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Theoretical Investigation of Zero Field Splitting Parameters of Mn^{2+} doped YAP Crystal at Orthorhombic Symmetry Site

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Abstract
The crystal field parameters (CFPs) of Mn^{2+} doped yttrium orthoaluminate (YAP) single crystal are obtained with the help of superposition model (SPM). The zero field splitting parameters (ZFSPs) D and E are then calculated using perturbation and microscopic spin Hamiltonian (SH) theory. D and E thus determined show reasonable matching with the experimental values obtained from electron paramagnetic resonance. The results conclude that the Mn^{2+} ion enters the lattice substitutionally at Y^{3+} site in YAP. The method employed here may be applied for the modeling of other ion-host systems.

Keywords: *A. Inorganic compounds; A. Single Crystal; C. Crystal structure and symmetry; D. Crystal and ligand fields; D. Optical properties; E. Electron paramagnetic resonance.*
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I. INTRODUCTION

Superposition model (SPM) is used to find physical and geometrical information present in crystal field parameters of different ion-host systems [1, 2]. As the positions of ligands are required to apply this model, the theories of local distortion in crystals are quite important. This model provided the reasonable results for $Fe^{3+}$and Mn^{2+} spin Hamiltonian parameters [3, 4].

Various mechanisms have been suggested for the ground state splitting of the magnetic ions incorporated in crystals [5-8]. In most of the systems, cubic field and the diagonal part of free-ion Hamiltonian are taken to be 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 [9].

Yttrium orthoaluminate ($YAlO_3$), known as yttrium aluminum perovskite (YAP), is largely used as a host material for solid-state lasers and scintillators. The manganese doped YAP is of particular interest due to its application in holographic recording and optical data storage [10−13].

EPR study of Mn^{2+} doped YAP single crystals has been reported [14]. Two possibilities, substitutional and interstitial, for Mn^{2+} ion location in the YAP crystal may be considered. It was indicated [14] that Mn^{2+} ion enters the lattice of YAP substitutionally at Y^{3+} site. In this investigation, the zero-field splitting parameters (ZFSPs) D and E are determined for the Mn^{2+} ion at substitutional Y^{3+} site in YAP; using crystal field parameters (CFPs) evaluated from SPM and perturbation equations [15]. The values of D and E obtained with the help of this model show reasonable matching with the experimental ones (evaluated after gamma irradiation) [14].

II. CRYSTAL STRUCTURE

The crystal structure of YAP single crystal has a perovskite-like orthorhombic crystal structure with lattice parameters a = 0.5330(2) nm, b = 0.7375(2) nm, c = 0.5180(2) nm; space group Pnma-D_{2h}^{16} [16]. The oxygen coordination around Y^{3+} is shown in Fig. 1. The site symmetry around Mn^{2+}ions may be considered as approximately orthorhombic, as suggested by EPR investigation of Mn^{2+}: YAP [14].

III. THEORETICAL INVESTIGATION

The resonance magnetic fields can be found employing the spin Hamiltonian [17, 18]

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

$$+\frac{F}{180}\{35\,S_z^4-30\,S(S+1)S_z^2+25S_z^2-6S(S+1)+3S^2(S+1)^2\}+\frac{K}{4}[\{7S_z^2-S(S+1)-5\}(S_+^2+S_-^2)+(S_+^2+S_-^2)\{7S_z^2-S(S+1)-5\}]+\mathcal{A}S_zI_z+\mathcal{B}(S_xI_x+S_yI_y) \quad (1)$$

where g is the isotropic spectroscopic splitting factor, μ_B is the Bohr magneton, $\boldsymbol{B}$ is the external magnetic field. D and E are the second-rank axial and rhombic ZFSPs, while a, F, and K are the fourth-rank cubic, axial and rhombic ones, respectively. The last two terms in Eq. (1) provide the hyperfine (I = 5/2) interaction. The F and K terms are deleted as their effect is quite small [17, 19, 20]. The isotropic assumption for the electronic Zeeman interaction is normally valid for 3d^5 ions [17, 21]. The above two assumptions may slightly affect the value of a [22]. The maximum overall splitting direction of EPR spectrum is taken as the z axis and that of the minimum as the x axis [23]. The laboratory axes (x, y, z) determined from EPR spectra are found to coincide with the crystallographic axes (CAS), a, b, c. The z-axis of the local site symmetry axes, i.e. the symmetry adapted axes (SAA) is along the metal oxygen O (1'') bond and the other two axes (x, y) are normal to the z-axis.

In YAP, yttrium ion is located within a distorted octahedron of oxygen ions [14, 16] and the local symmetry is taken approximately as orthorhombic of first kind (OR-I) [24]. In an OR-I symmetry, the ZFSPs D and E of 3d^5 ions are determined [15, 25] 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 are the Racah parameters. Eqs. (2) and (3) are good for weak-field cases, and are also valid for the low-symmetry components [15].

Considering the covalency effect, the parameters B, C and ξ are given in terms of the average covalency parameter N as [26-27]

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

Here B$_0$, C$_0$, and ξ_d^0 are the free ion Racah and spin-orbit coupling parameters, respectively [26-27]. B$_0$ = 960 cm^{-1}, C$_0$ = 3325 cm^{-1}, ξ_d^0 = 336 cm^{-1} for free Mn^{2+} ion [17].

From optical absorption of Mn^{2+} doped crystal with oxygen ligands [28]: B = 917cm^{-1} and C = 2254 cm^{-1}were found. The average value [27] of N = $\left(\sqrt{B/B_0}+\sqrt{C/C_0}\right)/2$ = 0.911 is used to find the ZFSPs D and E from Eqs. (2) and (3).

The SPM is used to calculate the CFPs, B$_{kq}$ for Mn^{2+} ion in YAP single crystal and ZFSPs are then calculated using these CFPs.

The SPM has well explained the crystal-field splitting of 4f^n ions [29] and also of some 3d^n ions [30-32]. The model yields the CFPs as [15, 29]

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

Here R_j are the distances between the Mn^{2+} ion and the ligand ion j, R$_0$ is the reference distance, normally taken near a value of the R_j's. θ_j provide the bond angles in a chosen axis system (symmetry adapted axes system (SAAS)) [33, 34]. The summation is over all the nearest neighbour ligands. The coordination factor K$_{kq}$

(θ_j , ϕ_j) are the explicit functions of angular position of ligand [15, 33, 35-36]. The intrinsic parameter $\overline{A_k}$ (R_j) is given by the power law [9, 24] as:

$$\overline{A_k}\,(R_j) = \overline{A_k}\,(R_0)\,(R_0 / R_j)^{t_k} \qquad (6)$$

where $\overline{A_k}$ (R_0) is intrinsic parameter for a given ion host system. The symbol t_k is power law exponent. The crystal-field parameters B_{kq} are obtained using Eq. (5) [37].

For 3d^5 ions, the ratio $\overline{A_2}$ (R_0) / $\overline{A_4}$ (R_0) is in the range 8 -12 [8, 31]. In this study, we have taken the ratio $\overline{A_2}$ (R_0) / $\overline{A_4}$ (R_0) = 10. For 3d^N ions in the 6-fold cubic coordination $\overline{A_4}$ (R_0) can be found from the relation: $\overline{A_4}$ (R_0) = (3/4) Dq [22]. As $\overline{A_4}$ (R_0) is independent of the coordination [38], the above relation is used to obtain $\overline{A_4}$ (R_0) with Dq = 756 cm^{-1} [28].

IV. RESULT AND DISCUSSION

In order to check the substitution at Y^{3+} site, the origin of Mn^{2+} was shifted at the Y^{3+} ion. As the ionic radius of the impurity Mn^{2+} ion (0.080 nm) is slightly smaller than that of the host Y^{3+} (0.090 nm), a small distortion may take place [39]. From the coordinates x, y, z; the bond distances of different ligands, R_j along with the angles θ_j and ϕ_j are calculated and are shown in Table 1. In adjusting the Mn-O distances to match the experimental values, the site symmetry is preserved as well as the energy is minimized and hence the structural stability is taken into consideration. Taking R_0 as slightly smaller than the minimum of R_j [40], i.e. R_0 = 0.170 nm, $\overline{A_2}$ (R_0) / $\overline{A_4}$ (R_0) = 10, t_2= 3, t_4= 7 [8]; considering no distortion, we obtain B_{kq} and then |D| and |E| which are inconsistent with the experimental values as shown in Table 2. Hence, we have taken into account the distortion. The bond distances of different ligands R_j and the angles θ_j and ϕ_j calculated for this case are also given in Table 1. The calculated B_{kq} from Eq. (5) and transformation S2 for standardization [23] as well as ZFSPs |D| and |E| taking other parameters as above are given in Table 2. From Table 2, |D| and |E| show reasonable match with the experimental values when distortion is taken into account. Such model calculations have been done earlier in case of Mn^{2+} and Fe^{3+} doped anatase TiO$_2$ crystal [41]. The interstitial sites for Mn^{2+} ions in YAP were also studied but ZFSPs found are inconsistent with the experimental values and so are not being given here.

Using calculated CFPs [42] with OR-I symmetry of the crystal field and CFA program the optical absorption spectra of Mn^{2+} doped YAP crystals are calculated. The energy levels of the Mn^{2+} ion are evaluated by diagonalizing the complete Hamiltonian within the 3d^N basis of states in the intermediate crystal field coupling scheme. The calculated energy values are shown in Table 3 together with the experimental values for comparison. From Table 3 a reasonable match between the two is seen. Therefore, the result obtained employing SPM with distortion supports the experimental conclusion that Mn^{2+} ions substitute at Y^{3+} site in YAP crystal [14].

V. CONCLUSIONS

The zero field splitting parameters (ZFSPs) have been determined using the superposition model and perturbation formulae. The calculated ZFSPs for Mn^{2+} ion in YAP single crystal at the substitutional Y^{3+} site are in reasonable match with the experimental ones. We conclude that the Mn^{2+} ion occupies substitutional Y^{3+} site in YAP crystal .The theoretical results support the reported experimental conclusion.

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TABLE AND FIGURE CAPTIONS:

Table 1. Coordinates of oxygen ligands, Mn-oxygen bond distances R_j and coordination angles θ_j and ϕ_j for Mn^{2+} ion doped YAP single crystals.

Table 2. CFPs and ZFSPs calculated by the superposition model for Mn^{2+} ion doped YAP single crystal with experimental values.

Table 3. Experimental and calculated (CFA package) energy band positions of Mn^{2+} doped YAP single crystal.

Fig. 1: Coordination around Mn^{2+} in YAP single crystal.

Table 1

Position of Mn^{2+}	Ligands	x	y (Å)	z	R(nm)	θ^0	φ^o
	Without distortion						
Site I: Substitutional	O(1)	0 .4752	0.25	0.0862	0.5193 R_1	100.01 θ_1	85.26 φ_1
Y (0.0526, 0.25, 0.9896)	O(1’)	-0.4752	0.75	-0.0862	0.7250 R_2	98.53 θ_2	94.22 φ_2
	O(1’’)	0.0248	0.75	0.5862	0.4241 R_3	95.45 θ_3	90.37 φ_3
	O(2)	0.2932	0.0442	0.7032	0.2479 R_4	96.63 θ_4	84.39 φ_4
	O(2’)	0.7932	0.4558	-0.2032	0.7487 R_5	99.16 θ_5	84.25 φ_5
	O(2’’)	-0.7932	0.5442	-0.7032	1.0095 R_6	99.65 θ_6	94.87 φ_6
	With distortion						
	O(1)				0.5163 $R_1+\Delta R_1$		
	O(1’)				0.7230 $R_2+\Delta R_2$		
	O(1’’)				0.4221 $R_3+\Delta R_3$		
	O(2)				0.2380 $R_4+\Delta R_4$		
	O(2’)				0.7387 $R_5+\Delta R_5$		
	O(2’’)				0.9895 $R_6+\Delta R_6$		

Table 2

		Crystal- field parameters (cm^{-1})					Zero-field splitting parameters ($\times10^{-4}cm^{-1}$)		
Site	R_0(nm)	B_{20}	B_{22}	B_{40}	B_{42}	B_{44}	|D|	|E |	|E|/|D|
		Without distortion							
Site I $\frac{\overline{A}_2}{\overline{A}_4}=10$	0.170	-2445.7	-3038.61	108.2412	115.3268	2141.723	176.7	69.0	0.390
		With distortion							
Site I $\frac{\overline{A}_2}{\overline{A}_4}=10$	0.170	-3009.77	2358.034	143.0249	152.3732	2142.087	174.3	55.7	0.319
							Exp. 174.3	97.1	0.557

Table 3

Transition from $^6A_{1g}(S)$	Observed wave number (cm^{-1})	Calculated wave number (cm^{-1})
$^4T_{1g}(G)$	16044	
$^4T_{2g}(G)$	20433	20477, 20480, 21249, 21263, 21406, 21427
$^4E_g(G)$	24108	22678, 23428
$^4A_{1g}(G)$	24242	23440
$^4T_{2g}(D)$	26724	26693, 26762, 26839, 26911, 27311, 27325
$^4E_g(D)$	30451	30434, 30543
$^4T_{1g}(P)$	33956	32760, 32812, 32990, 33355, 33374, 33897
$^4A_{2g}(F)$	36846	36863
$^4T_{1g}(F)$	38521	37344, 37631, 37688, 37776, 37807, 39600

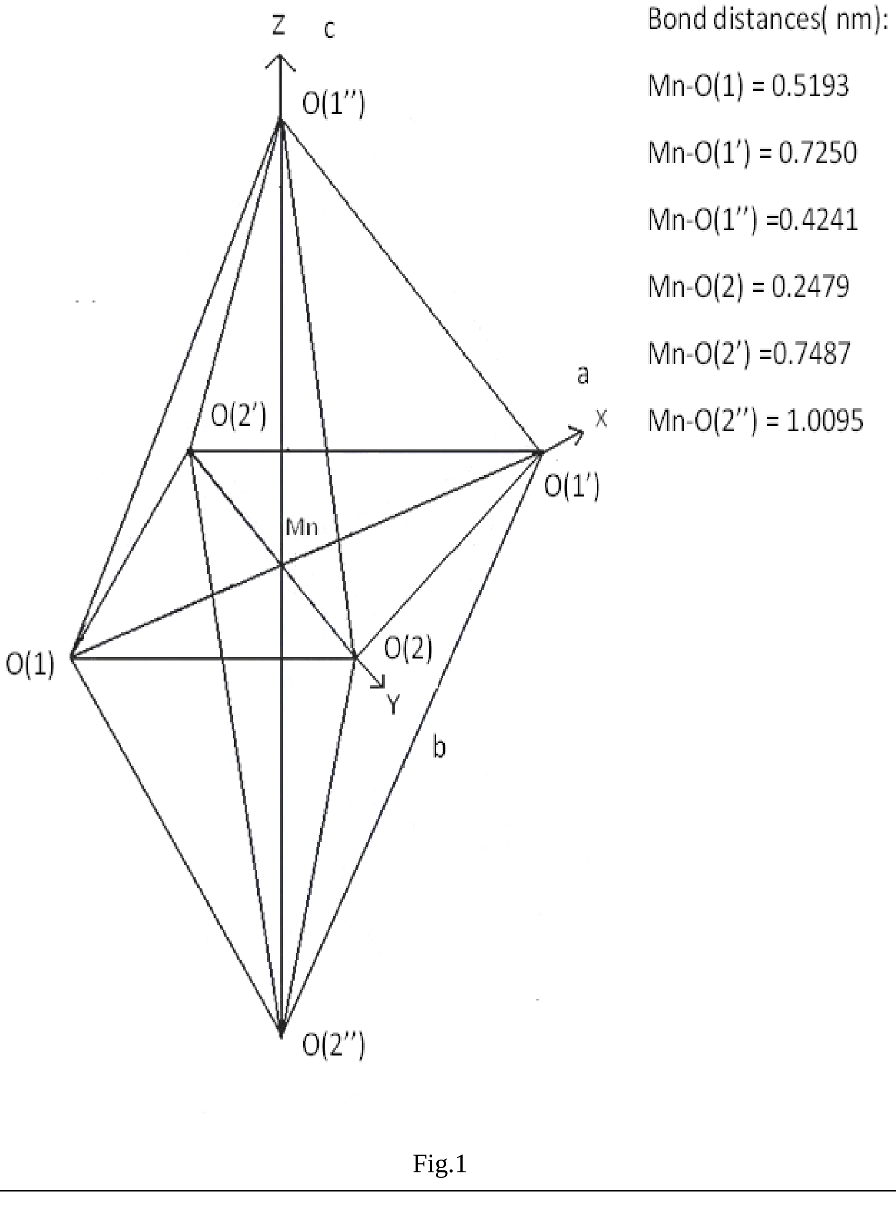

Fig.1