

# Modeling of crystal field and zero field splitting parameters of $\text{Mn}^{2+}$ doped $\beta\text{-Ga}_2\text{O}_3$ single crystal

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Crystal field (CF) parameters and zero field splitting (ZFS) parameters of  $\text{Mn}^{2+}$  doped  $\beta\text{-Ga}_2\text{O}_3$  single crystals are obtained using the superposition model (SPM) and perturbation theory. The determined ZFS parameters show good agreement with the experimental values suggesting that the  $\text{Mn}^{2+}$  ion substitutes at  $\text{Ga}^{3+}$  site in  $\beta\text{-Ga}_2\text{O}_3$  single crystal. The CF energy levels of the  $\text{Mn}^{2+}$  ion computed by diagonalizing the complete Hamiltonian are in reasonable agreement with the experimental values. The approach used may be applied for the modeling of other ion-host systems to explore the crystals for scientific and industrial applications.

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## 1. Introduction

The gallium oxide,  $\beta\text{-Ga}_2\text{O}_3$  is a large band gap ( $E_g = 4.9$  eV) material [1] and has a potential application as transparent conducting oxide [2, 3]. When gallium oxide is synthesized in reduction condition, it becomes an  $n$ -type semiconductor because of oxygen vacancies [4]. The  $\text{Zr}^{4+}$  ion doping increases the electrical conductivity and the blue luminescence as well as the oxygen vacancies [5]. The doped impurities producing the microscopic structural change can affect the optical properties of the crystal depending on the location of site and symmetry of impurities. The  $\text{Mn}^{2+}$  ion is important probe to obtain information for the  $\beta\text{-Ga}_2\text{O}_3$  crystal having various applications.

The electron paramagnetic resonance (EPR) Spectroscopy is quite useful for the analysis of ground state energy of paramagnetic ions. EPR is a sensitive technique to know the site location and local site symmetry of impurities in the host crystal. The iron group transition metal ions  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  are detected with high sensitivity by the EPR method as they have the  $S$ -state electron spin system. The EPR spectra of  $\text{Mn}^{2+}$  ions doped  $\beta\text{-Ga}_2\text{O}_3$  are analyzed using monoclinic spin Hamiltonian with the effective spin  $S = 5/2$  [6]. The local site symmetry, ground-state energy levels of  $\text{Mn}^{2+}$  as well as substitutional site of  $\text{Mn}^{2+}$  ion are determined [6]. Since  $\text{Ga}^{3+}$  cations are located in the distorted octahedral and tetrahedral sites in  $\beta\text{-Ga}_2\text{O}_3$  crystal, the local site symmetry about  $\text{Ga}^{3+}$  cations may be lower than rhombic [7]. The laboratory axes  $x$ ,  $y$ ,  $z$  used for the spin Hamiltonian analysis coincide with the modified crystallographic axes  $a$ ,  $b$ ,  $c^*$ . The magnetic axes are labeled as  $X$ ,  $Y$ ,  $Z$ . The computer program EPR-NMR [8] gives spin Hamiltonian parameters  $g$ ,  $D$ ,  $E$  and  $A$  using exact diagonalization. One of the principal axes  $Y$  of both

$g$  and  $D$  tensors is parallel to the crystallographic axis  $b$  ( $C_2$  axis). However, the principal axes of the  $g$  and  $D$  tensors in the plane normal (monoclinic plane) to the  $C_2$  axis are not coincident.

It is concluded that the  $\text{Mn}^{2+}$  spectrum is originated from only one EPR center. This implies that  $\text{Mn}^{2+}$  ions substitute for only one site either tetrahedral or octahedral site. The radius of the  $\text{Ga}^{2+}$  ion  $0.62$  Å in an octahedral site is much larger than that of  $0.47$  Å in a tetrahedral site  $\text{Ga}^{3+}$  [9]. The ionic radius of the octahedrally coordinated  $\text{Mn}^{2+}$  ion favors the octahedral  $\text{Ga}^{2+}$  site. When the  $\text{Mn}^{2+}$  ion substitutes for the  $\text{Ga}^{2+}$  ion, charge mismatch is produced. However, charge compensation can be made remotely as seen in other crystals [10, 11].  $\text{Ga}_2\text{O}_3$  crystal is not purely ionic, it is partially covalent. There was no indication of nearby charge compensation in EPR signals. Therefore, it is concluded that the  $\text{Mn}^{2+}$  ion substitutes for the  $\text{Ga}^{2+}$  ion in octahedral site without nearby charge compensation, rather with remote charge compensation consistent with the earlier work [12].

In reference to its applications in electron paramagnetic resonance (EPR) of transition metal ions in crystals, the superposition model (SPM) has been reviewed earlier [13]. SPM gives semi-empirical modeling of the crystal field (CF) parameters and zero field splitting (ZFS) parameters used in optical and [14–16] EPR spectroscopy [17–20], respectively. The origin of the physical CF Hamiltonian, and the effective spin Hamiltonians (SH) with ZFS Hamiltonian are described in [21–22].

In the present investigation, the ZFS parameters  $D$  and  $E$  for the  $\text{Mn}^{2+}$  ion at substitutional  $\text{Ga}^{2+}$  octahedral site in  $\beta\text{-Ga}_2\text{O}_3$  are calculated using CF parameters and perturbation formulae [23]. The theoretical values of  $D$  and  $E$  are in good agreement with the experimental ones [6]. The optical energy levels for  $\text{Mn}^{2+}$  ions in  $\beta\text{-Ga}_2\text{O}_3$  are

determined using CF parameters and Crystal Field Analysis (CFA) program. There is reasonable agreement between the theoretical and experimental optical energy levels. The present approach may be useful in future modeling of other crystals for technological and industrial applications.

## 2. Crystal structure

The crystal structure of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is monoclinic having space group  $C2/m$  [7]. The lattice parameters are  $a = 1.2214$  nm,  $b = 0.30371$  nm,  $c = 0.57981$  nm,  $\beta = 103.83^\circ$  and  $Z = 4$ . Two chemically distinct cation sites are either coordinated tetrahedrally or octahedrally with oxygen ions. The structure shows double chains of GaO<sub>6</sub> octahedra (Ga2) parallel to the  $b$  axis, which are connected by GaO<sub>4</sub> tetrahedra (Ga1). The crystal structure of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> together with symmetry adapted axis system (SAAS) is given in Fig. 1.

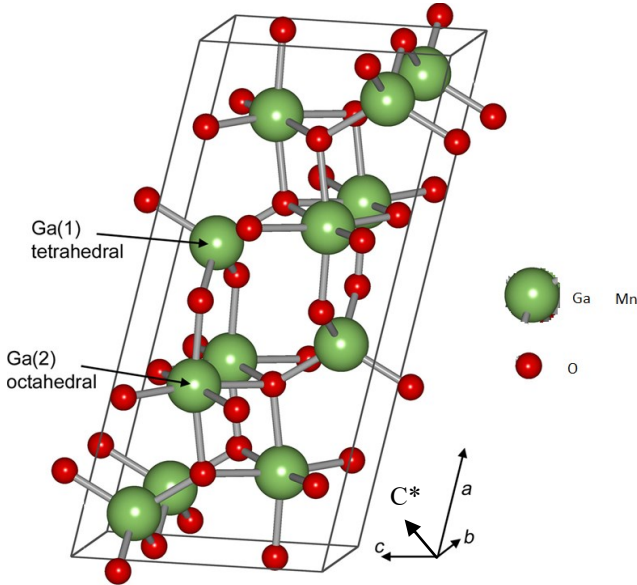


Fig. 1. Crystal structure of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> with symmetry adapted axis system (SAAS) (color online)

The site symmetry around Mn<sup>2+</sup> ions substituting for Ga<sup>3+</sup> is assumed to be approximately orthorhombic [6].

## 3. Theoretical investigation

The resonance magnetic fields can be obtained using the following spin Hamiltonian [14, 17]

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

where  $g$ ,  $\mu_B$ ,  $\mathbf{B}$  are the isotropic spectroscopic splitting factor, Bohr magneton, and external magnetic field, respectively.  $D$  and  $E$  are the second-rank axial and rhombic ZFS parameters, whereas  $a$  is the fourth-rank cubic one.  $\mathcal{A}$  and  $\mathcal{B}$  in Eq. (1) give the hyperfine ( $I = 5/2$ ) interaction constants. The electronic Zeeman interaction is taken to be isotropic for 3d<sup>5</sup> ions [17, 24-26]. The maximum overall splitting direction of EPR spectrum is taken as the  $z$  axis and that of the minimum as the  $x$  axis [27, 28]. 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 (the symmetry adapted axes (SAA)) is along the Mn-O<sub>2</sub> bond and the other two axes ( $x, y$ ) are normal to the  $z$ -axis.

Ga<sup>2+</sup> ion in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystal exists within a distorted octahedron of oxygen ions [6, 7] and the local symmetry is assumed to be orthorhombic of first kind (OR-I) [29]. In an OR-I symmetry, the ZFS parameters  $D$  and  $E$  of 3d<sup>5</sup> ions are obtained [23, 30] as:

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

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

where  $P = 7B + 7C$ ,  $G = 10B + 5C$ , and  $D = 17B + 5C$ ;  $B$  and  $C$  being the Racah parameters.

The parameters  $B, C$  and  $\xi$ , in terms of the average covalency parameter  $N$ , are given as [31-33]

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

where  $B_0, C_0$ , and  $\xi_d^0$  are the free ion Racah and spin-orbit coupling parameters, respectively [25-26].  $B_0 = 960$  cm<sup>-1</sup>,  $C_0 = 3325$  cm<sup>-1</sup> and  $\xi_d^0 = 336$  cm<sup>-1</sup> for free Mn<sup>2+</sup> ion are used [17].

Using optical absorption of Mn<sup>2+</sup> doped crystal with oxygen ligands; zinc ammonium phosphate hexahydrate (ZAPH),  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> [34-36]:  $B = 917$  cm<sup>-1</sup> and  $C = 2254$  cm<sup>-1</sup> are taken. The average value [27] of  $N = (\sqrt{B/B_0} + \sqrt{C/C_0})/2 = 0.911$  is used to obtain  $D$  and  $E$  from Eqs. (2) and (3).

The SPM is used to obtain the CF parameters,  $B_{kq}$  for Mn<sup>2+</sup> ion in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystal and ZFS parameters are then evaluated using these  $B_{kq}$ .

The crystal-field splitting of rare-earth ions [37] and also of transition ions [38-40] have been explained earlier by SPM. This model gives the CF parameters as [23, 37]

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

where  $R_j$  are the distances between the Mn<sup>2+</sup> ion and the ligand ion  $j$ ,  $R_0$  is the reference distance, near a value of the  $R_j$ 's.  $\theta_j$  are the bond angles in a chosen axis system

(SAAS) [41, 42]. The summation is taken over all the nearest neighbour ligands and the coordination factor  $K_{kq}$  ( $\theta_j, \phi_j$ ) are the explicit functions of angular position of ligand [23, 41, 43-45]. The intrinsic parameter  $\overline{A}_k(R_j)$  is found by the power law [29] as:

$$\overline{A}_k(R_j) = \overline{A}_k(R_0) (R_0/R_j)^{t_k} \quad (6)$$

where  $\overline{A}_k(R_0)$  is intrinsic parameter for a given ion host system. The symbol  $t_k$  is called power law exponent. The CF parameters,  $B_{kq}$  are obtained from Eq. (5) [46].

For 3d<sup>5</sup> ions, the ratio  $\overline{A}_2(R_0)/\overline{A}_4(R_0)$  lies in the range 8-12 [39]. In the present study, we have taken  $\overline{A}_2(R_0)/\overline{A}_4(R_0) = 10$ . For 3d<sup>5</sup> ions in the 6-fold cubic

coordination  $\overline{A}_4(R_0)$  can be obtained from the relation:  $\overline{A}_4(R_0) = (3/4) Dq$  [26]. Since  $\overline{A}_4(R_0)$  is independent of the coordination [47], the above relation is used to find  $\overline{A}_4(R_0)$  taking  $Dq = 756 \text{ cm}^{-1}$  [32-34].

#### 4. Results and discussion

The ionic radius of the Mn<sup>2+</sup> ion (0.080 nm) is larger than the Ga<sup>3+</sup> (0.062 nm) ion, a small distortion is expected [48] when Mn<sup>2+</sup> introduces at Ga<sup>3+</sup> site. The bond distances of different ligands,  $R_j$  along with the angles  $\theta_j$  and  $\phi_j$  are calculated from the crystal structure data of β-Ga<sub>2</sub>O<sub>3</sub> and are given in Table 1.

Table 1. Coordinates of ligands, Mn-ligand bond distances  $R_j$  and coordination angles  $\theta_j$  and  $\phi_j$  for Mn<sup>2+</sup> ion doped β-Ga<sub>2</sub>O<sub>3</sub> single crystals

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 : Interstitial	O1	0.16452	0	0.10983	0.1937	R <sub>1</sub>	96.05	$\theta_1$	89.82	$\phi_1$
Ga2	O2	0.17332	0	0.56324	0.2074	R <sub>2</sub>	83.10	$\theta_2$	89.59	$\phi_2$
(0.15866, 0.5, 0.31402)	O3	-0.00412	0.5	0.25663	0.1936	R <sub>3</sub>	91.69	$\theta_3$	94.82	$\phi_3$
	O1 v	0.16452	1.0	0.10983	0.1937	R <sub>4</sub>	96.05	$\theta_4$	89.82	$\phi_4$
	O2 iii	0.32668	0.5	-0.06324	0.3338	R <sub>5</sub>	96.49	$\theta_5$	87.09	$\phi_5$
	O2 v	0.17332	1.0	0.56324	0.2074	R <sub>6</sub>	83.10	$\theta_6$	89.59	$\phi_6$
With distortion										
I	O1				0.3337	R <sub>1</sub> +ΔR <sub>1</sub>				
	O2				0.3474	R <sub>2</sub> +ΔR <sub>2</sub>				
	O3				0.3336	R <sub>3</sub> +ΔR <sub>3</sub>				
	O1 v				0.3337	R <sub>4</sub> +ΔR <sub>4</sub>				
	O2 iii				0.5188	R <sub>5</sub> +ΔR <sub>5</sub>				
	O2 v				0.3924	R <sub>6</sub> +ΔR <sub>6</sub>				

Taking  $R_0$  as slightly smaller than the sum of ionic radii of Mn<sup>2+</sup> (0.080 nm) and O<sup>2-</sup> (0.140 nm) [49] i.e.  $R_0 = 0.200 \text{ nm}$ ,  $\overline{A}_2(R_0)/\overline{A}_4(R_0) = 10$ ,  $t_2 = 3$ ,  $t_4 = 7$ ; no distortion, we obtain  $B_{kq}$  and then  $|D|$  and  $|E|$  which are larger than the experimental values as shown in Table 2. Taking other parameters as above and  $t_2 = 3$ ,  $t_4 = 7$  [41], the values of  $|D|$  and  $|E|$  are inconsistent with the experimental ones and also the ratio  $|E|/|D|$  comes out to be larger than 0.401 and therefore  $t_2 = 3$ ,  $t_4 = 4$  were taken for calculation. Because  $|D|$  and  $|E|$  evaluated with no distortion were much different than the experimental values, the distortion

was included into calculation. The bond distances of different ligands  $R_j$  and the angles  $\theta_j$  and  $\phi_j$  calculated for this case are also given in Table 1. The calculated CF parameters,  $B_{kq}$  from Eq. (5) and transformation S2 for standardization [27, 28] as well as ZFS parameters  $|D|$  and  $|E|$  using other parameters as above are shown in Table 2. From Table 2,  $|D|$  and  $|E|$  are in good agreement with the experimental values when distortion is included into calculation. Such model calculations have been reported in case of Mn<sup>2+</sup> and Fe<sup>3+</sup> doped anatase TiO<sub>2</sub> crystal [50]. The interstitial sites for Mn<sup>2+</sup> ions in β-Ga<sub>2</sub>O<sub>3</sub> were also

studied but ZFS parameters obtained were inconsistent here. with the experimental values and so have not been given

Table 2. CF parameters and ZFS parameters calculated by the SPM for  $Mn^{2+}$  ion doped  $\beta$ - $Ga_2O_3$  single crystal with experimental values

Site	$R_0$ (nm)	Crystal- field parameters ( $cm^{-1}$ )					Zero-field splitting parameters ( $\times 10^{-4} cm^{-1}$ )		
		$B_{20}$	$B_{22}$	$B_{40}$	$B_{42}$	$B_{44}$	$ D $	$ E $	$ E / D $
Without distortion									
Site I $\frac{\overline{A_2}}{\overline{A_4}} = 10$	0.200	-29194.5	-36389.2	8205.632	8797.045	11654.09	10816.8	5488.6	0.401
With distortion									
Site I $\frac{\overline{A_2}}{\overline{A_4}} = 10$	0.200	-6337.66	4948.765	900.0414	965.5287	3365.179	504.3	168.0	0.333
						Exp.	504.0	120.0	0.238

Using calculated CF parameters [51] and CFA program the optical absorption spectra of  $Mn^{2+}$  doped  $\beta$ - $Ga_2O_3$  single crystals are calculated. The CF energy levels of the  $Mn^{2+}$  ion are obtained by diagonalizing the complete Hamiltonian in the intermediate crystal field coupling scheme. The calculated energy values are given in Table 3

together with the experimental ones for comparison. It is found from Table 3 that there is a reasonable agreement between the two values. Hence, the result obtained using SPM with distortion supports the experimental conclusion that  $Mn^{2+}$  ions substitute at  $Ga^{3+}$  sites in  $\beta$ - $Ga_2O_3$  single crystal [6].

Table 3. Experimental and calculated (CFA program) energy band positions of  $Mn^{2+}$  doped  $\beta$ - $Ga_2O_3$  single crystal

Transition from ${}^6A_{1g}(S)$	Observed wave number ( $cm^{-1}$ )		Calculated wave number ( $cm^{-1}$ )
	$\beta$ - $Ga_2O_3:Mn^{2+}$ [35]	ZAPH: $Mn^{2+}$ [34]	
${}^4T_{1g}(G)$	16667 ( $Ga_2O_3:Mn^{2+}$ ) [34]	16044	19288, 19299, 19743, 19774, 20612, 20664
${}^4T_{2g}(G)$	20970	20433	20824, 20852, 21111, 21133, 21337, 21362
${}^4E_g(G)$	24197	24108	23228, 23263, 23443, 23479
${}^4A_{1g}(G)$		24242	25747, 25778
${}^4T_{2g}(D)$		26724	25971, 26020, 27301, 27324, 28060, 28096
${}^4E_g(D)$		30451	30115, 30247, 30477, 30641
${}^4T_{1g}(P)$		33956	33098, 33256, 33638, 34220, 34798, 34863
${}^4A_{2g}(F)$		36846	36610, 36882
${}^4T_{1g}(F)$		38521	37683, 37916, 37941, 37966, 38131, 38827

## 5. Conclusions

The zero field splitting (ZFS) parameters have been determined using the superposition model and perturbation theory. The calculated ZFS parameters for Mn<sup>2+</sup> ion in β-Ga<sub>2</sub>O<sub>3</sub> single crystal at the substitutional Ga<sup>3+</sup> site are in good agreement with the experimental values. The CF energy levels of the Mn<sup>2+</sup> ion obtained using CF parameters and CFA program are in reasonable agreement with the experimental ones. We conclude that the Mn<sup>2+</sup> ion substitutes at Ga<sup>3+</sup> site in β-Ga<sub>2</sub>O<sub>3</sub> single crystal hence the theoretical results support the experimental conclusion. The approach used in the present study may be applied for the modeling of other ion-host systems to explore the applications of different crystals in technology and industry.

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