

# Theoretical Investigation of Zero field splitting parameter of $\text{Fe}^{3+}$ in $\text{CsCdF}_3$ single crystals at axial symmetry site

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**Abstract:** A theoretical investigation of crystal field parameters and zero-field splitting parameter of  $\text{Fe}^{3+}$  doped  $\text{CsCdF}_3$  (CCF) single crystals is performed employing superposition model and the perturbation theory. The zero-field splitting parameter obtained matches well with the experimental value determined from EPR. The theoretical study supports the experimental finding that  $\text{Fe}^{3+}$  ions substitute at  $\text{Cd}^{2+}$  site in  $\text{CsCdF}_3$  single crystal with charge compensation.

**Keywords:** A. Inorganic compounds; A. Single crystal; D. Crystal fields; D. Optical properties; D. Electron paramagnetic resonance.

## 1. Introduction

Electron paramagnetic resonance (EPR) gives information about structural distortions and local site symmetry of transition ions doped in different host crystals [1-3]. The spin Hamiltonian (SH) parameters determined from EPR are correlated with optical and structural parameters using microscopic spin-Hamiltonian (MSH) theory. The above studies suggest that the spin Hamiltonian parameters of transition ions ( $d^5$ ) in crystals are quite sensitive to local distortions. Hence, the SH theory is frequently used in the study of crystals.

The crystal-field (CF) parameters of  $d^5$  ion can be determined with the help of superposition model (SPM) [4, 5]. The zero field splitting (ZFS) parameters are then obtained employing CF parameters [6].  $\text{Fe}^{3+}$  ion is interesting due to its  ${}^6S_{5/2}$  ground state [7-10]. The electron spins become free in external magnetic field with high order interaction of crystalline electric field [11, 12].

The materials with perovskite structures find applications in several areas of science and technology because of their electro-optic, electro-mechanical and non-linear properties. When trivalent magnetic impurity ions are doped in perovskite fluorides, the magnetic impurity ions substitute for divalent cations of the crystal. A part of the impurity ions are associated with the nearest divalent-cation vacancies due to charge compensation, which forms the impurity- $V_M$  complex center. When  $\text{Li}^+$  ions are co-doped with the impurity ions, some impurity ions are associated with  $\text{Li}^+$  ion very near to the divalent-cation site, which forms the impurity- $\text{Li}^+$  complex center.

EPR study of  $\text{Fe}^{3+}$  centers in doped and  $\text{Li}^+$  co-doped perovskite fluoride  $\text{CsCdF}_3$  (CCF) have been done [13]. In this crystal two kinds of tetragonal (axial) centers associated with  $\text{Cd}^{2+}$  vacancy,  $\text{Fe}^{3+}-V_{\text{Cd}}$  (A) and  $\text{Li}^+$  ion,

$\text{Fe}^{3+}-\text{Li}^+$  (B) are found. The magnitude of ZFS parameter D for  $\text{Fe}^{3+}$  ion at the B center is larger than that at the A center. This may be due to the deviations of coordinated ligands to the magnetic ion [13]. In this investigation, the CF parameters are found with the help of SPM and these parameters with MSH theory then give ZFS parameter for  $\text{Fe}^{3+}$  ions at the two centers A and B in CCF single crystal at room temperature (RT). The ZFS parameter D evaluated using SPM provides good match with the experimental value [13].

## 2. Crystal Structure

CCF has a cubic perovskite structure at room temperature. The crystal structure of CCF is illustrated in Fig. 1. The lattice parameter is reported to be  $a = 4.465 \text{ \AA}$  [14]. The crystal structure belongs to the space group  $\text{Pm}\bar{3}\text{m}$  (221) with Cs at (0.5, 0.5, 0.5), Cd at (0, 0, 0) and F at (0.5 0 0) positions and the origin is chosen to be at (0, 0, 0) [14]. The fluorine coordination around  $\text{Cd}^{2+}$  is shown in Fig. 1. The site symmetry around  $\text{Fe}^{3+}$  ions may be considered to be tetragonal (axial), as suggested by EPR study of  $\text{Fe}^{3+}$ : CCF [13].

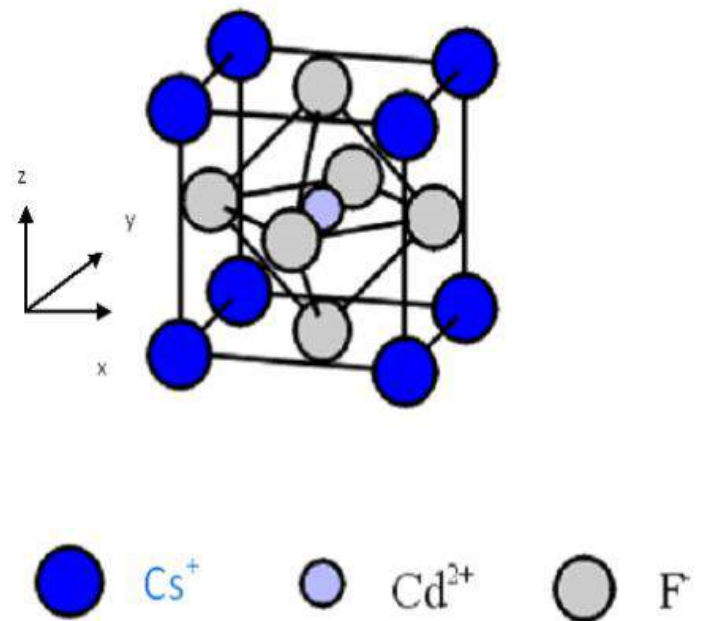


Fig. 1: Crystal structure of CCF.

## 3. Theoretical Investigation

The SH of  $3d^5$  ion in crystal field of axial (tetragonal) symmetry is given by [15-17]

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

where the first term represents electronic Zeeman interaction, B is the external magnetic field, g is the spectroscopic splitting factor and  $\mu_B$  is Bohr magneton. The second, third, and fourth terms are the second order axial, fourth-rank cubic and fourth-rank axial ZFS terms [9]. The fifth term gives the hyperfine interaction term. S, D, a, F are the effective spin vector, second order axial, fourth-rank cubic and fourth-rank axial ZFS parameters, respectively. An isotropic approximation for the electronic Zeeman interaction is considered for Fe<sup>3+</sup> ions [9, 18, 19].

The Hamiltonian for a d<sup>5</sup> ion is given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{cf} + \mathcal{H}_{so}$$

$$\text{where } \mathcal{H}_{cf} = \sum_{kq} B_{kq} C_q^k \quad (2)$$

is the crystal field Hamiltonian and  $\mathcal{H}_0$  and  $\mathcal{H}_{so}$  represent free ion Hamiltonian and spin-orbit (SO) coupling, respectively. Because the spin-spin coupling is very small [20-22], its contribution has been neglected in Eq. (2). The crystal field of SO interaction is considered as perturbation term [23-25]. The SO contribution to the ZFS parameter D for 3d<sup>5</sup> ions in axial symmetry is given by [24]

$$D^{(4)}(SO) = \left(\frac{\xi^2}{63F^2G}\right) [14B_{44}^2 - 5B_{40}^2] - \left(\frac{3\xi^2}{70F^2D}\right) B_{20} [B_{20} - 14\xi] \quad (3)$$

where P = 7(B+C), G = 10B+5C and D = 17B+5C. P, G, and D represent the energy separations between the excited quartets and the ground sextet. Racah parameters B and C give the electron-electron repulsion. Only fourth order term is taken in Eq. (3) because other perturbation terms are negligible [24]. The parameters B, C and  $\xi$ , in terms of the average covalency parameter N, are given as, B = N<sup>4</sup>B<sub>0</sub>, C = N<sup>4</sup>C<sub>0</sub> and  $\xi = N^2 \xi_0$ , where B<sub>0</sub>, C<sub>0</sub> and  $\xi_0$  are the Racah parameters and the spin-orbit coupling parameter for free ion [26, 27], respectively. B<sub>0</sub> = 1130 cm<sup>-1</sup>, C<sub>0</sub> = 4111

cm<sup>-1</sup>,  $\xi_0 = 589 \text{ cm}^{-1}$  [9] for Fe<sup>3+</sup> ion are taken in this study. Using equation

$$N = (\sqrt{B/B_0} + \sqrt{C/C_0}) / 2 \quad (4)$$

N can be determined taking the values of Racah parameters (B = 840 cm<sup>-1</sup>, C = 3360 cm<sup>-1</sup>) found from optical absorption study of Fe<sup>3+</sup> ion in crystal having fluorine ligands [28].

With the help of SPM the CF parameters for Fe<sup>3+</sup> in CCF single crystal are evaluated and then from Eq. (3) ZFS parameter D is determined. Similar method has been considered for obtaining ZFS parameters by several other workers [29].

In order to interpret the crystal-field splitting, the SPM model has also been applied for 3d<sup>n</sup> ions [30]. The crystal field parameters, using this model, are obtained from the equations [31]

$$B_{20} = -2\bar{A}_2 \left(\frac{R_0}{R_{10} + \Delta R_1}\right)^{t_2} - 4\bar{A}_2 \left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_2} \quad (5)$$

$$B_{40} = 16\bar{A}_4 \left(\frac{R_0}{R_{10} + \Delta R_1}\right)^{t_4} + 12\bar{A}_4 \left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_4} \quad (6)$$

$$B_{44} = 2\sqrt{70}\bar{A}_4 \left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_4} \quad (7)$$

where R<sub>0</sub> is the reference distance, normally taken as the average value of all four bond lengths (for axial symmetry).

#### 4. Results and Discussion

The position of transition metal ion Fe<sup>3+</sup> and spherical coordinates of ligands are shown in Table 1. The average of two out of four Fe<sup>3+</sup>-O bond lengths are found as R<sub>10</sub> = 0.22325 nm and the average value of the rest two bond lengths are determined as R<sub>20</sub> = 0.22325

nm.  $\Delta R_1$  and  $\Delta R_2$  are the distortion parameters.  $\bar{A}_2$ ,  $\bar{A}_4$  and  $t_k$  are the intrinsic parameter and power law exponent, respectively. In octahedral coordination,

$$\bar{A}_4(R_0) = (3/4)Dq \quad [6]. \text{ For } 3d^5 \text{ ions, } \frac{\bar{A}_2}{\bar{A}_4} \text{ lies in the}$$

range 8-12 [30]. The power law exponent for Fe<sup>3+</sup> ion is taken as  $t_2 = 3$ ,  $t_4 = 7$ .

**Table 1** Atomic coordinates in CCF crystal and spherical coordinates of ligands R θ, φ.

Position of Fe <sup>3+</sup> (Fractional)	Ligands			Spherical co-ordinates of ligands			
				R(nm)	θ <sup>0</sup> (degree)	φ <sup>0</sup>	
Site : Substitutional Cd (0, 0, 0)	F1 (1)	0.5000	0	0	0.22325	90.0	0
	F1 (2)	0	0.5000	0	0.22325	90.0	90.0
	F1 (3)	0	0	0.5000	0.22325	0	0
	F1 (4)	-0.5000	0	0	0.22325	90.0	90.0

Further, taking local distortions as  $\Delta R_1 = -0.20944$  nm and  $\Delta R_2 = -0.20980$  nm,  $R_0 = 0.220$  nm and ratio  $\frac{A_2}{A_4} = 10$ , the  $B_{kq}$  parameters are obtained as given in Table 2 and the value of D as:  $D = -548.8 \times 10^{-4} \text{ cm}^{-1}$ , in good match with the experimental one:  $D = -548.8 \times 10^{-4} \text{ cm}^{-1}$  for center A. Similarly taking distortions as  $\Delta R_1 = -$

$0.17590$  nm,  $\Delta R_2 = -0.17618$  nm and other parameters as above, the  $B_{kq}$  parameters are found as shown in Table 2 and the value of D as:  $D = -800.9 \times 10^{-4} \text{ cm}^{-1}$ , also in good match with the experimental value:  $D = -800.9 \times 10^{-4} \text{ cm}^{-1}$  for center B. Using  $B_{kq}$  parameters and CFA program [32-33], the optical spectra of Fe<sup>3+</sup>

**Table 2.** Crystal field parameters and zero field splitting parameters of Fe<sup>3+</sup> doped CCF single crystal.

	Crystal- field parameters (cm <sup>-1</sup> )				Zero-field splitting parameter (10 <sup>-4</sup> cm <sup>-1</sup> )		
	$\Delta R_1$ (nm)	$\Delta R_2$ (nm)	$R_0$ (nm)	$B_{20}$	$B_{40}$	$B_{44}$	D
A	-0.20944	-0.20980	0.220	-8208.1	255.7838	152.3518	-548.8
	0.0000	0.0000	0.220	-59857.8	26342.23	15742.5	-17346.9
B	-0.17590	-0.17618	0.220	-10458.7	450.1192	268.2434	-800.9
	0.0000	0.0000	0.220	-59857.8	26342.23	15742.5	-17346.9

A = Fe<sup>3+</sup>-V<sub>Cd</sub>, B = Fe<sup>3+</sup>-Li<sup>+</sup>

doped CCF crystal are calculated. The energy levels of the impurity 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 Hamiltonian consists of the Coulomb interaction (in terms of B and C parameters), Trees correction, the spin-orbit interaction, the crystal field Hamiltonian, the spin-spin interaction and the spin-other orbit interaction. The calculated energy values are shown in Table 3 (input parameters are given below the Table)

together with the experimental values [28] for comparison. It can be seen from Table 3 that there is a reasonable agreement between the calculated and experimental energy values. The energy values calculated without considering distortion were different from the experimental ones and hence are not being given here. Thus our theoretical study supports the results obtained from the experimental investigation.

**Table 3.** Experimental and calculated (CFA package) energy band positions of Fe<sup>3+</sup> doped CCF single crystal.

Transition from <sup>4</sup> A <sub>2</sub> (F)	Observed energy bands (cm <sup>-1</sup> )	Calculated energy bands (cm <sup>-1</sup> )	
		With distortion A	B
Transition from <sup>4</sup> A <sub>2</sub> (F)	Observed energy bands (cm <sup>-1</sup> )	Calculated energy bands (cm <sup>-1</sup> )	
		With distortion A	B

${}^4T_{1g}(G)$	16300			
${}^4T_{2g}(G)$	22000			
${}^4A_{1g}(G)$	25100	26106, 26148	25589, 25659	
${}^4E_g(G)$	26750	26521, 26634, 26445, 26610,		
		26747, 26816	26729, 26936	
${}^4T_{2g}(D)$	29600	28287, 29451, 29453, 29573,		
		29566, 30767, 30429, 30480,		
		30835, 30894	30554, 30578	
${}^4E_g(D)$	31850	31574, 31693, 31578, 31705,		
		32519, 32860	32935, 33250	
${}^4T_{1g}(P)$	37050	39313, 39335, 38955, 38994,		
		39345, 39371, 39007, 39041,		
		39437, 39483	39119, 39183	

Input parameters: Numbers of free ion parameters = 5, number of d shell electrons = 3, number of fold for rotational site symmetry = 1; Racah parameters in A, B and C, spin-orbit coupling constant and Trees correction are 0, 840, 3360, 520 and  $90 \text{ cm}^{-1}$ , respectively; number of crystal field parameters = 3;  $B_{20}$ ,  $B_{40}$ ,  $B_{44}$  are taken from Table 2, spin-spin interaction parameter,  $M_0 = 0.2917$ ; spin-spin interaction parameter,  $M_2 = 0.0229$ ; spin-other-orbit interaction parameter,  $M_{00} = 0.2917$ ; spin-other-orbit interaction parameter,  $M_{22} = 0.0229$ ; magnetic field,  $B = 0.0$  Gauss; angle between magnetic field B and z-axis =  $0.00$  degree.

## 5. Conclusions

Axial (tetragonal) symmetry zero-field splitting parameter D for  $\text{Fe}^{3+}$  in CCF single crystal has been determined using superposition model and perturbation theory. The theoretical D matches well with the experimental value for both centers A and B when we consider the distortion. The theoretical study shows that  $\text{Fe}^{3+}$  ion occupies  $\text{Cd}^{2+}$  site with charge compensation which supports the inference of the experimental EPR investigation.

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