

ZERO FIELD SPLITTING PARAMETER OF Fe^{3+} IN CaF_2 SINGLE CRYSTALS**Ram Kripal**

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Abstract

A theoretical investigation of crystal field parameters and zero-field splitting parameter of Fe^{3+} doped CaF_2 single crystals is performed using superposition model and the perturbation theory. The zero-field splitting parameter D obtained theoretically agrees well with the experimental value determined from EPR study. The theoretical study supports the experimental result that Fe^{3+} ions substitute at Ca^{2+} site in CaF_2 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 distortions in the lattice and local site symmetry of transition ions doped in different crystals [1-3]. Employing microscopic spin-Hamiltonian (MSH) theory, the spin Hamiltonian (SH) parameters estimated from EPR can be correlated with optical and structural parameters. The above studies indicate 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 evaluated with the help of superposition model (SPM) [4, 5]. The zero field splitting (ZFS) parameters are then determined using CF parameters [6]. Fe^{3+} ion of iron group is important due to its ${}^6S_{5/2}$ ground state [7-9]. The electron spins are freely oriented in external magnetic field with high order interaction of crystalline electric field [10, 11].

Crystals with fluorite structure (Fig. 1) give the possibility of studying impurity ions in eightfold cubic coordination, when the ions are substituted on cation sites. Transition metal ions in sixfold and fourfold cubic coordination as well as rare-earth ions in eightfold cubic coordination have been studied for a long time, whereas d^n ions in eightfold cubic coordination were the subject of research in the last decade. The physical properties of crystals with fluorite structure have been discussed in [12]. In the group of crystals having fluorite structure only the compounds CaF_2 , SrF_2 , BaF_2 , CdF_2 , PbF_2 , and $SrCl_2$ were used as host for the study of transition metal impurities till now. The optical and EPR spectra can be described within the framework of the crystal field theory and the concept of the spin Hamiltonian (SH).

EPR measurements on the Fe^{3+} centers in alkaline ions (Na, K, Li) co-doped CaF_2 at 4.2K have been

reported [13]. CaF_2 crystals containing Fe^{3+} ions were prepared by doping alkaline ions (Na, K, and Li) as charge compensators [14]. In the present investigation, the CF parameters are evaluated using SPM and these parameters with MSH theory then provide ZFS parameter for Fe^{3+} ions at the axial center in CaF_2 single crystal at 4.2K The ZFS parameter D obtained with the help of SPM shows good agreement with the experimental value [13].

2. Crystal Structure

The crystal structure of CaF_2 is cubic as illustrated in Fig. 1. The lattice parameter is reported to be $a = 5.4629 \text{ \AA}$ [15]. The crystal structure belongs to the space group O_h^5 ($\text{Fm}\bar{3}\text{m}$). The fluorine coordination around Ca^{2+} is shown in Fig. 1. The site symmetry around Fe^{3+} ions may be considered to be axial, as suggested by EPR study of $\text{Fe}^{3+}:\text{CaF}_2$ [13].

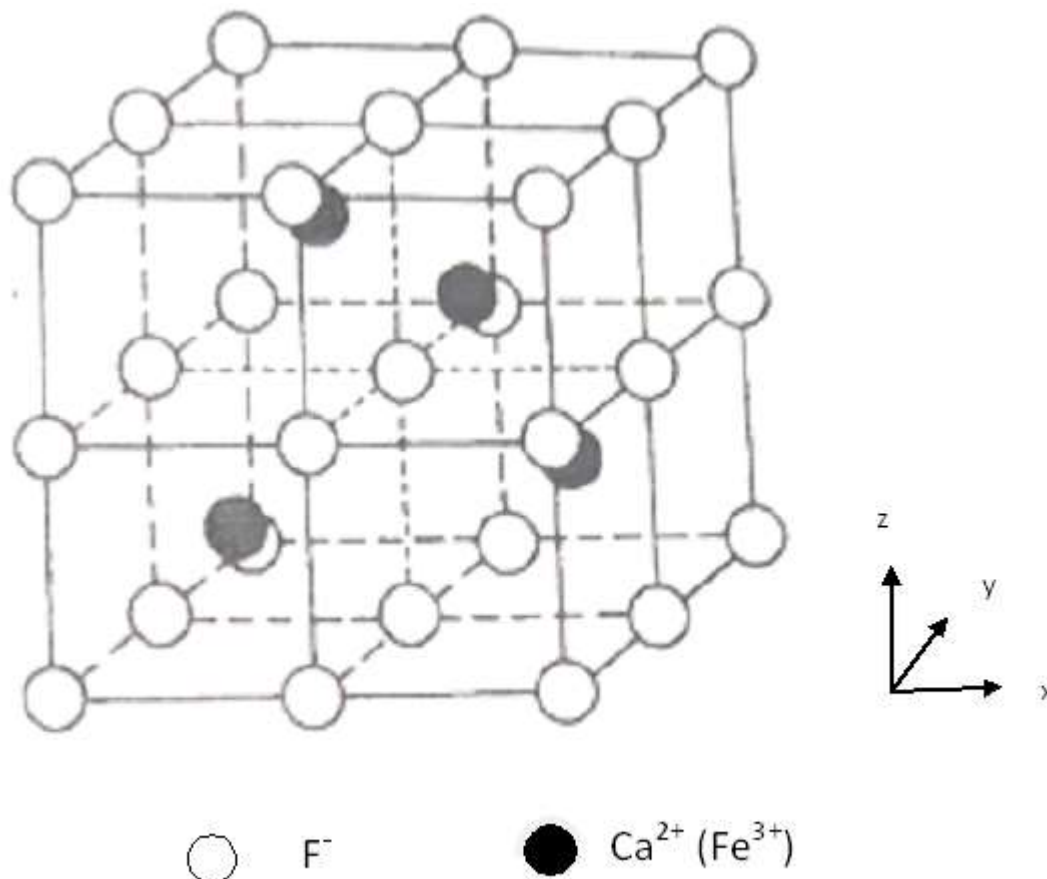


Fig. 1: Crystal structure of CaF_2 together with axes (SAAS-symmetry adopted axes system).

3. Theoretical Investigation

The SH of $3d^5$ ion in crystal field of axial symmetry is written as [16-18]

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

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 [8]. The fifth term represents 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. The electronic Zeeman interaction is taken to be isotropic for Fe^{3+} ions [8, 19, 20].

The Hamiltonian for a d^5 ion is given as

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

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

is the crystal field Hamiltonian whereas \mathcal{H}_0 and \mathcal{H}_{so} are free ion Hamiltonian and spin-orbit (SO) coupling, respectively. As the spin-spin coupling is very small [21-23], its contribution is 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 given by Macfarlane [27]. The SO contribution to the ZFS parameter D for $3d^5$ ions in axial symmetry is given by [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 provide 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) as other perturbation terms are negligible [25, 27]. The parameters B, C and ξ , in terms of the average covalency parameter N, are given 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. $B_0 = 1130 \text{ cm}^{-1}$, $C_0 = 4111 \text{ cm}^{-1}$, $\xi_0 = 589 \text{ cm}^{-1}$ [8] for Fe^{3+} ion are taken in our 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].

Using SPM the CF parameters for Fe^{3+} in CaF_2 single crystal are evaluated and then from Eq. (3) ZFS parameter D is determined. Similar method has been used for obtaining ZFS parameters by various other workers [31].

In order to interpret the crystal-field splitting, the SPM is effectively considered. This model has also been applied for $3d^n$ ions [27, 32]. The crystal field parameters B_{kq} , using this model, are obtained 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 Fe^{3+} ion and spherical coordinates of ligands are shown in Table 1. The average of two out of four Fe^{3+} -F bond lengths are found as $R_{10} = 0.6041 \text{ nm}$ and the average value of the rest two bond lengths are obtained as $R_{20} = 0.6041 \text{ nm}$. 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, the same method is used here.

*Table 1 Atomic coordinates in CaF₂ crystal and spherical coordinates of ligands R
θ, φ.*

Position of Fe ³⁺ (Fractional)	Ligands			Spherical co-ordinates of ligands			
				R(nm)	θ ⁰	φ ⁰	
	x	y	z		(degree)		
	(Å)						
Site : Substitutional	F (1)	0.2500	0.2500	0.2500	0.3021	54.73	45.00
Ca (0, 0, 0)	F (2)	0.7500	0.7500	0.7500	0.9063	54.73	45.00
	F (3)	-0.2500	-0.2500	-0.2500	0.3021	125.26	45.00
	F (4)	-0.7500	-0.7500	-0.7500	0.9063	125.26	45.00

The values of B, C and Dq are determined 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

$\frac{\overline{A_2}}{\overline{A_4}} = 10$ and $R_0 = 0.211$ nm, which is slightly larger than the sum of ionic radii of Fe³⁺ = 0.0645 nm

and $F^- = 0.133$ nm, the B_{kq} parameters are found as: $B_{20} = -2663.99$ cm⁻¹, $B_{40} = 18.49042$ cm⁻¹, $B_{44} = 11.05014$ cm⁻¹ and the value of D as: $|D| = 114.37 \times 10^{-4}$ cm⁻¹. EPR study provides the experimental value of D as: $|D| = 1471.0 \times 10^{-4}$ cm⁻¹ [13]. From above it is found that the theoretical value is quite smaller than the experimental one.

Now, taking local distortions as $\Delta R_1 = -0.2654$ nm and $\Delta R_2 = -0.2662$ nm, $R_0 = 0.211$ nm and ratio

$\frac{\overline{A_2}}{\overline{A_4}} = 10$, the B_{kq} parameters are found as given in Table 2 and the value of D as: $|D| = 1471.73 \times 10^{-4}$

cm⁻¹, in good agreement with the experimental one: $|D| = 1471.0 \times 10^{-4}$ cm⁻¹. Taking B_{kq} parameters and CFA program [34-35], the optical spectra of Fe³⁺

Table 2. Crystal field parameters and zero field splitting parameters of Fe³⁺ doped CaF₂ 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
-0.2654	-0.2662	0.211	-15181.0	1068.324	644.4901	1471.73
0.0000	0.0000	0.211	-2663.99	18.49042	11.05014	114.37
Exptl.						1471.0

doped CaF₂ crystals are calculated. The energy levels of Fe³⁺ 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 calculated energy values are given in Table 3 (input parameters are given below the Table) together with the experimental values [30] for comparison. It is seen from Table 3 that there is a reasonable agreement between the calculated and experimental energy values. The energy values evaluated without considering distortion were inconsistent from the experimental ones and so are not being shown here. Thus our theoretical investigation supports the results of the experimental study.

Table 3. Experimental and calculated (CFA package) energy band positions of Fe³⁺ doped CaF₂ single crystal.

Transition from ⁶ A _{1g} (S)	Observed energy bands (cm ⁻¹)	Calculated energy bands (cm ⁻¹) With distortion
⁴ T _{1g} (G)	16300	
⁴ T _{2g} (G)	22000	24111, 24118, 24349, 24371, 24482, 24588
⁴ A _{1g} (G)	25100	24907, 25145
⁴ E _g (G)	26750	26831, 26862, 26880, 26945
⁴ T _{2g} (D)	29600	29508, 29629, 29890, 29892, 29985, 30008
⁴ E _g (D)	31850	31584, 31720, 33706, 33964
⁴ T _{1g} (P)	37050	37824, 37921, 37928, 37991, 38138, 38237

Input parameters: Numbers of free ion parameters = 5, number of d shell electrons = 5, 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; B₂₀, B₄₀, B₄₄ are taken from Table 2, spin-spin interaction parameter, M₀ = 0.2917; spin-spin interaction parameter, M₂ = 0.0229; spin-other-orbit interaction parameter, M₀₀ = 0.2917; spin-other-orbit interaction parameter, M₂₂ = 0.0229; magnetic field, B = 0.0 Gauss; angle between magnetic field B and z-axis = 0.00 degree.

5. Conclusions

Zero-field splitting parameter D for Fe³⁺ in CaF₂ single crystal has been determined using superposition model and perturbation theory. The theoretical D agrees well with the experimental value when distortion is taken into account. The theoretical investigation shows that Fe³⁺ ion occupies Ca²⁺ site with

charge compensation which supports the results of the experimental EPR study.

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