

# Theoretical Zero Field Splitting Parameters of Mn<sup>2+</sup> doped SAH Single Crystals

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## Abstract

Superposition model (SPM) has been used to evaluate the crystal field parameters (CFPs) of Mn<sup>2+</sup> doped strontium acetate hemihydrate (SAH) single crystals. Further, employing perturbation and microscopic spin Hamiltonian (SH) theory the zero field splitting parameters (ZFSPs) D and E are determined. Calculated D and E give reasonable agreement with the experimental values. The results show that the Mn<sup>2+</sup> ion enters the lattice substitutionally at Sr<sup>2+</sup> site in SAH.

**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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## 1. INTRODUCTION

The physical and geometrical information contained in crystal field parameters of different ion-host systems can be obtained using superposition model (SPM) [1, 2]. This model has been successfully used for spin Hamiltonian parameters of 3d<sup>5</sup> ions [3, 4].

There are different mechanisms for the splitting of the ground state of magnetic ions doped in crystals [5-8]. In majority of the cases, the spin-orbit coupling, the low-symmetry field, and the off-diagonal part of free-ion Hamiltonian are taken to be the perturbation terms while cubic field and the diagonal part of free-ion Hamiltonian are considered as unperturbed terms [9].

Metal acetates and formates are found in a number of crystallographic forms and states of hydration. These have proved to be popular subjects of investigation by solid-state <sup>13</sup>C NMR [10-17] in order to understand the influence of metal ion, structural type, and packing on shielding. Calcium acetate hemihydrate (CAH), strontium acetate hemihydrate (SAH), and barium acetate monohydrate (BAM) have been studied using both solid-state NMR and single-crystal X-ray diffraction [18].

EPR absorption study of Mn<sup>2+</sup> (3d<sup>5</sup> ion) doped strontium acetate hemihydrate, Sr (CH<sub>3</sub>COO)<sub>2</sub> ·  $\frac{1}{2}$  H<sub>2</sub>O (SAH) single crystal has been performed at 295K (RT), 77K and 4.2K [19]. For Mn<sup>2+</sup> ion location in the SAH crystal, both substitutional and interstitial sites may be adopted. It was suggested [19] that Mn<sup>2+</sup> ion enters the lattice of SAH substitutionally at Sr<sup>2+</sup> site. In the present study, the zero-field splitting parameters (ZFSPs) D and E are evaluated for the Mn<sup>2+</sup> ion at substitutional Sr<sup>2+</sup> site in SAH at RT; employing perturbation equations and crystal field parameters (CFPs) determined from SPM [20]. The values of D and E obtained using SPM are in reasonable agreement with the experimental values [19].

## 2. CRYSTAL STRUCTURE

The crystal structure of SAH single crystal is triclinic with lattice parameters a = 7.2321 Å, b = 9.9271 Å, c = 10.6431 Å; α = 83.58°, β = 82.04°, γ = 73.98°; space group P $\bar{1}$  and Z = 2 [18]. The oxygen coordination about Sr<sup>2+</sup> is shown in Fig. 1. The site symmetry around Mn<sup>2+</sup> ions is taken to be orthorhombic, as indicated by EPR study of Mn<sup>2+</sup>: SAH [19].

### 3. THEORETICAL INVESTIGATION

The resonance magnetic fields can be obtained using the spin Hamiltonian [21, 22]

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

where  $g$  is the isotropic spectroscopic splitting factor,  $\mu_B$  is the Bohr magneton,  $\mathbf{B}$  is the external magnetic field.  $D$  and  $E$  are the second-rank axial and rhombic ZFSPs, whereas  $a$ ,  $F$ , and  $K$  are the fourth-rank cubic, axial and rhombic ZFSPs, respectively. The last two terms in Eq. (1) give the hyperfine ( $I = 5/2$ ) interaction. The  $F$  and  $K$  terms are neglected as their effect is very small [21, 23, 24]. The electronic Zeeman interaction is assumed to be isotropic for 3d<sup>5</sup> ions [21, 25]. The above two assumptions can slightly affect the value of  $a$  [26]. The direction of maximum overall splitting of EPR spectrum is taken as the  $z$  axis and that of the minimum as the  $x$  axis [27]. The laboratory axes ( $x, y, z$ ) obtained from EPR spectra coincide with the modified crystallographic axes (CAS\*),  $a, b^*, c^*$ . The  $z$ -axis of the local site symmetry axes, i.e. the symmetry adapted axes (SAA) is along the metal oxygen O (22) bond and the other two axes ( $x, y$ ) are perpendicular to the  $z$ -axis as shown in Fig. 1. A common axis system ( $a//x, b^*//y, c^*//z$ ) is considered to simplify the calculations.

In SAH, strontium ion is located in a distorted octahedron of oxygen ions [18] and the local symmetry is considered approximately as orthorhombic of first kind (OR-I) [28]. In an OR-I symmetry, the ZFSPs  $D$  and  $E$  of 3d<sup>5</sup> ions are obtained [20, 29] as:

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

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

where  $P = 7B + 7C$ ,  $G = 10B + 5C$ , and  $D = 17B + 5C$ ;  $B$  and  $C$  are the Racah parameters. Eqs. (2) and (3) are good for weak-field cases as well as for the low-symmetry components [20].

Taking the covalency effect, the parameters  $B, C$  and  $\xi$  are written in terms of the average covalency parameter  $N$  as [30-31]

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

where  $B_0, C_0$ , and  $\xi_d^0$  are the free ion Racah and spin-orbit coupling parameters, respectively [30-31]. For free Mn<sup>2+</sup> ion, the above parameters are:  $B_0 = 960 \text{ cm}^{-1}$ ,  $C_0 = 3325 \text{ cm}^{-1}$ ,  $\xi_d^0 = 336 \text{ cm}^{-1}$  [21].

From optical absorption study of Mn<sup>2+</sup> doped crystal having oxygen ligands [32]:  $B = 917 \text{ cm}^{-1}$  and  $C = 2254 \text{ cm}^{-1}$  were determined. The average value [31] of  $N = (\sqrt{B/B_0} + \sqrt{C/C_0})/2$  is used in our calculation.

The SPM is employed to calculate the CFPs,  $B_{kq}$  for Mn<sup>2+</sup> ion in SAH single crystal and ZFSPs are then evaluated with the help of these CFPs.

The SPM has been used to explain the crystal-field splitting of 4f<sup>*n*</sup> ions [33] and some 3d<sup>*n*</sup> ions [34-36]. Using this model the CFPs are given as [20, 33]

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

where  $R_j$  are the distances between the Mn<sup>2+</sup> ion and the ligand ion j,  $R_0$  is the reference distance, generally taken near a value of the  $R_j$ 's.  $\theta_j$  give the bond angles in symmetry adapted axes system (SAAS) [37, 38]. 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 [20, 37, 39-40]. The intrinsic parameter  $\bar{A}_k(R_j)$  is written [9, 28] 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 power law exponent. The crystal-field parameters  $B_{kq}$  are determined using Eq. (5) [41].

For 3d<sup>5</sup> ions, the ratio  $\bar{A}_2(R_0)/\bar{A}_4(R_0)$  falls in the range 8 -12 [8, 35]. In the present study, the ratio  $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 10$  is considered. For 3d<sup>N</sup> ions in the 6-fold coordination  $\bar{A}_4(R_0)$  is obtained from the relation:  $\bar{A}_4(R_0) = (3/4) Dq$  [26]. Since  $\bar{A}_4(R_0)$  is independent of the coordination [42], it is obtained from the above relation with  $Dq = 756 \text{ cm}^{-1}$  [32].

#### 4. RESULTS AND DISCUSSION

The origin of Mn<sup>2+</sup> ion was shifted at the Sr<sup>2+</sup> ion to check the substitution at Sr<sup>2+</sup> site. As the ionic radius of the impurity Mn<sup>2+</sup> ion (0.083 nm) is smaller than that of the host Sr<sup>2+</sup> (0.118 nm), a small distortion is expected [43]. Using the coordinates x, y, z; the bond distances of different ligands,  $R_j$  together with the angles  $\theta_j$  and  $\phi_j$  are calculated and are given in Table 1. In adjusting the Mn-O distances to match the experimental values, the site symmetry is preserved and the energy is minimized to have the structural stability. Taking  $R_0$  as slightly smaller than the minimum of  $R_j$  [44], i.e.  $R_0 = 0.170 \text{ nm}$ ,  $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 10$ ,  $t_2 = 4$ ,  $t_4 = 3$  (different from the values in [8]; taking  $t_2 = 3$ ,  $t_4 = 7$  as in [8] the ratio  $|E|/|D|$  was greater than the standard value 0.33); with no distortion, we obtain  $B_{kq}$  and then  $|D|$  and  $|E|$  which are different from the experimental values as given in Table 2. Therefore, we have taken into consideration the distortion. The bond distances of various ligands  $R_j$  and the angles  $\theta_j$  and  $\phi_j$  computed for this are also presented in Table 1. The computed  $B_{kq}$  from Eq. (5) and transformation S2 for standardization [27] as well as ZFSPs  $|D|$  and  $|E|$  taking other parameters as above are shown in Table 2. From Table 2, it is seen that  $|D|$  and  $|E|$  are in reasonable agreement with the experimental values when distortion is taken into consideration. Such calculations have been done by other workers for Mn<sup>2+</sup> and Fe<sup>3+</sup> doped anatase TiO<sub>2</sub> crystal [45]. The interstitial sites for Mn<sup>2+</sup> ions in SAH were also considered but ZFSPs obtained are quite different from the experimental values and so have not been presented here.

Using evaluated CFPs [46] and CFA program the optical spectra of Mn<sup>2+</sup> doped SAH crystals are computed. The energy levels of the Mn<sup>2+</sup> ion are determined by diagonalizing the complete Hamiltonian within the 3d<sup>N</sup> basis of states in the intermediate crystal field coupling scheme. The computed energy values are given in Table 3 along with the experimental values for comparison. From Table 3 a reasonable agreement between the computed and experimental energy values is found. Hence, the result obtained using SPM with distortion supports the experimental observation that Mn<sup>2+</sup> ions substitute at Sr<sup>2+</sup> site in SAH crystal [19].

#### 5. CONCLUSIONS

The zero field splitting parameters (ZFSPs) have been obtained using the superposition model and perturbation equations. The evaluated ZFSPs for Mn<sup>2+</sup> ion in SAH single crystal at the substitutional Sr<sup>2+</sup> site at RT are in reasonable agreement with the experimental values. It is confirmed that the Mn<sup>2+</sup> ion occupies substitutional Sr<sup>2+</sup> site in SAH crystal. The theoretical results support the experimental finding reported by earlier workers. The method used here may be applied for the modeling of other ion-host systems.

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**TABLE AND FIGURE CAPTIONS:**

**Table 1.** Coordinates of oxygen ligands, Mn-oxygen bond distances  $R_j$  and coordination

angles  $\theta_j$  and  $\phi_j$  for Mn<sup>2+</sup> ion doped SAH single crystals.

**Table 2.** CFPs and ZFSPs calculated by the superposition model for Mn<sup>2+</sup> ion doped SAH single crystal with experimental values.

Table 3. Experimental and calculated (CFA package) energy band positions of Mn<sup>2+</sup> doped SAH single crystal.

**Fig. 1.** Coordination around Mn<sup>2+</sup> in SAH single crystal.

**Table 1**

Position of Mn <sup>2+</sup>	Ligands	Spherical co-ordinates of ligands								
		x	y	z	R(nm)	$\theta^\circ$	$\phi^\circ$			
		(Å)								
		Without distortion								
Site I: Substitutional	O(12)	0.1720	0.8056	0.7817	0.2472	R <sub>1</sub>	91.16	$\theta_1$	95.40	$\phi_1$
Sr(1)	O(21)	0.1685	0.8610	1.0376	0.2722	R <sub>2</sub>	85.67	$\theta_2$	94.99	$\phi_2$
(0.4050, 0.9275, 0.8321)	O(22)	0.3000	1.0231	1.0796	0.2832	R <sub>3</sub>	84.98	$\theta_3$	92.13	$\phi_3$
	O(31)	0.2401	1.1993	0.8181	0.2628	R <sub>4</sub>	90.30	$\theta_4$	93.59	$\phi_4$
	O(32)	0.3259	1.1154	0.6312	0.2690	R <sub>5</sub>	94.28	$\theta_5$	91.68	$\phi_5$
	Ow(1)	0.6299	0.8348	0.6377	0.2538	R <sub>6</sub>	94.39	$\theta_6$	84.90	$\phi_6$
		With distortion								
	O(12)				0.2672	R <sub>1</sub> + $\Delta$ R <sub>1</sub>				
	O(21)				0.2922	R <sub>2</sub> + $\Delta$ R <sub>2</sub>				
	O(22)				0.3032	R <sub>3</sub> + $\Delta$ R <sub>3</sub>				
	O(31)				0.2828	R <sub>4</sub> + $\Delta$ R <sub>4</sub>				
	O(32)				0.2890	R <sub>5</sub> + $\Delta$ R <sub>5</sub>				
	Ow(1)				0.2688	R <sub>6</sub> + $\Delta$ R <sub>6</sub>				

**Table 2**

Site	R <sub>0</sub> (nm)	Crystal- field parameters (cm <sup>-1</sup> )					Zero-field splitting parameters (×10 <sup>4</sup> cm <sup>-1</sup> )			
		B <sub>20</sub>	B <sub>22</sub>	B <sub>40</sub>	B <sub>42</sub>	B <sub>44</sub>	D	E	E / D	
Without distortion										
Site I										
$\frac{A_2}{A_4} = 10$	0.170	-5835.09	-7122.82	2628.404	2762.62	3621.629	574.4	322.6	0.561	
With distortion										
Site I										
$\frac{A_2}{A_4} = 10$	0.170	-4898.51	3924.435	2130.449	2239.404	2936.344	306.7	84.0	0.273	
							Exp. 306.2	21.3	0.069	

**Table 3**

Transition from <sup>6</sup> A <sub>1g</sub> (S)	Observed wave number (cm <sup>-1</sup> )	Calculated wave number (cm <sup>-1</sup> )
<sup>4</sup> T <sub>1g</sub> (G)	16044	
<sup>4</sup> T <sub>2g</sub> (G)	20433	19488, 19496, 19627, 19634, 21198, 21212
<sup>4</sup> E <sub>g</sub> (G)	24108	21964, 21968, 23759, 23772
<sup>4</sup> A <sub>1g</sub> (G)	24242	24223, 24432
<sup>4</sup> T <sub>2g</sub> (D)	26724	25960, 25973, 26549, 26577, 27284, 27321
<sup>4</sup> E <sub>g</sub> (D)	30451	29979, 30156, 30213, 30442
<sup>4</sup> T <sub>1g</sub> (P)	33956	32403, 32784, 32902, 33142, 33291, 33899
<sup>4</sup> A <sub>2g</sub> (F)	36846	36798, 36929
<sup>4</sup> T <sub>1g</sub> (F)	38521	37944, 37974, 38147, 38183, 39079, 39246

