

ZERO FIELD SPLITTING PARAMETER STUDY OF Fe^{3+} IN $RbCdF_3$ SINGLE CRYSTALS AT AXIAL SYMMETRY SITE**Ram Kripal**EPR Laboratory, Department of Physics, University of Allahabad, Allahabad-211002, India
Tel: 91-532-2470532; Fax: 91-532-2460993**ABSTRACT**

A theoretical study of crystal field parameters and zero-field splitting parameter of Fe^{3+} doped $RbCdF_3$ (RCF) single crystals is done employing superposition model and the perturbation theory. The zero-field splitting parameter evaluated matches well with the experimental value obtained from EPR investigation. The theoretical study supports the experimental observation that Fe^{3+} ions substitute at Cd^{2+} site in $RbCdF_3$ single crystal with charge compensation.

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

INTRODUCTION

Electron paramagnetic resonance (EPR) studies give information about structural distortions and local site symmetry of transition ions introduced in different hosts [1-3]. Using microscopic spin-Hamiltonian (MSH) theory, the spin Hamiltonian (SH) parameters determined from EPR are correlated with optical and structural parameters. These studies suggest that the spin Hamiltonian parameters of transition ions (d^5) in crystals are very sensitive to local distortions. Therefore, the SH theory is largely used in the study of crystals.

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

It is well known that materials with perovskite structures find applications in many areas of science and technology due to their electro-optic, electro-mechanical and non-linear properties. When trivalent magnetic impurity ions are incorporated 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 because of charge compensation, forming the impurity- V_M complex center. When Li^+ ions are co-doped with the impurity ions, some impurity ions are associated with Li^+ ion near the divalent-cation site, forming the impurity- Li^+ complex center.

EPR measurements on the Fe^{3+} centers in doped and Li^+ co-doped perovskite fluoride $RbCdF_3$ (RCF) have been carried out [13]. In this crystal two kinds of tetragonal (axial) centers associated with Cd^{2+} vacancy, $Fe^{3+}-V_{Cd}$ (A) and Li^+ ion, $Fe^{3+}-Li^+$ (B) are observed. The magnitude of ZFS parameter D for Fe^{3+} ion in the B center is larger than that in the A center, which may be due to the deviations of coordinated ligands to the magnetic ion [13]. In the present study, the CF parameters are determined using SPM and these parameters with MSH theory then yield ZFS parameter for Fe^{3+} ions at the two centers A and B in RCF single crystal at room temperature (RT). The ZFS parameter D obtained using SPM gives good agreement with the experimental value [13].

2. Crystal Structure

RCF has a cubic perovskite structure at room temperature and undergoes a structural phase transition at 124 K from cubic to tetragonal. The crystal structure of RCF is cubic as illustrated in Fig. 1. The lattice parameter is reported to be $a = 4.398 \text{ \AA}$ [14]. The crystal structure belongs to the space group $Pm\bar{3}m$ (221) with Rb 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) [15]. The fluorine coordination around Cd^{2+}

is shown in Fig. 1. The site symmetry around Fe³⁺ ions may be considered to be tetragonal (axial), as suggested by EPR study of Fe³⁺: RCF [13].

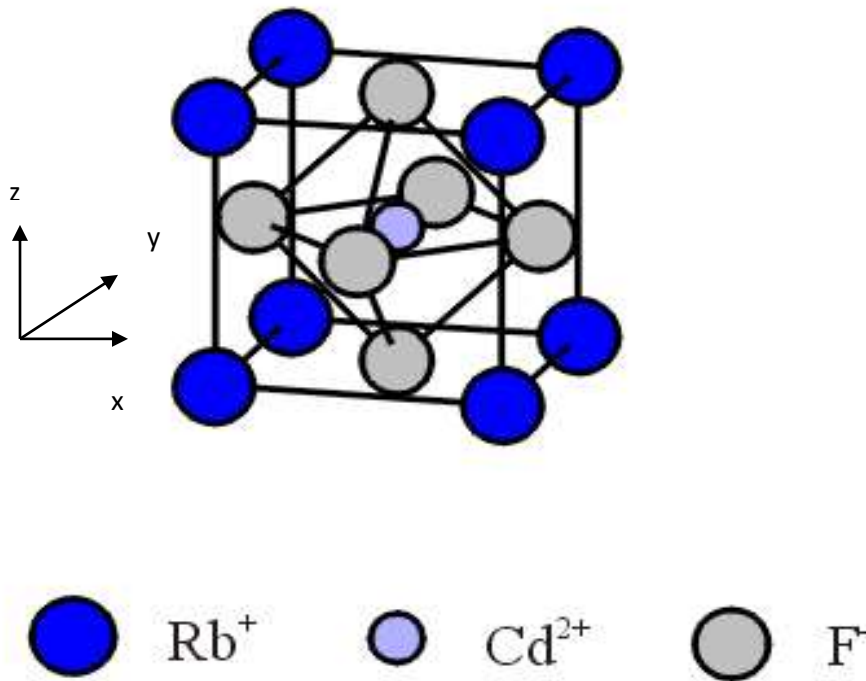


Fig. 1: Crystal structure of RCF.

3. Theoretical Investigation

The SH of 3d⁵ ion in crystal field of axial symmetry is given by [16-18]

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

where the first term gives electronic Zeeman interaction, B is the external magnetic field, g is the spectroscopic splitting factor and μ_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 provides 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 taken for Fe³⁺ ions [9, 19, 20].

The Hamiltonian for a d^5 ion is given by

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

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

is the crystal field Hamiltonian whereas \mathcal{H}_0 and \mathcal{H}_{so} represent free ion Hamiltonian and spin-orbit (SO) coupling, respectively. Since the spin-spin coupling is very small [21-23], its contribution has been neglected in Eq. (2). The crystal field of SO interaction is considered as perturbation term [24-26]. The strong-field scheme calculation for F-state ions was done by Macfarlane [27]. The SO contribution to the ZFS parameter D for $3d^5$ ions in axial symmetry is given as [25]

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

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 considered in Eq. (3) as other perturbation terms are negligible [25, 27]. The parameters B, C and ξ , in terms of the average covalency parameter N, are written as, $B = N^4B_0$, $C = N^4C_0$ and $\xi = N^2 \xi_0$, where B_0 , C_0 and ξ_0 are the Racah parameters and the spin-orbit coupling parameter for free ion [28, 29], respectively. $B_0 = 1130 \text{ cm}^{-1}$, $C_0 = 4111 \text{ cm}^{-1}$, $\xi_0 = 589 \text{ cm}^{-1}$ [9] for Fe^{3+} ion are taken in the present calculation. Using equation

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

N can be found taking the values of Racah parameters ($B = 840 \text{ cm}^{-1}$, $C = 3360 \text{ cm}^{-1}$) obtained from optical study of Fe^{3+} ion in crystal having fluorine ligands [30].

Employing SPM the CF parameters for Fe^{3+} in RCF single crystal are determined and then from Eq. (3) ZFS parameter D is evaluated. Similar method has been used for obtaining ZFS parameters by various earlier workers [31].

In order to interpret the crystal-field splitting, the SPM is effectively used. This model has also been applied for $3d^n$ ions [27, 32]. The crystal field parameters, using this model, are determined from the equations [33]

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

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

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

where R_0 is the reference distance, generally taken as the average value of all four bond lengths (for axial symmetry).

4. Results and Discussion

The position of transition metal ion Fe^{3+} and spherical coordinates of ligands are given in Table 1. The average of two out of four Fe^{3+} -O bond lengths are obtained as $R_{10} = 0.2199 \text{ nm}$ and the average value of the rest two bond

lengths are found as $R_{20} = 0.2199$ nm. ΔR_1 and ΔR_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, $\bar{A}_4(R_0) = (3/4)Dq$ [6]. For $3d^5$ ions, the ratio $\frac{\bar{A}_2}{\bar{A}_4}$ lies in the range 8-12 [27, 32]. The power law exponent for Fe^{3+} ion is taken as $t_2 = 3$, $t_4 = 7$.

Semi-ab initio calculations are done for other transition ions to obtain the intrinsic parameter values in SPM, Table 1 Atomic coordinates in RCF crystal and spherical coordinates of ligands R θ , ϕ .

Position of Fe^{3+} (Fractional)	Ligands	Spherical co-ordinates of ligands						
		x	y	z				
					R(nm)	θ^0	ϕ^0	
			(\AA)			(degree)		
Site : Substitutional	F1 (1)	0.5000	0	0	0.2199	90.0	0	
Cd (0, 0, 0)	F1 (2)	0	0.5000	0	0.2199	90.0		90.0
	F1 (3)	0	0	0.5000	0.2199	0	0	
	F1 (4)	-0.5000	0	0	0.2199	90.0	90.0	

The values of B, C and Dq are found from optical absorption study [30] as 840, 3360 and 1390 cm^{-1} , respectively.

First no local distortion is considered and the value of D is evaluated. For this, taking $\frac{\bar{A}_2}{\bar{A}_4} = 10$ and $R_0 = 0.220$ nm, which is slightly larger than the sum of ionic radii of $Fe^{3+} = 0.0645$ nm and $F^- = 0.133$ nm, the B_{kq} parameters are found as: $B_{20} = -62635.4 \text{ cm}^{-1}$, $B_{40} = 29283.05 \text{ cm}^{-1}$, $B_{44} = 17499.97 \text{ cm}^{-1}$ and the value of D as: $D = -18902.7 \times 10^{-4} \text{ cm}^{-1}$. EPR study gives the experimental value of D as: $D = -422.2 \times 10^{-4} \text{ cm}^{-1}$ and $D = -603.6 \times 10^{-4} \text{ cm}^{-1}$ for center A and B, respectively [13]. From above it is seen that the theoretical value is quite larger than the experimental one.

Now, taking local distortions as $\Delta R_1 = -0.2390$ nm and $\Delta R_2 = -0.2386$ nm, $R_0 = 0.220$ nm and ratio $\frac{\bar{A}_2}{\bar{A}_4} = 10$, the

B_{kq} parameters are found as shown in Table 2 and the value of D as: $D = -422.2 \times 10^{-4} \text{ cm}^{-1}$, in good agreement with the experimental one: $D = -422.2 \times 10^{-4} \text{ cm}^{-1}$ for center A. Similarly taking distortions as $\Delta R_1 = -0.20396$ nm, $\Delta R_2 = -0.20430$ nm and other parameters as above, the B_{kq} parameters are obtained as given in Table 2 and the value of D as: $D = -603.6 \times 10^{-4} \text{ cm}^{-1}$, also in good agreement with the experimental value: $D = -603.6 \times 10^{-4} \text{ cm}^{-1}$ for center B. Using B_{kq} parameters and CFA program [34-35], the optical spectra of Fe^{3+}

Table 2. Crystal field parameters and zero field splitting parameters of Fe³⁺ doped RCF single crystal.

	Crystal- field parameters (cm ⁻¹)					Zero-field splitting parameter (10 ⁻⁴ cm ⁻¹)	
	ΔR_1 (nm)	ΔR_2 (nm)	R ₀ (nm)	B ₂₀	B ₄₀	B ₄₄	D
A	-0.2390	-0.2386	0.220	-6897.95	170.4839	101.5284	-422.2
	0.0000	0.0000	0.220	-62635.4	29283.05	17499.97	-18902.7
B	-0.20396	-0.2043	0.220	-8732.36	295.524	176.0432	-603.6
	0.0000	0.0000	0.220	-62635.4	29283.05	17499.97	-18902.7

A = Fe³⁺-V_{Cd}, B = Fe³⁺-Li⁺

doped RCF crystal are computed. The energy levels of the impurity ion are evaluated by diagonalizing the complete Hamiltonian within the 3d^N basis of states in the intermediate crystal field coupling scheme. The Hamiltonian contains 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 computed energy values are shown in Table 3 (input parameters are given below the Table) along with the experimental values [30] for comparison. It is observed from Table 3 that there is a reasonable agreement between the computed and experimental energy values. The energy values determined without considering distortion were inconsistent from the experimental ones and so are not being given here. Thus our theoretical investigation supports the results obtained from the experimental study.

Table 3. Experimental and calculated (CFA package) energy band positions of Fe³⁺ doped RCF single crystal.

Transition from ⁴ A ₂ (F)	Observed energy bands (cm ⁻¹)	Calculated energy bands (cm ⁻¹)	
		With distortion A	B
⁴ T _{1g} (G)	16300		
⁴ T _{2g} (G)	22000	24590, 24612, 24706, 24772	24254, 24292, 24382, 24421, 24501
⁴ A _{1g} (G)	25100	25052, 25087	25075, 25140
⁴ E _g (G)	26750	27416, 27658, 27923, 28319	25238, 26875, 27135, 27426
⁴ T _{2g} (D)	29600	29244, 29376, 30389, 30470, 30522, 30525	29237, 29375, 30064, 30142, 30213, 30230
⁴ E _g (D)	31850	31032, 31166, 31818, 32187	31035, 31181, 32175, 32518
⁴ T _{1g} (P)	37050	35915, 35978, 36007, 36079, 36124, 36187	35786, 35851, 35965, 36023, 36123, 36193

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 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 symmetry zero-field splitting parameter D for Fe^{3+} in RCF single crystal has been evaluated using superposition model and perturbation theory. The theoretical D agrees well with the experimental value for both centers A and B when distortion is taken into consideration. This theoretical investigation shows that Fe^{3+} ion occupies Cd^{2+} site with charge compensation which supports the results of the experimental EPR study.

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