions [37-39]. The model gives the CFPs as [23, 36]

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

Here R_j are the distances between the Mn^{2+} ion and the ligand ion j, R_0 is the reference distance, generally taken near a value of the R_j's. θ_j present the bond angles in a chosen axis system (symmetry adapted axes system (SAAS)) [40, 41]. The summation is over all the nearest neighbour ligands. The coordination factor $K_{kq} (\theta_j, \phi_j)$ are the explicit functions of angular position of ligand [23, 40, 42-43]. The intrinsic parameter $\overline{A}_k (R_j)$ is provided by the power law [20, 31] as:

$$\overline{A}_k (R_j) = \overline{A}_k (R_0) (R_0 / R_j)^{t_k} \qquad (6)$$

where $\overline{A}_k (R_0)$ is intrinsic parameter for a given ion host system. The symbol t_k is power law exponent. The crystal-field parameters B_{kq} are determined using Eq. (5) [44].

For $3d^5$ ions, the ratio $\overline{A}_2 (R_0) / \overline{A}_4 (R_0)$ lies in the range 8 -12 [19, 38]. In the present study, we have taken the ratio $\overline{A}_2 (R_0) / \overline{A}_4 (R_0) = 10$. For $3d^N$ ions in the 6-fold cubic coordination $\overline{A}_4 (R_0)$ can be obtained from the relation: $\overline{A}_4 (R_0) = (3/4)$ Dq [29]. As $\overline{A}_4 (R_0)$ is independent of the coordination [45], the above relation is used to get $\overline{A}_4 (R_0)$ with Dq = 716 cm^{-1} [35].

IV. RESULTS AND DISCUSSION

In order to consider the substitution at Cd^{2+} site, the origin of Mn^{2+} was taken at the Cd^{2+} ion. Since the ionic radius of the dopant Mn^{2+} ion (0.080 nm) is slightly smaller than that of the host Cd^{2+} (0.095 nm), a small distortion may occur on doping [46]. From the coordinates x, y, z; the bond distances of various ligands, R_j together with the angles θ_j and ϕ_j are calculated for sites I and II and are given in Table 1A and 1B, respectively.

Table 1A. Coordinates of ligands, Mn-ligand bond distances R_j and coordination angles θ_j and ϕ_j for Mn^{2+} ion doped ACD single crystals (site I).

Position of Mn²⁺	Ligands				Spherical co-ordinates of ligands		
		x	y	z	R(nm) (Å)	θ^0	ϕ^0
				Without distortion			
Site I: Substitutional	O(1)	0.1399	0.2757	0.0875	0.2368 R_1	87.88 θ_1	86.61 ϕ_1
Cd(1) (0, 0, 0)	O(1')	0.1399	-0.2757	0.0875	0.2368 R_2	87.88 θ_2	86.61 ϕ_2
	O(2)	0.0705	0.5000	0.3362	0.3850 R_3	84.99 θ_3	88.94 ϕ_3
	O(3)	0.2842	0.5000	0.3689	0.4816 R_4	85.60 θ_4	86.60 ϕ_4
	N(1)	0.0006	0.0000	0.2894	0.2193 R_5	82.41 θ_5	89.98 ϕ_5
	N(2)	0.3298	0.0000	0.3087	0.4071 R_6	85.65 θ_6	85.34 ϕ_6
				With distortion			
	O(1)			0.3168 $R_1 + \Delta R_1$			
	O(1')			0.3168 $R_2 + \Delta R_2$			
	O(2)			0.4650 $R_3 + \Delta R_3$			
	O(3)			0.4216 $R_4 + \Delta R_4$			
	N(1)			0.1715 $R_5 + \Delta R_5$			
	N(2)			0.4891 $R_6 + \Delta R_6$			

Table 1B. Coordinates of ligands, Mn-ligand bond distances R_j and coordination angles θ_j and ϕ_j for Mn^{2+} ion doped ACD single crystals (site II).

Position of Mn²⁺	Ligands				Spherical co-ordinates of ligands		
		x	y	z	R(nm) (Å)	θ^0	ϕ^0
				Without distortion			
Site II: Substitutional	O(1)	0.1399	0.2757	0.0875	0.2368 R_1	177.88 θ_1	176.61 ϕ_1
Cd(1) (0, 0, 0)	O(1')	0.1399	-0.2757	0.0875	0.2368 R_2	177.88 θ_2	176.61 ϕ_2
	O(2)	0.0705	0.5000	0.3362	0.3850 R_3	174.99 θ_3	178.94 ϕ_3
	O(3)	0.2842	0.5000	0.3689	0.4816 R_4	175.60 θ_4	176.60 ϕ_4
	N(1)	0.0006	0.0000	0.2894	0.2193 R_5	172.41 θ_5	179.98 ϕ_5
	N(2)	0.3298	0.0000	0.3087	0.4071 R_6	175.65 θ_6	175.34 ϕ_6
				With distortion			
	O(1)			0.2868 $R_1 + \Delta R_1$			
	O(1')			0.2868 $R_2 + \Delta R_2$			
	O(2)			0.4290 $R_3 + \Delta R_3$			
	O(3)			0.3996 $R_4 + \Delta R_4$			
	N(1)			0.1389 $R_5 + \Delta R_5$			
	N(2)			0.4991 $R_6 + \Delta R_6$			

In adjusting the Mn-ligand distances to match the experimental values, the site symmetry is preserved as well as the energy is minimized and so the structural stability is taken into account. Taking R_0 as slightly smaller than the minimum of R_j [47], i.e. $R_0 = 0.173$ nm, $\overline{A}_2 (R_0) / \overline{A}_4 (R_0) = 10$, $t_2 = 3$, $t_4 = 7$ [19]; considering no distortion, we find B_{kq} and then |D| and |E| which are different than the experimental values as shown in Table 2. Hence, we have taken into consideration the distortion. The bond distances

of different ligands R_j and the angles θ_j and ϕ_j calculated for this case are also given in Table 1A and 1B for sites I and II, respectively. The computed B_{kq} from Eq. (5) and transformation S2 for standardization [30] in case of site I as well as ZFSPs |D| and |E| taking other parameters as above for both sites I and II are given in Table 2. From Table 2 it is seen that |D| and |E| show reasonable agreement with the experimental values when distortion is taken into consideration. Such modeling has been done earlier for Mn^{2+} and Fe^{3+} doped anatase TiO_2 crystal [48]. The calculations of interstitial sites for Mn^{2+} ions in ACD were also done but ZFSPs obtained are inconsistent with the experimental values and therefore are not being given here.

Table 2. CFPs and ZFSPs calculated by the superposition model for Mn^{2+} ion doped ACD single crystal with experimental values.

Site |E|	R_0(nm) |E|/|D|	B_{20}	B_{22}	B_{40}	B_{42}	B_{44}	Crystal- field parameters (cm^{-1})	|D|	Zero-field splitting parameters ($\times 10^{-4} cm^{-1}$)
Without distortion									
Site I									
0.173	-7791.55	-9642.24	616.965	659.5878	3065.515	1049.2			
517.9	0.493								
Site II									
0.173	15760.46	71.71391	1721.902	36.24277	0.202769	438.2			
4.94	0.010								
With distortion									
Site I									
0.173	-8824.53	6833.377	1469.031	1608.293	4525.302	1037.2			
336.5	0.324								
						Exp. 1037.0			
216.5	0.208								
Site II									
0.173	26891.98	231.2806	18485.38	801.8007	3.191669	733.6			
27.0	0.036								
						Exp. 733.4			
149.0	0.189								

Using calculated CFPs [49] with OR-I symmetry of the crystal field and CFA program the optical absorption spectra of Mn^{2+} doped ACD single crystals are calculated. The energy levels of the Mn^{2+} ion are determined by diagonalizing the complete Hamiltonian within the $3d^N$ basis of states in the intermediate crystal field coupling scheme. The calculated energy values for sites I and II are given in Table 3 along with the experimental values of band positions for comparison. From Table 3 a reasonable agreement between the two can be seen. Hence, the result found using SPM with distortion supports the experimental observation that Mn^{2+} ions substitute at Cd^{2+} site in ACD crystal [22].

Table 3. Experimental and calculated (CFA package) energy band positions of Mn^{2+} doped ACD single crystal.

Transition from $^6A_{1g}(S)$	Observed wave number (cm^{-1})	Calculated wave number (cm^{-1})	
		Site I	Site II
$^4T_{1g}(G)$	13889 15385	16580, 16585, 17235, 17263, 18189, 18247	17418, 17597, 17718, 17815, 18541, 18717
$^4A_{1g}(G)$	19417	19312, 19320	19279, 19547
$^4E_g(G)$	20833	20822, 20825, 20834, 20836	20757, 20820, 20882, 20884
$^4T_{2g}(G)$	21739	21714, 21741, 22941, 22981, 23282, 23307	21453, 21777, 21849, 21933, 22015, 22099
$^4T_{2g}(D)$	23529	23445, 23500, 25148, 25184, 25639, 26497	22424, 22825, 22841, 22899, 22914, 25179
$^4E_g(D)$	25157	26522, 26863, 27241, 27289	25194, 28236, 28456, 28812
$^4T_{1g}(P)$	28986	28189, 28556, 28627, 28856, 28949, 29015	29451, 29865, 30209, 30261, 30283, 30450
$^4T_{1g}(F)$	32216	31346, 31484, 31852, 31986, 32009, 32576	30821, 30931, 31152, 31653, 31663, 32339
$^4A_{2g}(F)$	38986 40193	38456, 38881	38502, 39365

V. CONCLUSION AND FUTURE SCOPE

The zero field splitting parameters (ZFSPs) have been evaluated using the superposition model and perturbation formulae. The calculated ZFSPs for Mn^{2+} ion in ACD single crystal at the substitutional Cd^{2+} site are in reasonable agreement with the experimental ones. We confirm that the Mn^{2+} ion occupies substitutional Cd^{2+} site in ACD crystal .The theoretical results support the experimental observation. Computation approaches employed for this study may be useful in future to correlate EPR and optical data for several ion-host systems. The combined approaches: SPM/CF, SPM/ZFS and Microscopic Spin Hamiltonian/Zero Field Splitting (MSH/ZFS) may yield better correlation of EPR and optical data.

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