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Zero field splitting parameter of Fe^{3+} in $CdGa_2Se_4$ single crystals

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Abstract

Theoretical investigation of crystal field parameters and zero-field splitting parameter of Fe^{3+} doped $CdGa_2Se_4$ single crystals is performed using superposition model and perturbation theory. The zero-field splitting parameter obtained agrees well with the experimental value determined from EPR. The theoretical investigation supports the experimental result that Fe^{3+} ions substitute at Ga^{3+} site in $CdGa_2Se_4$ single crystal. Using crystal field parameters and CFA program, the optical spectra of Fe^{3+} doped $CdGa_2Se_4$ crystal are computed. There is a reasonable agreement between the computed and experimental energy values. Thus our theoretical investigation supports the results of the experimental study.

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

Introduction

Electron paramagnetic resonance (EPR) studies are important to obtain structural distortions and local site symmetry of transition ions doped in crystals [1-3]. The spin Hamiltonian (SH) parameters determined from EPR with the help of microscopic spin-Hamiltonian (MSH) theory, may be correlated with optical and structural parameters. The above studies indicate that the spin Hamiltonian parameters of transition ions (d^5) in crystals are quite sensitive to local distortions.

The crystal-field (CF) parameters of d^5 ion can be obtained employing superposition model (SPM) [4, 5]. The zero field splitting (ZFS) parameters are then estimated using CF parameters [6-10]. The electron spins of Fe^{3+} ion orient freely in external magnetic field with high order interaction of crystalline electric field [11, 12].

$CdGa_2Se_4$ exhibits thiogallate structure of space group I and belongs therefore to the family of defect tetrahedral structures [13]. There is a great interest in ternary, tetrahedral compounds due to their non-linear optical properties and semiconductivity [14].

EPR measurements on the Fe^{3+} centers in $CdGa_2Se_4$ have been carried out at 35 GHz frequency and 300 K temperature [15]. In this crystal 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 magnitude of ZFS parameter D for Fe^{3+} ion in the II center is larger than that in the I center, which may be due to the deviations of coordinated ligands to the magnetic ion [15]. In the present investigation, the CF parameters are computed using SPM and these parameters with MSH theory then provide ZFS parameter for Fe^{3+} ions at the two centers I and II in $CdGa_2Se_4$ single crystal at 300 K. The ZFS parameter D obtained using SPM matches well with the experimental value [15].

Crystal Structure

The crystal structure of $CdGa_2Se_4$ is tetragonal. The lattice parameters are a = 5.7432 Å, c = 10.7564 Å, Z = 2 [16]. The crystal structure belongs to the space group $I\bar{4}$. The Se coordination around Ga (1) and Ga (2) is shown in Fig. 1. The site symmetry around Ga^{3+} (Fe^{3+}) ions is considered to be axial, as presented by EPR study of Fe^{3+}: $CdGa_2Se_4$ [15].

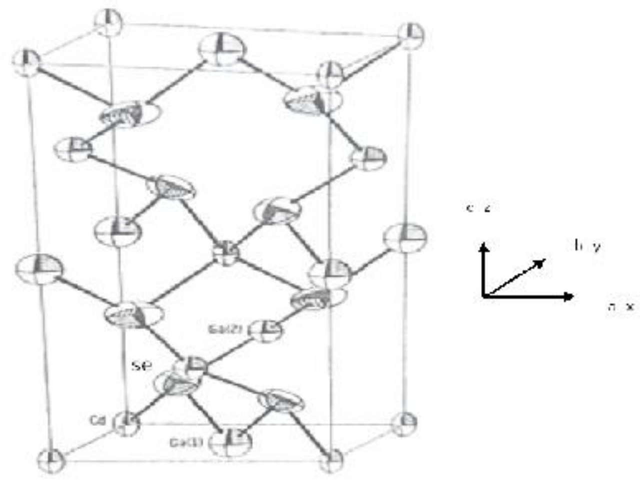

Fig 1: Crystal structure of $CdGa_2Se_4$ together with axes (SAAS-symmetry adopted axes system).

Theoretical Investigation

The SH of $3d^5$ Fe^{3+} ion in crystal field of axial symmetry is given as [17-19]

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

where the first term provides 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 as discussed in [9]. The fifth term gives 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 taken for Fe^{3+} ions [9, 20, 21].

The Hamiltonian for a d^5 ion is written as

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

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

is the crystal field Hamiltonian whereas $\mathcal{H}_0$ and $\mathcal{H}_{so}$ represent free ion Hamiltonian and spin-orbit (SO) coupling, respectively. As the spin-spin coupling is very small [22-24], its contribution is neglected in Eq. (2). The crystal field of SO interaction is taken as perturbation term [25-27]. The strong-field scheme calculation for F-state ions has been done by Macfarlane [28]. The SO contribution to the ZFS parameter D for $3d^5$ ions in axial symmetry is given by [26]

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

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 represent the electron-electron repulsion. Only fourth order term is taken in Eq. (3) as other perturbation terms are quite small [26, 28]. 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 [29, 30], respectively. $B_0 = 1130$ cm^{-1}, $C_0 = 4111$ cm^{-1}, $\xi_0 = 589$ cm^{-1} [9] for free Fe^{3+} ion are taken here for calculation. Using equation

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

N can be obtained taking the values of Racah parameters (B =720 cm^{-1}, C = 2500 cm^{-1}) found from optical study of Fe^{3+} ion in crystal having Se ligands [31].

Using SPM the CF parameters for Fe^{3+} in $CdGa_2Se_4$ single crystal are evaluated and then from Eq. (3) ZFS parameter D is determined. Similar method has been used for finding ZFS parameters by earlier workers [32].

The SPM is effectively applied to interpret the crystal-field splitting. This model has also been used for $3d^n$ ions [28, 33]. The crystal field parameters, using this model, are obtained from the equations [34]

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

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

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

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

Results and Discussion

The position of Fe^{3+} ion and spherical coordinates of ligands are given in Table 1A and B. The average of two out of four Fe^{3+}-Se^{2-} bond lengths are found as $R_{10} = 0.5829$ nm for center I (Ga (1)) and $R_{10} = 0.3520$ nm for center II (Ga (2)); the average value of the other two bond lengths are obtained as $R_{20} = 0.4449$ nm for center I (Ga (1)) and $R_{20} = 0.4817$ 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, $\overline{A_4}(R_0) = -(27/16)Dq$ [6]. For $3d^5$ ions, the ratio $\frac{\overline{A_2}}{\overline{A_4}}$ lies in the range 8-12 [28, 33]. The power law exponent for Fe^{3+} ion is taken as $t_2 = 3$, $t_4 = 7$. Semi-ab initio calculations are done for other transition ions to obtain the intrinsic parameter values in SPM, the same method is used here:

Table 1A and B. Atomic coordinates in $CdGa_2Se_4$ crystal and spherical coordinates of ligands R θ, φ.

Table 1A

Position of Fe^{3+} (Fractional)	Ligands				Spherical co-ordinates of ligands		
					R(nm)	Θ^0	Φ^0
	x	y		z	(degree)		
	(Å)						
Site: Substitutional	Se (1)	0.2753	0.2593	0.1390	0.4449	50.7	43.3
Ga(1) (0, 0, 0.5)	Se (2)	0.2753	0.2593	0.1390	0.4449	50.7	43.3
	Se (3)	0.2753	0.2593	0.1390	0.4449	50.7	-46.7
	Se (4)	0.2753	0.2593	0.1390	0.4449	50.7	-46.7

Table 1B

Position of Fe^{3+} (Fractional)	Ligands				Spherical co-ordinates of ligands		
					R(nm)	Θ^0	Φ^0
	x	y		z	(degree)		
	(Å)						
Site: Substitutional	Se (1)	0.2753	0.2593	0.1390	0.2416	119.6	-42.2
Ga(2) (0, 0.5, 0.25)	Se (2)	-0.2753	-0.2593	0.1390	0.4789	104.4	70.1
	Se (3)	0.2593	-0.2793	0.1390	0.4844	104.2	-71.5
	Se (4)	-0.2593	0.2793	-0.1390	0.4625	154.7	40.9

The values of B, C and Dq are found from optical absorption study [31] as 720, 2500 and 720 cm^{-1}, respectively. First no local distortion is considered and the value of D is determined. 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 $Se^{2-} = 0.198$ nm, the B_{kq} parameters are found as: $B_{20} = 6336.211$ cm^{-1}, $B_{40} = -94.4905$ cm^{-1}, $B_{44} = -109.68$ cm^{-1} and the value of D as: $|D| = 41.2\times10^{-4}$ cm^{-1} for center I (Ga (1)) and $B_{20} = 9316.054$ cm^{-1}, $B_{40} = -585.211$ cm^{-1}, $B_{44} = -62.89$ cm^{-1} and the value of D as: $|D| = 143.6\times10^{-4}$ cm^{-1} for center II (Ga (2)). EPR study provides the experimental value of D as: $|D| = 2706.0\times10^{-4}cm^{-1}$ and $|D| = 5028.0\times10^{-4}cm^{-1}$ for center I and II, respectively [15]. From above it is noted that the theoretical value is quite smaller than the experimental one. Now, taking local distortions as $\Delta R_1 = 0.2105$ nm and $\Delta R_2 = 0.2101$ nm, $R_0 = 0.211$ nm and ratio $\frac{\overline{A}_2}{\overline{A}_4} = 10$, the B_{kq} parameters are obtained as shown in Table 2 and the value of D as: $|D| = 2706.5\times10^{-4}$ cm^{-1}, in good agreement with the experimental one: $|D| = 2706.0\times10^{-4}$ cm^{-1} for center I. Further, taking distortions as $\Delta R_1 = 0.1370$ nm, $\Delta R_2 = 0.1372$ nm and other parameters as above, the B_{kq} parameters are found as given in Table 2 and the value of D as: $|D| = 5028.8\times10^{-4}$ cm^{-1}, also in good agreement with the experimental value: $|D| = 5028.0\times10^{-4}$ cm^{-1} for center II. Using B_{kq} parameters and CFA program [35-36], the optical energy values of Fe^{3+} doped $CdGa_2Se_4$ 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 presented in Table 3 (input parameters are given below the Table) together with the experimental values [31] 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 are inconsistent with the experimental ones and hence are not given here. Thus the theoretical investigation supports the results of the experimental study.

Table 2: Crystal field parameters and zero field splitting parameters of Fe^{3+} doped $CdGa_2Se_4$ single crystal.

				Crystal- field parameters (cm^{-1})			Zero-field splitting parameter (10^{-4}cm
ΔR_1 (nm)		ΔR_2 (nm)	R_0 (nm)	B_{20}	B_{40}	B_{44}	|D|
I	0.2105	0.2101	0.211	39678.3	-7259.47	-9614..49	2706.5
	0.0000	0.0000	0.211	6336.211	-94.4905	-109.68	41.2
							Exptl. 2706.0
II	0.1370	0.1372	0.211	34118.94	-17491.3	-657.125	5028.8
	0.0000	0.0000	0.211	9316.054	-585.211	-62.89	143.6
							Exptl. 5028.0

Table 3: Experimental and calculated (CFA package) energy band positions of Fe^{3+} doped $CdGa_2Se_4$ single crystal.

Transition from	Observed wave number	Calculated wave number	Transition from
$^6A_{1g}(S)$	[cm^{-1}]		[cm^{-1}]
		i.	ii.
$^4T_{1g}(G)$	14489	14935, 15350,	13100, 13303,
	16389	15495, 15605,	14444, 16797,
		16068, 16259	16951, 17766
$^4T_{2g}(G)$	19300	17707, 18217,	18389, 19185,
		19497, 20932,	19927, 20026,
		20974, 21050	20300, 20681
$^4E_g(G)$		21236, 21493	21019, 21380,
		21531, 21585	21427, 21570
$^4A_{1g}(G)$		21586, 22935	21717, 22798
$^4T_{2g}(D)$	23803	23202, 23235,	23290, 23302,
		23242, 23288,	23343, 23367,
		23380, 23554	23635,24223
$^4E_g(D)$		25267, 25563,	25251, 25423,
		25918, 26664	25627, 26372

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.

Conclusions

Axial symmetry zero-field splitting parameter D for Fe^{3+} in $CdGa_2Se_4$ single crystal has been determined using superposition model and perturbation theory. The theoretical D matches well with the experimental value for both centers I and II when distortion is included into calculation. The theoretical D shows that Fe^{3+} ion occupies Ga^{3+} site which supports the results obtained from the experimental EPR study. Using CF parameters and CFA program, the optical energy values show a reasonable agreement with the experimental energy ones. Thus our theoretical investigation supports the results of the experimental study.

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