iJETRM
International Journal of Engineering Technology Research & Management

Crystal field parameters and zero field splitting parameter of Fe^{3+} in $CdGa_2S_4$ single crystals

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Abstract

Crystal field parameters and zero-field splitting parameter of Fe^{3+} doped $CdGa_2S_4$ single crystals are determined using superposition model and perturbation theory. The evaluated zero-field splitting parameter matches well with the experimental value obtained from EPR. The theoretical study supports the experimental result that Fe^{3+} ions replace Ga^{3+} site in $CdGa_2S_4$ single crystal. Using CFA program and crystal field parameters, the optical spectra of Fe^{3+} doped $CdGa_2S_4$ crystal are calculated. A reasonable agreement is noted between the calculated and experimental energy values. Thus our theoretical study supports the results of the experimental study.

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

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1. Introduction

Electron paramagnetic resonance (EPR) study is capable to give information about structural distortions and local site symmetry of transition ions introduced in crystals [1-2]. The spin Hamiltonian (SH) parameters from EPR are correlated with optical and structural parameters using microscopic spin-Hamiltonian (MSH) theory. It is noted from above studies that the spin Hamiltonian parameters of d^5 transition ions in crystals are very sensitive to local distortions.

The crystal-field (CF) parameters of d^5 ions can be estimated using superposition model (SPM) [3, 4]. The zero field splitting (ZFS) parameters are then evaluated with the help of CF parameters [5-8]. Due to high order interaction of crystalline electric field, the electron spins of Fe^{3+} ion are oriented freely in external magnetic field [9, 10].

$CdGa_2S_4$ presents thiogallate structure of space group $I\bar{4}$ and belongs to the family of defect tetrahedral structures [11]. There is a great interest in ternary, tetrahedral compounds due to their non-linear optical properties, semiconductivity, photoconductivity and vibrational spectra
[12,13].

EPR study on the Fe^{3+} centers in $CdGa_2S_4$ has been done at 35 GHz frequency and 300 K temperature [14]. In this system two axial centers are observed, for center I Fe^{3+} substitutes at Ga^{3+} (1) and for center II it substitutes at Ga^{3+} (2) site. The value of ZFS parameter D for Fe^{3+} ion in the center II is larger than that in the center I, due to the deviations of coordinated ligands to the magnetic ion [14]. In the present study, the CF parameters are calculated using SPM and these parameters with MSH theory then yield ZFS parameter for Fe^{3+} ions located at the two centers I and II in $CdGa_2S_4$ single crystal at 300 K. The ZFS parameter D evaluated in this way agrees well with the experimental value [14].

2. Crystal Structure

The crystal structure of $CdGa_2S_4$ is tetragonal. The lattice parameters are a = 5.5492 Å, c = 10.1624 Å, Z = 2 [15].

The crystal structure belongs to the space group $I\bar{4}$. The S coordination around Ga (1) and Ga (2) is shown in Fig. 1. The site symmetry around Ga^{3+} (Fe^{3+}) ions is taken to be axial, as shown by EPR study of Fe^{3+}: $CdGa_2S_4$ [14].

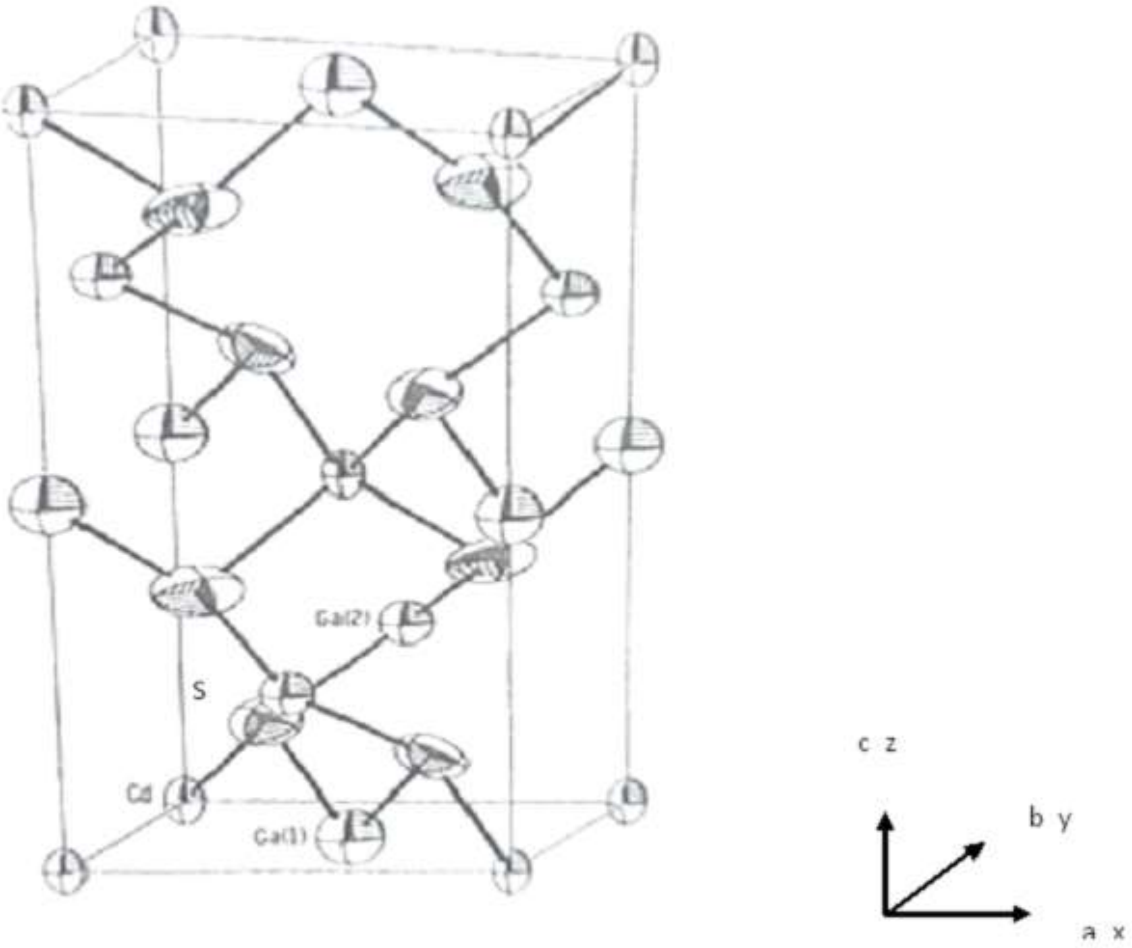

Fig. 1: Crystal structure of $CdGa_2S_4$ together with axes (S metry adopted axes system).

3. Theoretical Investigation

The SH of Fe^{3+} ion in crystal field of axial symmetry is given by [16-18]

$$
\begin{aligned}
\mathscr{H} = {} & g\ \mu_B B.S + D\{S_Z^2 - S(S+1)\} \\
& + \left(\frac{a}{6}\right)[S_X^4 + S_Y^4 + S_Z^4 - \frac{1}{5} S(S+1)(3S^2 + 3 \quad 1)] \\
& + \frac{F}{180}\{35S_Z^4 - 30S(S+1)S_Z^2 + 25S_Z^2 - 6S(S+1) + 3S^4(S+1)^2\} \\
& + A(I.S)
\end{aligned}
\qquad (1)
$$

where the first term is the electronic Zeeman interaction, B is the external magnetic field, g is the spectroscopic splitting factor and μ_B is Bohr magneton. The second, third, and fourth terms are the second order axial, fourth-rank cubic and fourth-rank axial ZFS terms [7]. The fifth term provides the hyperfine interaction term. S, D, *a*, F are the effective spin vector, second order axial, fourth-rank cubic and fourth-rank axial ZFS parameters, respectively. An isotropic electronic Zeeman interaction is supposed for Fe^{3+} ions [7, 19, 20].

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 while $\mathcal{H}_0$ and $\mathcal{H}_{so}$ are free ion Hamiltonian and spin-orbit (SO) coupling, respectively. Since the spin-spin coupling is quite small [21-23], its contribution in Eq. (2) is neglected. The crystal field of SO interaction is taken as perturbation term [24-26]. The strong-field calculation for F-state ions has been done by Macfarlane [27]. The SO contribution to the ZFS parameter D for $3d^5$ Fe^{3+} ions in axial symmetry is given by [25]

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

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 very small [25, 27]. The parameters B, C and ξ, in terms of the average covalency parameter N, are given as, $B = N^4B_0$, $C = N^4C_0$ 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 [28, 29], respectively. $B_0 = 1130\ cm^{-1}$, $C_0 = 4111\ cm^{-1}$, $\xi_0 = 589\ cm^{-1}$ [7] for free Fe^{3+} ion are taken in our calculation. From equation

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

N can be found taking the values of Racah parameters ($B = 720\ cm^{-1}$, $C = 2500\ cm^{-1}$) determined from optical study of Fe^{3+} ion in crystal having similar ligands [30].

Employing SPM, the CF parameters for Fe^{3+} ion in $CdGa_2S_4$ single crystal are calculated and then from Eq. (3) ZFS parameter D is found. Similar method has been used for evaluating ZFS parameters by earlier workers [31].

The SPM is effectively used to interpret the crystal-field splitting for $3d^n$ ions [27, 32]. The crystal field parameters, using this model, are determined from the equations [33]

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

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

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

where R_0 is the reference distance (the average of all four bond lengths for axial symmetry).

4. Results and Discussion

The position of Fe^{3+} ion and spherical coordinates of ligands are shown in Table 1A and B. The average of two out of four Fe^{3+}-S^{2-} bond lengths are obtained as R_{10} = 0.5486 nm for center I (Ga (1)) and R_{10} = 0.3340 nm for center II (Ga (2)); the average value of the other two bond lengths are found as R_{20} = 0.4198 nm for center I (Ga (1)) and R_{20} = 0.4569 nm for center II (Ga (2)), respectively. ΔR_1 and ΔR_2 are the distortion parameters. $\bar{A}_2$, $\bar{A}_4$ and t_k are the intrinsic parameter and power law exponent, respectively. In tetrahedral coordination, $\overline{A_4}(R_0) = -(27/16)Dq$ [5]. For $3d^5$ ions, $\frac{\overline{A_2}}{\overline{A_4}}$ lies in the range 8-12 [27, 32]. The power law exponent for Fe^{3+} 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 used here

Table 1A and B. Atomic coordinates in $CdGa_2S_4$ crystal and spherical coordinates of ligands R θ, φ.

Table 1 A

Position of Fe^{3+} (Fractional)	Ligands	x	y	z (Å)	Spherical co-ordinates of ligands R(nm)	θ^0 (degree)	ϕ^0
Site : Substitutional Ga(1) (0, 0, 0.5)	S (1)	0.2585	0.2513	0.1368	0.4198	151.3	44.2
	S (2)	-0.2585	-0.2513	0.1368	0.4198	151.3	44.2
	S (3)	0.2513	-0.2585	0.1368	0.4198	151.3	-45.8
	S (4)	-0.2513	0 .2585	-0.1368	0.6773	162.8	-45.8

Table 1 B

Position of Fe^{3+} (Fractional)	Ligands	x	y	z (Å)	Spherical co-ordinates of ligands R(nm)	θ^0 (degree)	ϕ^0	
Site : Substitutional Ga(2) (0, 0.5, 0.25)	S (1)	0.2585	0.2513	0.1368	0.2299	120.0	-43.9	
	S (2)	-0.2585	-0.2513	0.1368	0.4556	104.6		71.0
	S (3)	0.2513	-0.2585	0.1368	0.4581	104.5	-71.5	
	S (4)	-0.2513	0 .2585	-0.1368	0.4381	153.8	43.8	

The values of B, C and Dq are determined from optical absorption study [30] as 720, 2500 and 720 cm^{-1}, respectively. First no local distortion is considered and the value of D is obtained. For this, taking $\frac{\overline{A_2}}{\overline{A_4}} = 10$ and R_0 = 0.211 nm, which is slightly smaller than the sum of ionic radii of Fe^{3+} = 0.0645 nm and S^{2-} = 0.184 nm, the B_{kq} parameters are obtained as: B_{20} = 7552.292 cm^{-1}, B_{40} = -142.297 cm^{-1}, B_{44} = -164.671 cm^{-1} and the value of D as: $|D| = 75.6\times10^{-4}$ cm^{-1} for center I (Ga (1)) and B_{20} = 10914.09 cm^{-1}, B_{40} = -846.031 cm^{-1}, B_{44} = -91.1094 cm^{-1} and the value of D as: $|D| = 220.9\times10^{-4}$ cm^{-1} for center II (Ga (2)) . EPR study gives the experimental value of D as: $|D| = 168.0\times10^{-4} cm^{-1}$ and $|D| = 6285.0\times10^{-4} cm^{-1}$ for center I and II, respectively [14]. From above it is seen that the theoretical value is quite smaller than the experimental one.

Now, taking local distortions as $\Delta R_1 = 0.0390$ nm and $\Delta R_2 = 0.0385$ nm, $R_0 = 0.211$ nm and ratio $\frac{\overline{A}_2}{\overline{A}_4} = 10$, the B_{kq} parameters are obtained as given in Table 2 and the value of D as: $|D| = 168.2\times10^{-4}$ cm^{-1}, in good agreement with the experimental one: $|D| = 168.0\times10^{-4}$ cm^{-1} for center I. Further, taking distortions as $\Delta R_1 = 0.12351$ nm, $\Delta R_2 = 0.12375$ nm and other parameters as above, the B_{kq} parameters are found as given in Table 2 and the value of D as: $|D| = 6285.0\times10^{-4}$ cm^{-1}, also in good agreement with the experimental value: $|D| = 6285.0\times10^{-4}$ cm^{-1} for center II. Using B_{kq} parameters and CFA program [34-35], the optical energy values of Fe^{3+} doped $CdGa_2S_4$ single crystal are calculated 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 (input parameters are given below the Table) together with the experimental values [30] for comparison. It is observed from Table 3 that there is a reasonable agreement between the calculated and experimental energy values. The energy values determined without considering distortion are quite different from the experimental ones and hence are not presented here. Thus the theoretical study supports the results of the experimental one.

Table 2. Crystal field parameters and zero field splitting parameters of Fe^{3+} doped $CdGa_2S_4$ 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|
I	0.0390	0.0385	0.211	9958.382	-272.101	-322..868	168.2
	0.0000	0.0000	0.211	7552.292	-142.297	-164.671	75.6
						Exptl.	168.0
II	0.12351	0.12375	0.211	36828.35	-20370.8	-831..571	6285.0
	0.0000	0.0000	0.211	10914.09	-846.031	-91.1094	220.9
						Exptl.	6285.0

Table 3. Experimental and calculated (CFA package) energy band positions of Fe^{3+} doped $CdGa_2S_4$ single crystal.

Transition from $^6A_{1g}(S)$	Observed wave number [cm^{-1}]	Calculated wave number [cm^{-1}]	
		I	II
$^4T_{1g}(G)$	14489 16389		12293, 14596, 14728, 15971, 16591, 17507
$^4T_{2g}(G)$	19300	19671, 19871, 19991, 20000, 20143, 20166	18353, 18359, 18697, 19907, 19934, 20053
$^4E_g(G)$		21218, 21244 21329, 21417	21311, 21345, 21567, 21609
$^4A_{1g}(G)$		21504, 21512	21632, 21650
$^4T_{2g}(D)$	23803	22607, 22712, 24010, 24075, 24198, 24329	22704, 22886, 23182, 23291, 23303,23364
$^4E_g(D)$		25249, 25392, 26375, 26558	24553, 25367, 25536, 25741

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, 720, 2500, 520 and 90 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.

5. Conclusions

Zero-field splitting parameter D for Fe^{3+} in $CdGa_2S_4$ single crystal has been determined using superposition model and perturbation theory. The theoretical D agrees well with the experimental one for both centers I and II when distortion is considered into calculation. The theoretical D shows that Fe^{3+} ion substitutes Ga^{3+} sites. This supports the results of the experimental EPR study. Using CF parameters and CFA program, the optical energy values give a reasonable agreement with the experimental energy values. Thus our theoretical study supports the experimental results obtained earlier.

ACKNOWLEDGEMENT

The author is thankful to the Head, Department of Physics for giving the departmental facilities and to Prof. C. Rudowicz, Faculty of Chemistry, A. Mickiewicz. University, Poznan, Poland for CFA program.

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