

Crystal field parameters and zero field splitting parameter of Mn²⁺ doped CdGa₂S₄ single crystals

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Abstract

Using superposition model and the perturbation theory the crystal field parameters and zero-field splitting parameter of Mn²⁺ doped CdGa₂S₄ single crystals are calculated. The theoretical zero-field splitting parameter D matches well with the experimental value obtained from EPR study. The present study supports the experimental EPR result that Mn²⁺ ions replace Cd²⁺ ions in CdGa₂S₄ single crystal. The optical energy values for Mn²⁺ ions at Cd²⁺ sites found using CFA package and crystal field parameters are in reasonable agreement with the experimental ones. Hence the theoretical study supports the experimental observation.

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

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I. INTRODUCTION

The microscopic spin-Hamiltonian (MSH) theory is frequently used for the study of crystals as the spin Hamiltonian parameters of transition ions (d⁵) in crystals are quite sensitive to local distortions [1-3]. The spin Hamiltonian (SH) parameters obtained from electron paramagnetic resonance (EPR) can be correlated with optical and structural parameters of the crystals.

The crystal-field (CF) parameters of 3d⁵ Mn²⁺ ion may be determined employing superposition model (SPM) [4, 5]. The zero field splitting (ZFS) parameters can then be obtained with the help of CF parameters [6-10].

CdGa₂S₄ shows the well known 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 with reference to their non-linear optical properties, semiconductivity, photoconductivity, the electronic energy band structure and the vibrational spectra [12, 13].

EPR study of Mn²⁺ doped CdGa₂S₄ single crystals [14] at room temperature (RT) has been reported [15]. In the present work, the CF parameters are determined employing SPM and these parameters with MSH theory yield ZFS parameter for Mn²⁺ ions at the axial symmetry site in CdGa₂S₄ single crystal at RT. The ZFS parameter D evaluated in this manner gives good match with the experimental value [14].

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

II. RELATED WORK

The SPM studies have been done for different ion-host systems [16-31]. The crystal structure of CdGa₂S₄ is tetragonal. The lattice parameters are a = 5.5492 Å, c = 10.1624 Å, Z = 2 [14]. The crystal structure belongs to

the space group $I\bar{4}$. The S coordination around Cd²⁺ is shown in Fig. 1. The site symmetry around Cd²⁺ (Mn²⁺) ions is considered to be axial, as shown by EPR study of Mn²⁺: CdGa₂S₄ [14].

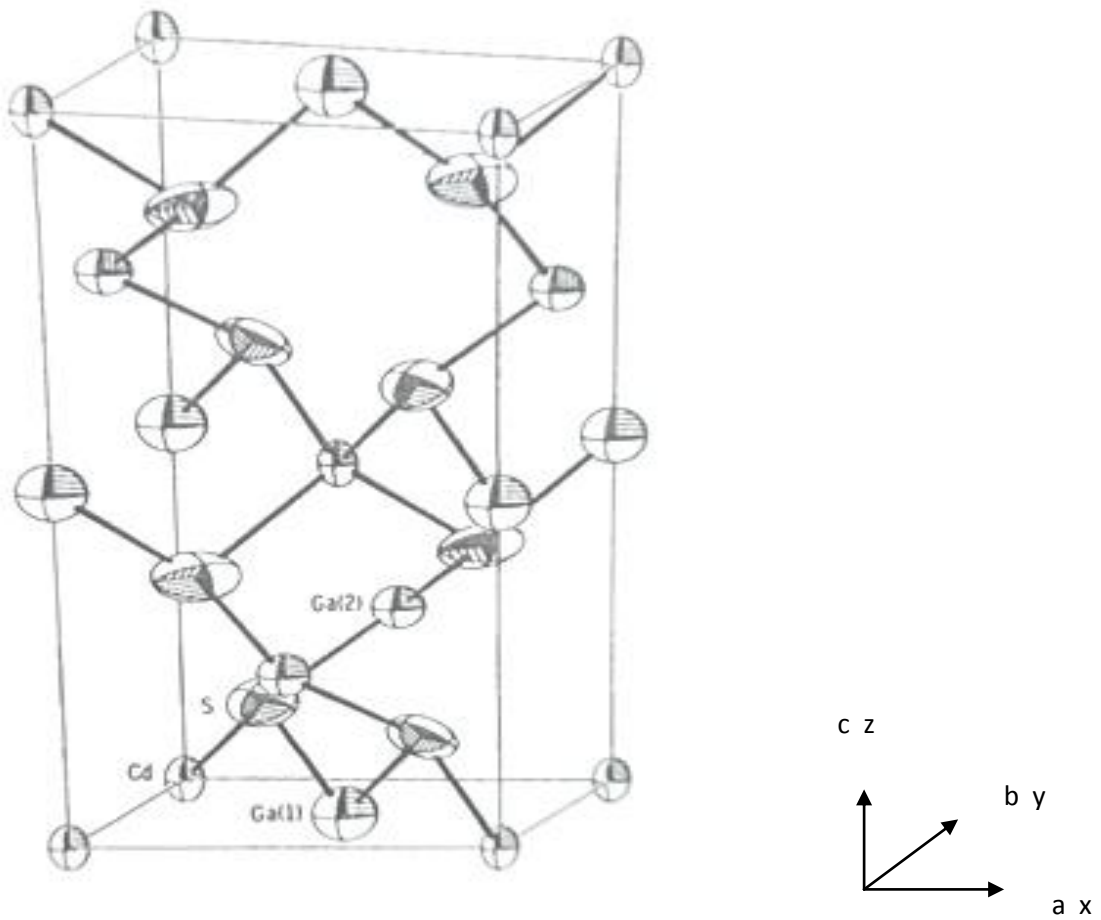


Fig. 1: Crystal structure of $CdGa_2S_4$ together with axes (SAAS-symmetry adopted axes system).

III. MATERIALS AND METHODS

The SH of $3d^5 Mn^{2+}$ ion in crystal field of axial symmetry [8]:

$$\begin{aligned} \mathcal{H} = & g \mu_B B \cdot S + D(S_z^2 - S(S+1)) \\ & + \left(\frac{\alpha}{6}\right)[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)] \\ & + A(I \cdot S) \end{aligned} \quad (1)$$

where the first term represents 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 give the second order axial and fourth-rank cubic ZFS terms [8]. The fourth term provides the hyperfine interaction term. S , D and a are the effective spin vector, second order axial and fourth-rank cubic ZFS parameters, respectively. The electronic Zeeman interaction is assumed to be isotropic for Mn^{2+} ions [8, 19, 20].

The Hamiltonian for a d^5 ion is given as

$$\begin{aligned} \mathcal{H} = & \mathcal{H}_0 + \mathcal{H}_{CF} + \mathcal{H}_{SO} \\ \text{where } \mathcal{H}_{CF} = & \sum_{kq} B_{kq} C_q^k \end{aligned} \quad (2)$$

is the crystal field Hamiltonian while \mathcal{H}_0 and \mathcal{H}_{SO} represent free ion Hamiltonian and spin-orbit (SO) coupling, respectively. Since the spin-spin coupling is very small [21-23], its effect is neglected in Eq. (2).

The crystal field of SO interaction is taken as perturbation term [24-26]. The strong-field scheme calculation for F-state ions is given by Macfarlane [27]. The SO contribution to the ZFS parameter D for 3d⁵ ions in axial symmetry is given as [25]

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

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) since other perturbation terms are very small [25, 27]. The parameters B, C and ζ , in terms of the average covalency parameter N, are: $B = N^4B_0$, $C = N^4C_0$ and $\zeta = N^2\zeta_0$, where B_0 , C_0 and ζ_0 are the Racah parameters and the spin-orbit coupling parameter for free ion [28, 29], respectively. $B_0 = 960 \text{ cm}^{-1}$, $C_0 = 3325 \text{ cm}^{-1}$, $\zeta_0 = 336 \text{ cm}^{-1}$ [8] are taken here for free Mn²⁺ ion. Using equation

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

N can be determined with the help of the values of Racah parameters ($B = 648 \text{ cm}^{-1}$, $C = 2475 \text{ cm}^{-1}$) found from optical study [30].

Using SPM the CF parameters for Mn²⁺ in CdGa₂S₄ single crystal are obtained and then from Eq. (3) ZFS parameter D is calculated. Similar method has been applied to find ZFS parameters by previous workers [31]. The SPM is effectively used to find the crystal-field splitting. It has also been used for 3dⁿ ions [27, 32]. The crystal field parameters B_{kq} , using this model, are evaluated from the equations [33]

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

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

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

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 are the intrinsic parameter and power law exponent, respectively.

IV. RESULTS AND DISCUSSION

The position of Mn²⁺ ion and spherical coordinates of ligands are given in Table 1. The average of two out of four Mn²⁺-S²⁻ bond lengths are: $R_{10} = 0.2436 \text{ nm}$ and the average value of other two bond lengths are: $R_{20} = 0.2436 \text{ nm}$. ΔR_1 and ΔR_2 are the distortion parameters. In tetrahedral coordination,

$\bar{A}_4(R_0) = (-27/16)Dq$ [6]. For 3d⁵ ions $\frac{\bar{A}_2}{\bar{A}_4}$ lies in the range 8-12 [27, 31]. The power law exponent for

Mn²⁺ ion is taken as $t_2 = 3$, $t_4 = 7$.

Table 1 Mn²⁺ ion position and spherical coordinates of ligands R, θ, φ in CdGa₂S₄ single crystal.

Position of Mn ²⁺ (Fractional)	Ligands	Spherical co-ordinates of ligands			
		R (nm)	θ ⁰ (degree)	φ ⁰	
	x y z (Å)				
Site : Substitutional Cd (0, 0, 0)	S (1)	0.2585 0.2513 0.1368	0.2436	55.2	44.2
	S (2)	-0.2585 -0.2513 0.1368	0.2436	55.2	44.2
	S (3)	0.2513 -0.2585 0.1368	0.2436	55.2	-45.8
	S (4)	-0.2513 0.2585 -0.1368	0.2436	124.7	-45.8

The values of B, C and Dq are obtained from optical study [30] as 648, 2475 and 810 cm⁻¹, respectively. First considering no local distortion the value of D is determined. For this, taking $\frac{\overline{A_2}}{\overline{A_4}} = 10$ and R₀ = 0.211 nm, which is slightly smaller than the sum of ionic radii of Mn²⁺ = 0.083 nm and S²⁻ = 0.184 nm, the B_{kq} parameters are found as: B₂₀ = 53283.0 cm⁻¹, B₄₀ = -13991.8 cm⁻¹, B₄₄ = -8361.7 cm⁻¹ and the value of D as: |D| = 8095.2 × 10⁻⁴ cm⁻¹. The experimental value of D from EPR is: |D| = 225.3 × 10⁻⁴ cm⁻¹ [14]. Thus it is noted that the theoretical value is quite larger than the experimental one.

Further, taking local distortions as ΔR₁ = -0.1720 nm and ΔR₂ = -0.1714 nm, R₀ = 0.211 nm and $\frac{\overline{A_2}}{\overline{A_4}} = 10$, the B_{kq} parameters are obtained as shown in Table 2 and the value of D as: |D| = 225.2 × 10⁻⁴ cm⁻¹, in good match with the experimental value: |D| = 225.3 × 10⁻⁴ cm⁻¹. Using B_{kq} parameters and CFA program [34-35], the optical energy values of Mn²⁺ doped CdGa₂S₄ crystals are calculated. The energy levels of Mn²⁺ ion are calculated by

Table 2. Crystal field parameters and zero field splitting parameter of Mn²⁺ doped CdGa₂S₄ 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
-0.1720	-0.1714	0.211	10762.02	-334.1	-200.818	225.2
0.0000	0.0000	0.211	53283.0	-13991.8	-8361.7	8095.2
						Exptl. 225.3

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 [29] for comparison purpose. It can be noted from Table 3 that there is a reasonable agreement between the calculated and experimental energy values. The energy values obtained without distortion were much different from the experimental ones and hence are not given here. Thus the theoretical study supports the experimental results.

Table 3. Experimental and calculated (CFA package) energy band positions of Mn²⁺ doped CdGa₂S₄ single crystal.

Transition from ⁶ A _{1g} (S)	Observed energy bands (cm ⁻¹)	Calculated energy bands (cm ⁻¹) With distortion
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⁴ T _{1g} (G)	17244	18485, 18503, 18624, 18703, 18735, 18800
⁴ T _{2g} (G)	20196	19322, 19526, 20115, 20151, 20211, 20303
⁴ E _g (G)	21519	20394, 20400, 20413, 21940
⁴ T _{2g} (D)	23374	22539, 22577, 22645, 22721, 23839, 23911
⁴ E _g (D)	25576	25348, 25471, 25580, 25673

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; B₂₀, B₄₀, B₄₄ 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

Crystal field parameters and Zero-field splitting parameter D for Mn²⁺ in CdGa₂S₄ single crystal have been determined with the help of superposition model and perturbation theory. The theoretical D agrees well with the experimental value when distortion is taken into consideration. The theoretical study suggests that Mn²⁺ ion replaces Cd²⁺ site which supports the experimental EPR results. The CF energy values for Mn²⁺ ions at Cd²⁺ sites calculated using CFA package and CF parameters show reasonable agreement with the experimental values. Thus the theoretical investigation supports the experimental observation. Modeling approach employed in the present study may be applied in future to other ion-host systems for correlating EPR and optical data.

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