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ZERO FIELD SPLITTING PARAMETER OF MN^{2+} IN PMN SINGLE CRYSTALS

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ABSTRACT

Crystal field parameters and zero-field splitting parameter of Mn^{2+} doped PMN single crystals are determined using superposition model and perturbation theory. The evaluated zero-field splitting parameter D matches well with the experimental value given by EPR study. The study performed supports the experimental result that Mn^{2+} ions substitute at Mg^{2+} site in PMN single crystal.

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

I. INTRODUCTION

Electron paramagnetic resonance (EPR) is used to find local site symmetry and distortions in the lattice of transition ions doped crystals [1-3]. The spin Hamiltonian (SH) parameters of transition ions in crystals are very sensitive to local distortions and may be correlated with optical and structural parameters using microscopic spin-Hamiltonian (MSH) theory.

The crystal-field (CF) parameters of d^5 ion are obtained using superposition model (SPM) [4, 5]. The zero field splitting (ZFS) parameters are evaluated using CF parameters and perturbation equations [6, 7-9]. For Mn^{2+} ions the electron spins are oriented freely in applied magnetic field [10, 11].

The hydrated double nitrates, M$_2$''' M$_3$'' (NO$_3$)$_{12}$ • 24 H$_2$O, where M''' is a trivalent cation (Bi or 4f group ion) and M'' is a divalent cation (Zn, Mg or 3d group ion), form an interesting isomorphous series of salts [12]. Double nitrate crystals are used widely in
experiments involving magnetic cooling, nuclear alignment, and EPR [13]. The EPR of Mn^{2+} in Pr$_2$Mg$_3$ (NO$_3$)$_{12}$ • 24 H$_2$O (PMN) single crystals is done from 298 K down to 77 K [14].

In the present work, the CF parameters are obtained at 298 K using SPM and these parameters with MSH theory then yield ZFS parameter at 298 K for Mn^{2+} ions in PMN single crystal at the axial symmetry site. The ZFS parameter D obtained using SPM matches well with the experimental value [14].

This section was dedicated to the brief introduction of the subject and objective of the study performed. The rest of the paper is organized as follows. Section II presents the related work associated with the SPM analysis. Section III describes the methods used for calculation of CF and ZFS parameters. Section IV gives the results and its discussion. Section V provides conclusion of the study and future scope for improvement.

II. RELATED WORK

The SPM analysis has been done for different ion-host systems [15-28]. The crystal structure of PMN is isomorphous with cerium magnesium nitrate hydrate [12]. The hexagonal cell has parameters as: a = 11.004 Å, c = 34.592 Å [12]

and the space group is R$\bar{3}$. The oxygen coordination around Mg^{2+} is illustrated in Fig. 1. The site symmetry around Mn^{2+}ions may be taken to be axial, as suggested by EPR study of Mn^{2+}: PMN [14].
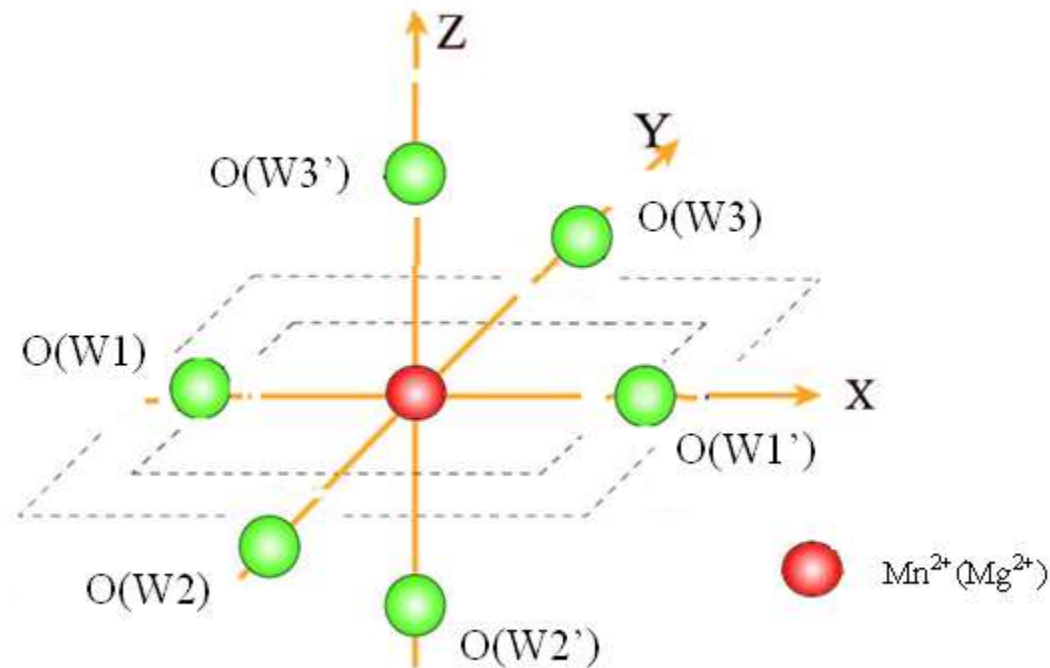
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Fig. 1: Crystal structure of PMN together with axes (SAA⌣ ⌣y........ry adopted axes system).

III. MATERIALS AND METHODS

The SH of Mn^{2+} ($3d^5$) ion in crystal field of axial symmetry is given as [15-17]

$$\mathcal{H} = g\,\mu_B B.S + D\{S_Z^2 - S(S+1)\}$$

$$+ \left(\frac{a}{6}\right)[S_X^4 + S_Y^4 + S_Z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)]$$

$$+ \frac{F}{180}\{35S_Z^4 - 30S(S+1)S_Z^2 + 25S_Z^2 - 6S(S+1) + 3S^2(S+1)^2\}$$

$$+ A(I.S) \tag{1}$$

where the first term provides electronic Zeeman interaction, the second, third, fourth and fifth terms are the second order axial, fourth-rank cubic, fourth-rank axial ZFS and hyperfine interaction terms, respectively [8]. g is the spectroscopic splitting factor, μ_B is Bohr magneton and B is the applied magnetic field. The term represents the. S, D, a, F are the effective spin vector, second order axial, fourth-rank cubic and fourth-rank axial ZFS

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parameters, respectively. The electronic Zeeman interaction is isotropic for Mn^{2+} ions [8, 18, 19].

The Hamiltonian for a d^5 ion is given as

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

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

is the crystal field Hamiltonian whereas $\mathcal{H}_0$ and $\mathcal{H}_{so}$ give free ion Hamiltonian and spin-orbit (SO) coupling, respectively. Because the spin-spin coupling is quite small [20-22], its contribution is almost zero in Eq. (2). The SO contribution to the ZFS parameter D for $3d^5$ ions in axial symmetry is obtained as [23-26]

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

(3)

where P = 7(B+C), G = 10B+5C and D = 17B+5C. P, G, and D are the energy separations between the excited quartets and the ground sextet. B and C, called Racah parameters, provide the electron-electron repulsion. Only fourth order term is taken in Eq. (3) as other perturbation terms are negligible [24, 26]. The parameters B, C and ξ are written in terms of the average covalency parameter N as: $B = N^4 B_0$, $C = N^4 C_0$ 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 [27, 28], respectively. $B_0 = 960$ cm^{-1}, $C_0 = 3325$ cm^{-1}, $\xi_0 = 336$ cm^{-1} [8] for Mn^{2+} free ion are used here. Using equation

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

(4)

N can be found taking the values of Racah parameters (B = 917 cm^{-1}, C = 2254 cm^{-1}) determined from optical study [29].

Using SPM the CF parameters for Mn^{2+} in PMN single crystal are obtained and then from Eq. (3) ZFS parameter D is evaluated. Similar method has been employed for obtaining ZFS parameters by other workers [30].

The SPM has been used for $3d^n$ ions to interpret the crystal-field splitting [26, 31]. The crystal field parameters B_{kq}, using this model, are found from the equations [32]

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

(5)

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

(6)

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

where R_0 is the reference distance, normally taken as the average value of all four bond lengths (for axial symmetry). $\bar{A}_2$, $\bar{A}_4$ and t_k represent the intrinsic parameter and power law exponent, respectively.

IV. RESULTS AND DISCUSSION

The position of Mn^{2+} ion and spherical coordinates of ligands are given in Table 1.The average of two out of four Mn^{2+}-O^{2-} bond lengths is found as $R_{10} = 0.2057$ nm and the average value of the rest two bond lengths is obtained as $R_{20} = 0.3240$ nm for site I. Similarly $R_{10} = 0.3062$ nm and $R_{20} = 0.2110$ nm for site II ΔR_1 and ΔR_2 are the distortion parameters. For octahedral coordination, $\overline{A_4}(R_0) = (3/4)Dq$ [6]. For $3d^5$ ions the ratio $\dfrac{A_2}{A_4}$ lies in the range 8-12 [26, 31]. The power law exponent for Mn^{2+} ion is taken as $t_2 = 3$, $t_4 = 7$.

Table 1(A and B). Atomic coordinates in PMN crystal and spherical coordinates of ligands R

θ, φ.

Table 1

Position of Mn^{2+} (Fractional)	Ligands				Spherical co-ordinates of ligands		
		x	y	z	R(nm)	θ^0	ϕ^0
			(Å)			(degree)	
Site : Substitutional	O(W1)	0.0128	0.1576	0.0058	0.1751	83.4	85.3
Mg(1) (0, 0, 0)	O (W2)	0.1607	0.0173	0.0656	0.2883	38.1	6.1
	O (W3)	0.1567	0.1548	0.0768	0.3596	42.4	44.6
	O (W1')	-0.1576	-0.1448	0.0058	0.2363	85.1	42.4

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Table 1 B

Position of Mn^{2+} (Fractional)	Ligands	Spherical co-ordinates of ligands		
		R(nm)	θ^0	ϕ^0
	x y z		(degree)	
	(Å)			
Site : Substitutional	O(W1) 0.0128 0.1576 0.0058	0.2856	142.5	85.3
Mg(2) (0, 0, 0.0713)	O (W2) 0.1607 0.0173 0.0656	0.1789	96.3	6.1
	O (W3) 0.1567 0.1548 0.0768	0.2431	85.5	44.6
	O (W1') -0.1576 -0.1448 0.0058	0.3268	133.9	42.5

The values of B, C and Dq are determined from optical absorption study [29] as 917, 2254 and 756 cm^{-1}, respectively. First no local distortion is considered and the value of D for site I is evaluated. For this, taking $\dfrac{\overline{A_2}}{A_4} = 10$ and $R_0 = 0.211$ nm, which is slightly smaller than the sum of ionic radii of Mn^{2+} = 0.083 nm and O^{2-} = 0.140 nm, the B_{kq} parameters are found as: B_{20} = -18495.5 cm^{-1}, B_{40} = 11158.54 cm^{-1}, B_{44} = 471.6356 cm^{-1} and the value of D as: $|D|$ = 2147.5×10^{-4} cm^{-1} for site I; B_{20} = -26377.2 cm^{-1}, B_{40} = 7464.368 cm^{-1}, B_{44} = 9476.095 cm^{-1} and the value of D as: $|D|$ = 985.7×10^{-4} cm^{-1} for site II. EPR study gives the experimental value of D as: $|D|$ = 187.6×10^{-4}cm^{-1} and $|D|$ = 20.63×10^{-4}cm^{-1} for sites I and II, respectively[14]. From above it is seen that the theoretical value is quite larger than the experimental one.

Now, taking local distortions as $\Delta R_1 = 0.1082$ nm and $\Delta R_2 = 0.1100$ nm, $R_0 = 0.211$ nm and ratio $\dfrac{\overline{A_2}}{A_4} = 10$, the

B_{kq} parameters are found as given in Table 2 and the value of D as: $|D|$ = 187.7×10^{-4} cm^{-1}, in good match with the experimental one: $|D|$ = 187.6×10^{-4} cm^{-1}for site I. Similarly taking distortions as $\Delta R_1 = 0.3920$ nm, $\Delta R_2 = 0.3970$ nm and other parameters as above, the B_{kq} parameters are obtained as given in Table 2 and the value of D as: $|D|$= 20.63×10^{-4} cm^{-1}, also in good match with the experimental value: $|D|$ = 20.63×10^{-4} cm^{-1} for site II. Taking B_{kq} parameters and CFA program [33-34], the optical spectra of Mn^{2+} doped PMN single crystals are calculated. The energy levels of Mn^{2+} ion are determined by

Table 2. Crystal field parameters and zero field splitting parameters of Mn^{2+} doped PMN

single crystal.

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	ΔR_1 (nm)	ΔR_2 (nm)	R_0(nm)	Crystal- field parameters (cm^{-1})			Zero-field splitting parameter (10^{-4}cm^{-1})
				B_{20}	B_{40}	B_{44}	$\mid D \mid$
I	0.1082	0.1100	0.211	-6049.23	605.5493	60..94274	187.7
	0.0000	0.0000	0.211	-18495.5	11158.54	471.6356	2147.5
						Exptl.	187.6
II	0.3920	0.3970	0.211	-1260.69	6.210751	5.74949	20.63
	0.0000	0.0000	0.211	-26377.2	7464.368	9476.085	985.7
						Exptl.	20.63

I and II represent two sites.

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 (input parameters are given below the Table) together with the experimental values [29] for comparison. It is noted from Table 3 that there is a reasonable agreement between the calculated and experimental energy values. The energy values obtained without considering distortion were different from the experimental ones and so are not given here. Thus the theoretical study supports the experimental results.

Table 3. Experimental and calculated energy band positions of Mn^{2+}

doped PMN single crystal.

Transition from $^6A_{1g}$(S)	Observed wave number [cm^{-1}]	Calculated wave number [cm^{-1}]	
		I	II

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Term	Value		
$^4T_{1g}(G)$	16044		
$^4T_{2g}(G)$	20433	21364, 21419, 21429 21435, 21458, 21478	21883, 21886, 21891, 21896, 21901, 21948
$^4E_g(G)$	24108	22024, 22045, 22076, 22156	22216, 22248, 22270, 22295
$^4A_{1g}(G)$	24242	22343, 22365	22344, 22365
$^4T_{2g}(D)$	26724	26722, 26754, 26787, 26811, 27241, 27273	27258, 27264, 27269, 27272, 27318, 27319
$^4E_g(D)$	30451	30610, 30866, 30924 30986	31275, 31277, 31280, 31284
$^4T_{1g}(P)$	33956	32525, 32534, 32570, 33248, 33249, 33788	32654, 32656, 32659, 33197, 33280, 33284
$^4A_{2g}(F)$	36846	36844, 36851	36829, 36836
$^4T_{1g}(F)$	38521	37725, 37861, 37982, 39192, 39501, 39708	36996, 37033, 39775, 39776, 39789, 39790

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, 917, 2254, 336 and 76 cm^{-1}, respectively; number of crystal field parameters = 3; B_{20}, B_{40}, B_{44} 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.

V. CONCLUSION AND FUTURE SCOPE

Zero-field splitting parameter D for Mn^{2+} in PMN single crystal has been evaluated with the help of superposition model and perturbation theory. The theoretical D matches well with the experimental one when distortion is considered in the calculation. The theoretical study shows that Mn^{2+} ion occupies Mg^{2+} site which supports the experimental results from EPR. The CF energy values for Mn^{2+} ions at Mg^{2+} sites found using CFA program and CF parameters show reasonable agreement with the experimental ones. Thus the theoretical study supports the experimental result. Modeling procedure used here may be applicable in future to correlate EPR and optical data for other ion-host systems.

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