

# Theoretical Zero Field Splitting Parameters of Fe<sup>3+</sup> doped TlGaSe<sub>2</sub> Single Crystal

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## Abstract

A theoretical study of crystal field parameters (CFPs) and zero-field splitting parameters (ZFSPs) D and E of Fe<sup>3+</sup> doped TlGaSe<sub>2</sub> (TGS) crystals at room temperature (RT) is carried out using superposition model and the perturbation theory. The ZFSPs D and E obtained here are in good agreement with the experimental values reported earlier. The conclusion of experimental investigation that Fe<sup>3+</sup> substitutes for Ga<sup>3+</sup> in TGS is supported by our theoretical study. The values of D and E without and with local distortion are evaluated. The theoretical values of D and E agree well with the experimental values when local distortion is taken into account.

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

## 1. INTRODUCTION

Electron paramagnetic resonance (EPR) is used to provide information about local site symmetry and zero field splitting parameters (ZFSPs) of transition ions doped in crystals [1,2]. Fe<sup>3+</sup> ion in the iron group is of interest due to just half filled 3d shell yielding the ground state <sup>6</sup>S with spin S = 5/2. The crystal field can only affect the electron spins through high order interaction, making them free to orient themselves in the external magnetic field.

The superposition model (SPM) was developed to find physical and geometrical information present in crystal field parameters [3, 4]. The positions of different ligands are required to apply this model. Therefore, the relation between the model and the theories of local distortion in crystals is important. A one-parameter model was used [5] to describe the position of the Fe<sup>3+</sup> ion relative to the surrounding oxygens.

Theoretical studies on the spin Hamiltonian parameters of d<sup>5</sup> ions have been done by many researchers [6-16]. Various mechanisms are suggested to contribute to the ground state splitting of the magnetic ions introduced in the crystals [17]. The effect of spin Hamiltonian is normally considered by perturbation procedures. In most of the perturbation procedure, cubic field and the diagonal part of free-ion Hamiltonian are taken as unperturbed terms whereas the spin-orbit coupling, the low-symmetry field, and the off-diagonal part of free-ion Hamiltonian are considered as the perturbation terms [18].

EPR studies of Fe<sup>3+</sup> doped tellurium gallium selenide, TlGaSe<sub>2</sub> (TGS) single crystals have been reported earlier [19]. Two possibilities are there for Fe<sup>3+</sup> site in the TGS crystal, namely substitutional and interstitial. It is interesting to investigate the site of the impurity. It was suggested [19] that Fe<sup>3+</sup> ion enters the crystal lattice substitutionally at Ga<sup>3+</sup> site. In the present study, the zero-field splitting parameters (ZFSPs) D and E are calculated for the Fe<sup>3+</sup> ion at substitutional Ga<sup>3+</sup> site in TGS; using crystal field parameters (CFPs) obtained from superposition model and perturbation expressions [20]. The aim of study is to obtain information whether Fe<sup>3+</sup> ion enters the crystal lattice substitutionally or interstitially and about the distortion produced in the lattice. The results obtained from this model are in good agreement with the experimental one when local distortion is taken into account for the Fe<sup>3+</sup> ion at substitutional Ga<sup>3+</sup> site in TGS crystal.

## 2. CRYSTAL STRUCTURE

Single crystals of TGS are monoclinic with a = 1.0772 nm, b = 1.0771 nm, c = 1.5636 nm, β = 100.6°, Z = 16, space group Cc [21, 22]. The system crystallizes with a layer structure with two anion layers perpendicular to c\* in the unit cell. The structural motive of the layers is large corner-linked Ga<sub>4</sub>Se<sub>10</sub> tetrahedra consisting of four corner-linked GaSe<sub>4</sub> tetrahedra. Two adjacent layers are turned relative to each other by 90°. They are kept together by Tl<sup>1+</sup> ions situated on straight lines parallel to the edges of the Ga<sub>4</sub>Se<sub>10</sub> groups. They are surrounded by six selenium atoms forming trigonal-prismatic TlSe<sub>6</sub> polyhedra.

## 3. THEORETICAL INVESTIGATION

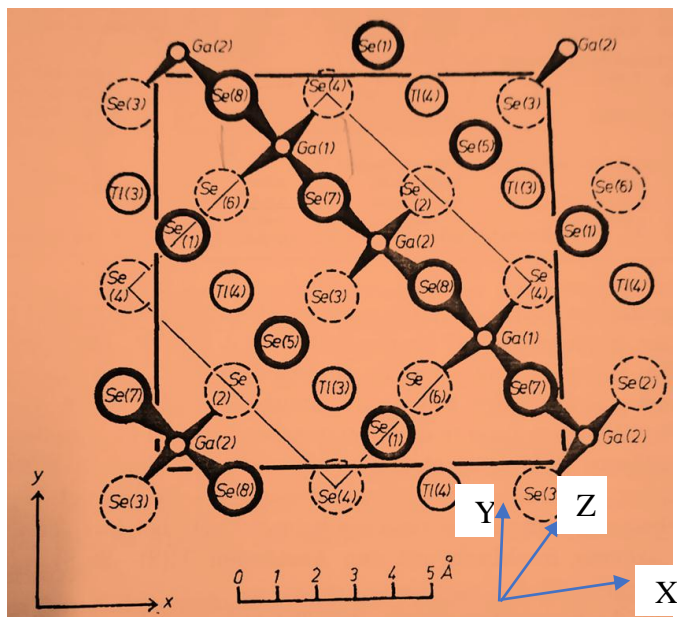
The experimental resonance fields are analyzed using the spin Hamiltonian [23, 24],

$$\mu_B B \cdot g \cdot S + D \left\{ S_z^2 - \frac{1}{3} S(S+1) \right\} + E(S_x^2 - S_y^2)$$
$$\mathcal{H} = + \frac{a}{6} [S_x^4 + S_y^4 + S_z^4 - \frac{1}{5} S(S+1)(3S^2 + 3S + 1)] \quad (1)$$

where g is the spectroscopic splitting factor, μ<sub>B</sub> is the Bohr magneton and B is the external magnetic field. The parameters D and E are the second rank axial and rhombic

ZFSPs, whereas  $a$  is the fourth rank cubic one [25, 26]. The direction of the maximum overall splitting of the EPR spectrum is taken along the  $z$  axis and the minimum along the  $x$  axis [27]. The laboratory axes ( $x, y, z$ ) are parallel to the crystallographic axes. The local site symmetry axes, i. e. the symmetry adopted axes (SAA) are the nearly orthogonal directions of metal-ligand bonds. The  $Z$ -axis of SAAS in four equivalent sites is coincident with the crystal  $c$ -axis and the other two axes ( $X, Y$ ) lie in the  $ab$  plane.

The  $Z$  axis of SAAS is along the metal-ligand bond Ga-Se (4), Ga-Se (2), Ga-Se (4) and GA-Se (2) for sites I, II, III and IV, respectively and the two other axes ( $X, Y$ ) are mutually perpendicular to the  $Z$  axes for all the four sites (Fig. 1). This indicates that  $Fe^{3+}$  substitutes  $Ga^{3+}$  in the crystal lattice. The ionic radius of  $Fe^{3+}$  ion 0.064 nm [28] is similar to the ionic radius of  $Ga^{3+}$  (0.062 nm), thus  $Fe^{3+}$  can fit at the location of  $Ga^{3+}$  with slight distortion.



**Fig 1.** Crystal structure of TGS in which symmetry adopted axis system (SAAS) is shown.

The ZFSPs of  $Fe^{3+}$  ion located at four equivalent sites in Fig. 1 are calculated using the perturbation theory [29, 30]. These calculated values are then compared with the experimental result.

Spin Hamiltonian of a  $d^5$  ( $^6S$  state) ion is written as sum of free ion ( $\mathcal{H}_o$ ), spin-orbit coupling ( $\mathcal{H}_{so}$ ), spin-spin coupling ( $\mathcal{H}_{ss}$ ) and crystal field ( $\mathcal{H}_c$ ) Hamiltonians,

$$\mathcal{H} = \mathcal{H}_o + \mathcal{H}_{so} + \mathcal{H}_{ss} + \mathcal{H}_c \quad (2)$$

$$\text{where } \mathcal{H}_c = \sum B_{kq} C_q^{(k)} \quad (3)$$

Here  $B_{kq}$  are the crystal-field parameters and  $C_q^{(k)}$  are the Wybourne spherical tensor operators. For the orthorhombic symmetry crystal field,  $B_{kq} \neq 0$  only with  $k = 2, 4, q = 0, 2, 4$ . The crystal-field theory has been extensively used to the study of the spin Hamiltonian parameters of transition ions in crystals [31-33]. In the present study, we have calculated the

CFPs,  $B_{kq}$  using SPM [29].

In TGS crystal the local symmetry around  $Fe^{3+}$  ions is orthorhombic of type I (OR-I) [19, 28]. In OR-I symmetry, the ZFSPs D and E are given by [34]

$$D^{(4)}(SO) = \left( \frac{3\xi^2}{70P^2D} \right) [-B_{20}^2 - 21\xi B_{20} + 2B_{22}^2] + \left( \frac{\xi^2}{63P^2G} \right) [-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2] \quad (4)$$

$$E^{(4)}(SO) = \left( \frac{\sqrt{6}\xi^2}{70P^2D} \right) [2B_{20} - 21\xi] B_{22} + \left( \frac{\xi^2}{63P^2G} \right) [3\sqrt{10}B_{40} + 2\sqrt{7}B_{44}] B_{42} \quad (5)$$

where  $P = 7B + 7C, G = 10B + 5C, D = 17B + 5C$ . B and C are Racah parameters, which describe electron-electron repulsion and  $\xi$  is the spin-orbit coupling parameter. In fact, the values of B and C for transition metal ion in a crystal are less than those of the free ion. By considering the average covalency parameter N, we can write the Racah parameters [29, 35] and spin-orbit coupling parameter as  $B = N^4 B_0, C = N^4 C_0, \xi = N^2 \xi_0$ , where  $B_0$  and  $C_0$  are Racah parameters for free ion and  $\xi_0$  is free ion spin-orbit coupling parameter. For free  $Fe^{3+}$  ion,  $B_0 = 1130 \text{ cm}^{-1}, C_0 = 4111 \text{ cm}^{-1}$  and  $\xi_0 = 589 \text{ cm}^{-1}$  are used [29].

Using the values of Racah parameters ( $B = 720 \text{ cm}^{-1}, C = 2500 \text{ cm}^{-1}$ ) evaluated from optical study of the system with Se ligand [36], the average parameter  $N = 0.789$  is obtained using  $N = (\sqrt{B/B_0} + \sqrt{C/C_0})/2$ .

The CFPs in SPM are given [34, 37] as

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

where the co-ordination factor  $K_{kq}(\theta_j, \phi_j)$  is an explicit function of the angular position of the ligand. The intrinsic parameter  $\overline{A}_k(R_j)$  is given by

$$\overline{A}_k(R_j) = \overline{A}_k(R_0) \left( \frac{R_0}{R_j} \right)^{t_k}$$

where  $R_j$  is the distance between the  $d^n$  ion and the ligand,  $\overline{A}_k(R_0)$  is the intrinsic parameter of the reference crystal,  $t_k$  is the power law exponent and  $R_0$  is reference distance between metal and ligand. For  $Fe^{3+}$  doped crystals having different ligands,  $t_2 = 3$  and  $t_4 = 5$  [33]. The same values are used here in our calculation. As the co-ordination around  $Fe^{3+}$

ion is tetrahedral,  $\overline{A}_4$  correlates Dq as [38]

$$\overline{A}_4(R_0) = -\frac{27}{16} Dq$$

From optical study [36], we have the value of  $Dq = 720 \text{ cm}^{-1}$ .

Thus, the relation gives the value of  $\overline{A}_4(R_0) = 1215 \text{ cm}^{-1}$ . It is seen that for  $3d^5$  ions the ratio of  $\overline{A}_2(R_0)$  and  $\overline{A}_4(R_0)$  lies between 8 to 12 [29, 39, 40]. In our study,  $\frac{\overline{A}_2}{\overline{A}_4} = 10$  is taken, which provides  $\overline{A}_2 = 12150 \text{ cm}^{-1}$ .

#### 4. RESULTS AND DISCUSSION

In SPM, the non-zero CFPs  $B_{kq}$  of  $\text{Fe}^{3+}$  ion at four equivalent sites is calculated by considering the parameters  $\overline{A}_2$  and

$\overline{A}_4$  as well as arrangement of Se ions around  $\text{Fe}^{3+}$  ion (Fig. 1). Atomic coordinates in TGS crystal together with bond length R (without and with distortion) and angle  $\theta$  (one site) are given in Table 1. The calculated CFPs and ZFS Ps together with reference distance  $R_0$  are shown in Table 2. Table 2 shows that the value of  $R_0 = 0.235 \text{ nm}$  near the average of four ligand distances from the central metal ion (0.2379 nm) together with local distortion yield ZFSPs for all the four equivalent sites in good agreement with the experimental values given here [19]. The ZFSPs obtained using  $R_0 = 0.235 \text{ nm}$  and without local distortion do not match with the experimental values. Thus, the inference drawn on the basis of superposition model supports the experimental result that  $\text{Fe}^{3+}$  ions take up substitutional  $\text{Ga}^{3+}$  site in the crystal [19]. For comparison we have also studied the interstitial sites for  $\text{Fe}^{3+}$  ions. The computed values of ZFSPs come out to be inconsistent with the experimental ones and hence we are not giving this result here.

**Table 1.** Atomic coordinates in TGS crystal together with bond length R (without and with distortion) and angle  $\theta$  (one site).

Position of $\text{Fe}^{3+}$	Ligands	Spherical co-ordinates of ligands					
		x	y	z	R(nm)	$\theta^0$	
(Å)							
Without distortion							
Site I: Substitutional	Se 4	0.0278	0.4468	0.3776	0.235	$R_1$	114.95 $\theta_1$
$\text{Ga1}(0.4249, 0.1907, 0.9584)$	Se 6	0.2697	0.3112	0.8767	0.232	$R_2$	112.08 $\theta_2$
	Se 7	0.0731	0.1864	0.5592	0.243	$R'_1$	112.48 $\theta'_1$
	Se 8	0.3261	0.0607	0.0526	0.241	$R'_2$	108.08 $\theta'_2$
With distortion							
	Se 4				0.26230	$R_1 + \Delta R_1$	114.95
	Se 6				0.23358	$R_2 + \Delta R_2$	112.08
	Se 7				0.25035	$R'_1 + \Delta R'_1$	112.48
	Se 8				0.26110	$R'_2 + \Delta R'_2$	108.08

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

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									
$\frac{\overline{A_2}}{\overline{A_4}}=10$	0.235	-27049.7	-4036.55	-2373.62	1868.264	14164.82	10359	1232	0.119
With distortion									
Site I									
$\frac{\overline{A_2}}{\overline{A_4}}=10$	0.235	-23141.9	-7022.85	-1791.7	1208.89	10997.6	7288	1569	0.215
							Exp. 7288	1560	0.214

## 5. CONCLUSIONS

CFPs and ZFSPs for Fe<sup>3+</sup> ion doped TGS have been calculated using superposition model and perturbation theory, respectively. The calculated parameters are in good agreement with the experimental ones. The inference drawn on the basis of superposition model supports the experimental result that Fe<sup>3+</sup> ions take up substitutional Ga<sup>3+</sup> position in the TGS crystal

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