



Theoretical Investigation of ZFS parameters of Mn²⁺ Doped CdSe Nanocrystals

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ABSTRACT

The superposition model and the perturbation theory are used to theoretically investigate the crystal field parameters (CFPs) and zero-field splitting (ZFS) parameter D of Mn²⁺ doped cadmium selenide (CdSe) nanocrystals. The obtained ZFS parameter D is very close to the experimental value reported earlier. The superposition model is applied to explain the crystal field (CF) splitting. The calculated value of D without taking distortion into account is $-79.50 \times 10^{-4} \text{ cm}^{-1}$ and when we consider local distortions the value of D is $-82.03 \times 10^{-4} \text{ cm}^{-1}$ which is in good agreement with the experimental value.

Keywords: Nanocrystal; Superposition model; Crystal fields; Zero-field splitting.

Introduction:

The spin-Hamiltonian theory is used to explain the electron paramagnetic resonance (EPR) of transition metal (TM) ions. Zero-field splitting (ZFS) parameters provide information about the structural distortions and local site symmetry around the transition metal ions in crystals [1-3]. ZFS parameters can be determined with the help of crystal-field parameters (CFPs) of d^5 ion in a crystal obtained using superposition model (SPM) [4, 5]. The experimental and theoretical results for transition metal ions reflect that the spin-Hamiltonian (SH) parameters are very sensitive to the local surrounding [6, 7].

To study the SH parameters for d^5 ions crystal-field (CF) theory has been comprehensively applied. Crystal field parameters contain geometrical and physical information of the system which can be found from the SPM [8]. This model needs the information of positions of various ligands. Thus, the theories regarding local distortions are extremely useful [9].

Mn²⁺ belongs to a class of ions called iron group. It is important because of its ground state

being S. High order interaction of external magnetic field and crystalline electric field affect the electronic spin of Mn²⁺ ion. At room temperature EPR of Mn²⁺ ion yields well resolved lines due to large spin-lattice relaxation time [10, 11].

Crystal Structure

The CdSe crystal has the wurtzite hexagonal structure. It belongs to the space group P6₃mc having unit cell dimensions: $a = b = 4.299 \text{ \AA}$, $c = 7.010 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The number of molecules per unit cell (Z) is 4 [12]. A tetrahedral environment is formed around Mn²⁺ ion by Se atoms as shown in Fig. 1.

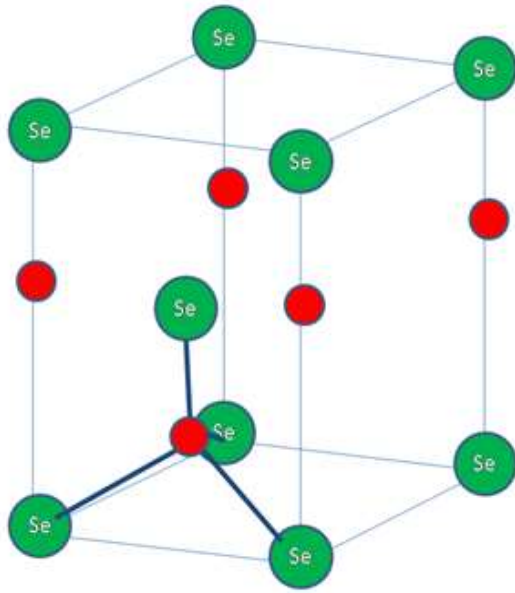


Fig. 1. Wurtzite CdSe: coordination of Cd²⁺ion [Cd²⁺(red), Se²⁻(green)]

Theoretical Investigation:

Doping of Mn²⁺ changes the coordination environment of the host. Here Mn²⁺ ion substitutes for Cd²⁺ ion and has a little distorted tetrahedral structure with Mn²⁺ ion in axial symmetry [13-16].

The Spin Hamiltonian of 3d⁵ ion in the crystal field of axial symmetry can be written as:

$$\mathcal{H} = \mu_B B \cdot g \cdot S + D(S_z^2 - \frac{1}{3}S(S+1)) + \left(\frac{a}{6}\right)[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)] + \frac{F}{180}(35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2) + A(I \cdot S) \dots (1)$$

where the first term is electronic Zeeman interaction term, g is spectroscopic splitting factor, B is the external magnetic field, and μ_B is the Bohr magneton. The second term is the second order axial ZFS term with S, D as the effective spin vector and second order axial ZFS parameter, third term is fourth-rank cubic ZFS term with a as fourth-rank cubic ZFS parameter, fourth term represents fourth-rank axial ZFS term with F as fourth-rank axial ZFS

parameter and fifth term is the hyperfine interaction term [17, 20].

The total Hamiltonian for Mn²⁺ ion can be written as:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{CF} + \mathcal{H}_{SO} + \mathcal{H}_{SS} \dots(2)$$

where \mathcal{H}_0 represents unperturbed or free ion Hamiltonian, \mathcal{H}_{CF} represents CF interactions, \mathcal{H}_{SO} stands for spin-orbit interaction and \mathcal{H}_{SS} is spin-spin coupling [21, 23]. The CF Hamiltonian in the Wybourne notation is written as [24]:

$$\mathcal{H}_{CF} = \sum_{kq} B_{kq} C_q^k \dots(3)$$

The B_{kq} in the equation are the crystal-field parameters which are the measure of strength of interaction between the outer-shell electrons of paramagnetic ions and their surrounding crystalline environment and C_q^k is the orbital angular momentum operator which is a tensor operator defined by:

$$C_q^k = \sqrt{\frac{4\pi}{2k+1}} Y_{kq} \dots(4)$$

with Y_{kq} denoting spherical harmonic function [25-27].

Spin-spin coupling (SS) here is very small thus its contribution to the Hamiltonian is negligible in equation (2). As a result we have only the crystal field and spin-orbit interaction (SO) as the perturbation term [28, 29]. In case of axial symmetry the ZFS parameter D⁽⁴⁾_(SO) for Mn²⁺ (3d⁵) ion is calculated by:

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

where P, G and D are given as: P = 7(B + C), G = 10B + 5C and D = 17B + C [30-31]. The Racah parameters B, C and spin-orbit coupling parameter ξ can be determined in terms of N, the average covalency parameter, and are given by: B = N⁴B₀, C = N⁴C₀ and ξ = N²ξ₀, where B₀, C₀ and ξ₀ are Racah parameters and spin-orbit coupling parameter for free Mn²⁺ ion. The values of these parameters are taken as: B₀

= 960 cm⁻¹, C₀ = 3325 cm⁻¹, ξ₀ = 336 cm⁻¹ [32, 33].
The value of N is determined using the relation:

$$N = \left(\sqrt{\frac{B}{B_0}} + \sqrt{\frac{C}{C_0}} \right) / 2 \quad \dots(6)$$

According to superposition model [12, 34, 35], the relationship between the CF parameters and local structure parameters can be expressed as:

$$B_{20} = -2\bar{A}_2 \left(\frac{R_0}{R_{10} + \Delta R_1} \right)^{t_2} - 4\bar{A}_2 \left(\frac{R_0}{R_{20} + \Delta R_2} \right)^{t_2} \dots(7)$$

$$B_{40} = 16\bar{A}_4 \left(\frac{R_0}{R_{10} + \Delta R_1} \right)^{t_4} + 12\bar{A}_4 \left(\frac{R_0}{R_{20} + \Delta R_2} \right)^{t_4} \dots(8)$$

$$B_{44} = 2\sqrt{70}\bar{A}_4 \left(\frac{R_0}{R_{20} + \Delta R_2} \right)^{t_4} \quad \dots(9)$$

where, R₀ symbolize the reference distance, value of which is taken in such a way that it is equal to the mean value of all four bond lengths for axial symmetry. When Mn²⁺ ions are doped into CdSe nanocrystal, Mn²⁺ replaces Cd²⁺ ion. The increment of bond lengths can be described by the distortion parameters ΔR₁ and ΔR₂, i.e., R₁ = R₁₀ + ΔR₁, R₂ = R₂₀ + ΔR₂. Mean value of two out of four Cd-Se bond lengths is denoted by R₁₀ and that of other two is denoted by R₂₀. \bar{A}_k and t_k represent the intrinsic parameter and power law exponent, respectively. The ratio of intrinsic parameters \bar{A}_2/\bar{A}_4 lies in the range 8- 12 for 3d⁵ ions [30, 36].

Results and Discussion:

The average value of the bond lengths R₁₀ and R₂₀ are calculated and are 0.4126 nm and 0.9126 nm, respectively. The ratio of intrinsic parameters \bar{A}_2/\bar{A}_4 is taken to be 12. t₂ = 3, t₄ = 7 are taken as the values of power law exponents. For the case of tetrahedral coordination $\bar{A}_4(R_0)$ and Dq are related to each other with the relation: $\bar{A}_4(R_0) = (-27/16)Dq$. Thus by using the value of Dq and ratio \bar{A}_2/\bar{A}_4 we can determine values of intrinsic parameters \bar{A}_2 and \bar{A}_4 which are -16402.5 and -1366.8, respectively. The value of R₀ is taken as 0.271 nm. This is less than the sum of ionic radii of Mn²⁺ ion and Se²⁻ ion which are 0.08 nm and 0.198 nm, respectively. B_{kq} parameters are calculated using equations (7), (8) and (9) and found as: B₂₀=

11014.96 cm⁻¹, B₄₀= -1157.07 cm⁻¹ and B₄₄= -4.66 cm⁻¹. Further, the value of D is estimated without considering local distortions which comes out to be -79.50 × 10⁻⁴ cm⁻¹. The experimental value [37] of D is -82 × 10⁻⁴ cm⁻¹. Taking local distortions into account, as ΔR₁ = 0.004 nm, ΔR₂ = -0.001 nm and ratio $\bar{A}_2/\bar{A}_4 = 12$, B_{kq} parameters are calculated as: B₂₀= 12052.35 cm⁻¹, B₄₀= -1441.46 cm⁻¹ and B₄₄= -5.44 cm⁻¹. Using these B_{kq}, the value of D is -82.03 × 10⁻⁴ cm⁻¹ which is very close to the experimental value mentioned above. Thus the theory is in good agreement with experimental findings.

Conclusion

Zero field splitting parameter D of Mn²⁺ doped CdSe nanocrystal is determined using perturbation theory and superposition model. The calculated value of D is compared with the experimental one and found in good agreement. The present study shows that Mn²⁺ substitutes for Cd²⁺ ion in the CdSe nanocrystal supporting the experimental inference.

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