Modeling of Mn^{2+} doped CdGa$_2$Se$_4$ single crystals

Maroj Bharati [a], Vikram Singh [a], Ram Kripal [b]

[a] *Department of Physics, Nehru Gram Bharti (DU), Jamunipur, Prayagraj, India*
[b] *EPR Laboratory, Department of Physics, University of Allahabad, Prayagraj-211002, India*

Abstract

The crystal field parameters and zero-field splitting parameter of Mn^{2+} doped CdGa$_2$Se$_4$ single crystals are determined using superposition model and the perturbation theory. The theoretically obtained zero-field splitting parameter D is similar to the experimental value found from EPR study. The present investigation supports the experimental finding that Mn^{2+} ions substitute Cd^{2+} ions in CdGa$_2$Se$_4$ single crystal.

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

I. INTRODUCTION

The spin Hamiltonian (SH) parameters from electron paramagnetic resonance (EPR) are correlated with optical and structural parameters with the help of microscopic spin-Hamiltonian (MSH) theory [1-3]. These studies show that the spin Hamiltonian parameters of transition ions (d^5) in crystals are very sensitive to local distortions due to which the SH theory is frequently employed for the study of crystals.

The crystal-field (CF) parameters of d^5 ion may be evaluated using superposition model (SPM) [4, 5]. The zero field splitting (ZFS) parameters may then be determined with the help of CF parameters [6]. Mn^{2+} ion belongs to iron group and is interesting because of its $^6S_{5/2}$ ground state [7-10].

CdGa$_2$Se$_4$ is a representative of the well known defect chalcopyrite structures (thiogallate structures), which are quite promising due to their optical and electrical properties [11, 12].

EPR measurements of Mn^{2+} doped CdGa$_2$Se$_4$ single crystals [13] at room temperature (RT) have been reported [14]. In the present investigation, the CF parameters are determined with the help of SPM and these parameters with MSH theory then provide ZFS parameter for Mn^{2+} ions at the axial symmetry site in CdGa$_2$Se$_4$ single crystal at RT. The ZFS parameter D thus obtained gives good agreement with the experimental value [13].

This section was dedicated to the brief introduction of the subject and objective of the investigation done. The remaining paper is organized as follows. Section II presents the related work associated with the SPM study. Section III provides the methods for calculating CF and ZFS parameters. Section IV gives the results and its discussion. In section V, conclusion of the investigation and future scope for improvement are provided.

II. RELATED WORK

The SPM studies have been performed for various ion-host systems [15-31]. The crystal structure of CdGa$_2$Se$_4$ is tetragonal. The lattice parameters are a = 5.7432 Å, c = 10.7564 Å, Z = 2 [14]. The crystal structure belongs to the space group I$\bar{4}$ The Se coordination around Cd^{2+} is illustrated in Fig. 1. The site symmetry around Cd^{2+} (Mn^{2+}) ions may be considered to be axial, as shown by EPR investigation of Mn^{2+}: CdGa$_2$Se$_4$ [13].
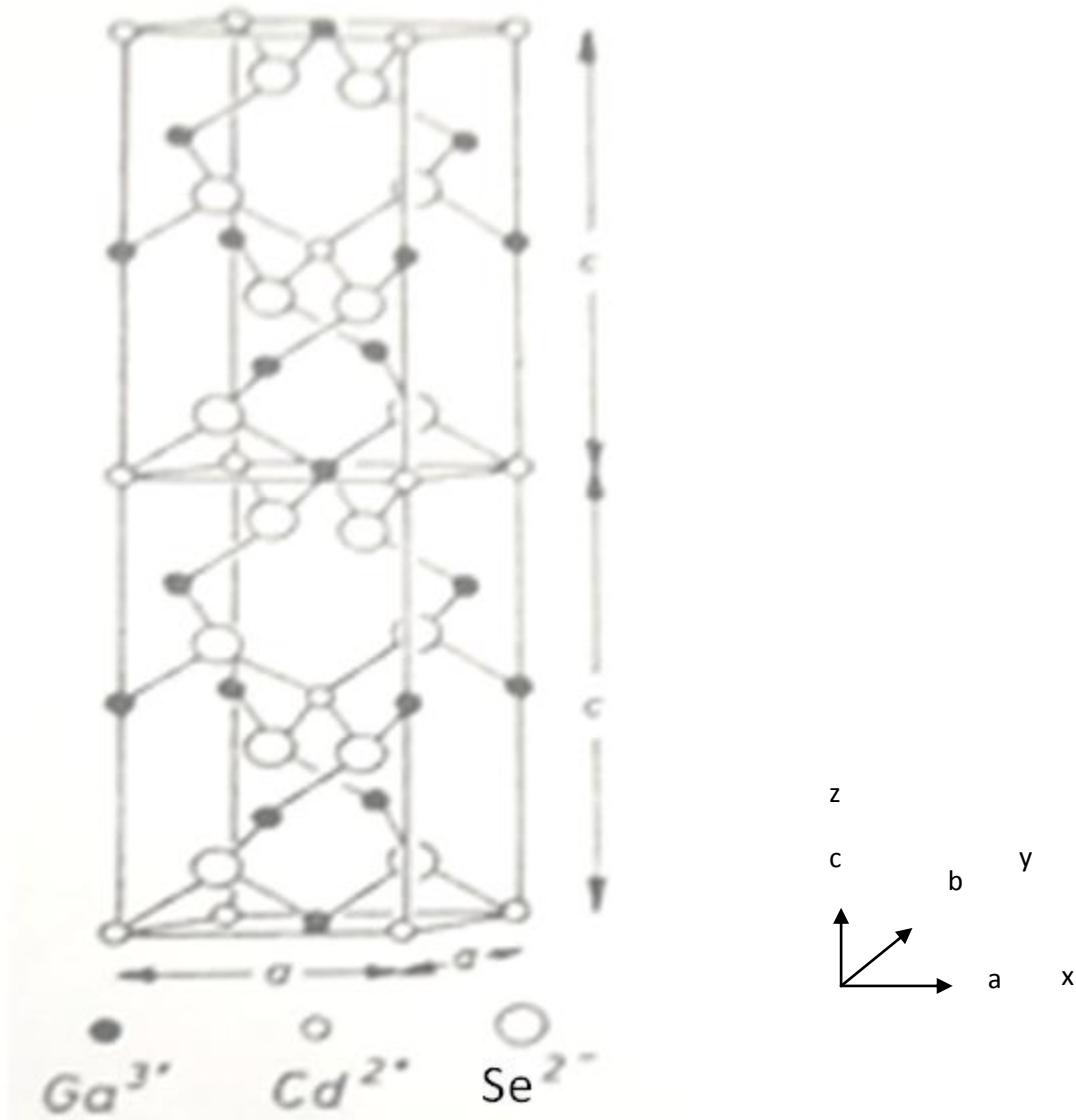
Fig. 1: Crystal structure of CdGa$_2$Se$_4$ together with axes (SAAS-symmetry adopted axes system).

III. MATERIALS AND METHODS

The SH of Mn^{2+}3d^5 ion in crystal field of axial symmetry is [15, 17]:

$$\mathcal{H} = g\,\mu_B B.S + D\{S_Z^2 - S(S+1)\}$$
$$+ \left(\frac{a}{6}\right)[S_X^4 + S_Y^4 + S_Z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)]$$
$$+ A(I.S) \tag{1}$$

where the first term provides electronic Zeeman interaction, B is the applied magnetic field, g is the spectroscopic splitting factor and μ_B is Bohr magneton. The second and third terms are the second order axial and fourth-rank cubic ZFS terms [8]. The fourth term gives the hyperfine interaction term. S, D and *a* give the effective spin vector, second order axial and fourth-rank cubic ZFS parameters, respectively. The electronic Zeeman interaction is considered to be isotropic for Mn^{2+} ions [8, 18, 19].

The Hamiltonian for a d^5 ion is written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{CF} + \mathcal{H}_{SO}$$

$$\text{where } \mathcal{H}_{CF} = \sum_{kq} B_{kq} C_q^k \tag{2}$$

is the crystal field Hamiltonian whereas $\mathcal{H}_0$ and $\mathcal{H}_{SO}$ represent free ion Hamiltonian and spin-orbit (SO) coupling, respectively. Since the spin-spin coupling is quite small [20-22], its effect is neglected in Eq. (2). The crystal field of SO interaction is taken as perturbation term [23-25]. The strong-field scheme computation for F-state ions is given by Macfarlane [26]. The SO contribution to the ZFS parameter D for $3d^5$ ions in axial symmetry is obtained as [24]

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

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. Racah parameters B and C give the electron-electron repulsion. Only fourth order term is taken in Eq. (3) as other perturbation terms are quite small [24, 26]. The parameters B, C and ς, in terms of the average covalency parameter N, are: $B = N^4 B_0$, $C = N^4 C_0$ and $\varsigma = N^2 \varsigma_0$, where B_0, C_0 and ς_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}, $\varsigma_0 = 336$ cm^{-1} [8] for Mn^{2+} ion are taken here. Using equation

$$N = \left(\sqrt{\frac{B}{B_0}} + \sqrt{\frac{C}{C_0}}\right)/2 \tag{4}$$

N can be found taking the values of Racah parameters (B = 648 cm^{-1}, C = 2475 cm^{-1}) obtained from optical study [29].

Using SPM the CF parameters for Mn^{2+} in $CdGa_2Se_4$ single crystal are determined and then from Eq. (3) ZFS parameter D is calculated. Similar method has been applied to find ZFS parameters by various other workers [30].

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

$$B_{20} = -2 \bar{A}_2 \left(\frac{R_0}{R_{10} + \Delta R_1}\right)^{t_2} - 4 \bar{A}_2 \left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_2} \tag{5}$$

$$B_{40} = 16 \bar{A}_4 \left(\frac{R_0}{R_{10} + \Delta R_1}\right)^{t_4} + 12 \bar{A}_4 \left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_4} \tag{6}$$

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

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

IV. RESULTS AND DISCUSSION

The Mn^{2+} ion position and spherical coordinates of ligands are given in Table 1. The average of two out of four Mn^{2+}-Se^{2-} bond lengths are: $R_{10} = 0.2637$ nm and the average value of the rest two bond lengths are: $R_{20} = 0.2637$ nm. ΔR_1 and ΔR_2 are the distortion parameters. In tetrahedral coordination, $\bar{A}_4(R_0) = (-27/16)Dq$ [6]. For $3d^5$ ions the ratio $\frac{\bar{A}_2}{\bar{A}_4}$ lies in the range 8-12 [26, 30]. The power law exponent for Mn^{2+} ion is taken as $t_2 = 3$, $t_4 = 7$. Semi-ab initio calculations are performed for other transition ions to find the intrinsic parameter values in SPM; the same method is utilized here.

Table 1 Mn^{2+}ion position and spherical coordinates of ligands R θ, φ in CdGa$_2$Se$_4$ single crystal.

Position of Mn^{2+} (Fractional)	Ligands				Spherical co-ordinates of ligands	
				R(nm)	θ^0	φ^0
		x y z (Å)			(degree)	
Site : Substitutional	Se (1)	0.2753	0.2593	0.1390	0.2637	55.4	43.2
Cd (0, 0, 0)	Se (2)	-0.2753	-0.2593	0.1390	0.2637	55.4	43.2
	Se (3)	0.2593	-0.2753	0.1390	0.2637	55.4	-46.7
	Se (4)	-0.2593	0.2753	-0.1390	0.2637	124.5	-46.7

The values of B, C and Dq are obtained from optical absorption study [29] as 648, 2475 and 810 cm^{-1}, respectively. First no local distortion is considered and the value of D is evaluated. For this, taking the ratio $\dfrac{\overline{A_2}}{A_4}$ = 10 and R$_0$ = 0.211 nm, which is slightly smaller than the sum of ionic radii of Mn^{2+} = 0.083 nm and Se^{2-} = 0.198 nm, the B$_{kq}$ parameters are obtained as: B$_{20}$ = -42020.53 cm^{-1}, B$_{40}$ = -8039.77 cm^{-1}, B$_{44}$ = -4804.68 cm^{-1} and the value of D as: |D| = 4926.1×10^{-4} cm^{-1}. But the experimental value of D from EPR is: |D| = 919.3×10^{-4}cm^{-1} [13]. Thus it is seen that the theoretical value is quite larger than the experimental one.

Further, taking local distortions as ΔR$_1$ = -0.0777 nm and ΔR$_2$ = -0.0776 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| = 919.5×10^{-4} cm^{-1}, in good agreement with the experimental value: |D| = 919.3×10^{-4} cm^{-1}. Using B$_{kq}$ parameters and CFA program [33-34], the optical spectra of Mn^{2+} doped CdGa$_2$Se$_4$ crystals are calculated. The energy levels of Mn^{2+} ion are determined by

Table 2. Crystal field parameters and zero field splitting parameter of Mn^{2+} doped CdGa$_2$Se$_4$ 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|
-0.0777	-0.0776	0.211	19374.98	-1319.83	-789..673		919.5
0.0000	0.0000	0.211	42020.53	-8039.77	-4804.68		4926.1
						Exptl.	919.3

diagonalizing the complete Hamiltonian within the 3d^N basis of states in the intermediate crystal field coupling scheme. The calculated energy values are given in Table 3 (input parameters are given below the Table) together with the experimental values [29] for comparison. It can be seen from Table 3 that there is a reasonable agreement between the calculated and experimental energy values. The energy values obtained without considering distortion were much different from the experimental values and so are not being shown here. Thus the theoretical investigation supports the experimental results.

Table 3. Experimental and calculated (CFA package) energy band positions of Mn^{2+}
doped CdGa$_2$Se$_4$ single crystal.

Transition from $^6A_{1g}(S)$	Observed energy bands (cm^{-1})	Calculated energy bands (cm^{-1}) With distortion
$^4T_{1g}(G)$	17244	15630, 15690, 16164, 16217, 16250, 16391
$^4T_{2g}(G)$	20196	19722, 19771, 19840, 19931, 20171, 20201
$^4Eg(G)$	21519	20375, 20379, 20382, 20385
$^4T_{2g}(D)$	23374	22111, 22153, 22161, 22199, 23840, 23911
$^4Eg(D)$	25576	25166, 25623, 25733, 25748

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, 648, 2475, 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 CdGa$_2$Se$_4$ single crystal has been evaluated with the help of superposition model and perturbation theory. The theoretical D matches well with the experimental value when distortion is taken into consideration. The theoretical study shows that Mn^{2+} ion replaces Cd^{2+} site which supports the experimental EPR results. The CF energy values for Mn^{2+} ions at Cd^{2+} sites determined using CFA package and CF parameters give reasonable agreement with the experimental values. Thus the theoretical investigation supports the experimental observation. Modeling approach used here may be applied in future to various other ion-host systems for correlating EPR and optical data.

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