

# Complete Diagonalization Calculation of the Optical and EPR Data for the Tetragonal $\text{Cu}^{2+}$ Center in $\text{Cu}^{2+}$ -Doped ZnSe Nanocrystals

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By using the complete diagonalization (of energy matrix) method based on the cluster approach (where the admixture between the  $d$  orbitals of  $d^n$  ion and  $p$  orbitals of ligands due to covalence effect is considered), the optical and electron paramagnetic resonance data (three optical band positions and four EPR parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$ ,  $A_{\perp}$ ) are calculated for the tetragonal  $\text{Cu}^{2+}$  center in  $\text{Cu}^{2+}$ -doped poly vinyl alcohol (PVA) passivated ZnSe nanocrystals with the defect model of  $\text{Cu}^{2+}$  in the interstitial octahedral site in ZnSe. The calculated results are near the experimental values. The tetragonal elongation of the  $\text{Cu}^{2+}$  octahedral cluster in ZnSe nanocrystals is obtained. The results are discussed.

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## 1. Introduction

II–VI semiconducting nanocrystals or nanoparticles, which have the different characteristics from the corresponding bulk crystals, have been extensively studied to explore their unique properties and potential applications [1–8]. The properties (particularly, the optical, electronic and magnetic ones) of nanocrystals and crystals can be modified by impurities (e.g., transition metal ( $3d^n$ ) ion impurities). The modifications of property are connected with the defect model and defect structure of impurity centers. The spectroscopic techniques are the important methods to study the defect model of impurity centers in nanocrystals and crystals. So, various spectroscopic measurements for  $3d^n$  ions in II–VI semiconducting nanocrystals and crystals have been made [9–16]. Among them, since the wide direct band gap II–VI semiconductor ZnSe is chemically more stable and has the applications in light-emitting diodes, photo-detectors and full color display [16–18], the spectroscopic studies of ZnSe nanocrystals doped with  $3d^n$  ions have attracted attention [13–15, 19].

Recently, the optical and electron paramagnetic resonance (EPR) spectra of  $\text{Cu}^{2+}$ -doped ZnSe nanocrystals prepared by simple chemical method at room temperature with poly vinyl alcohol (PVA) as the passivating (or capping) agent were measured by Begum et al. [15]. In these measurements, a tetragonal  $\text{Cu}^{2+}$  center with three optical absorption bands at about 8345, 12192, 14573  $\text{cm}^{-1}$  and four spin-Hamiltonian (or EPR) parameters ( $g$  factors  $g_{\parallel}$ ,  $g_{\perp}$  and hyperfine structure constants  $A_{\parallel}$ ,  $A_{\perp}$ ) was found [15]. Since the cubic crystal

field parameters  $Dq$  of  $\text{Cu}^{2+}$  tetrahedral clusters in crystals, e.g., II–VI semiconductors [20, 21], are about half those of  $\text{Cu}^{2+}$  octahedral clusters in crystals [22, 23], the optical band positions of  $\text{Cu}^{2+}$  tetrahedra are lower than 8000  $\text{cm}^{-1}$  [20, 21] and those of  $\text{Cu}^{2+}$  octahedra are in the range 8000–18000  $\text{cm}^{-1}$  [22, 23]. So, Begum et al. [15] suggested that  $\text{Cu}^{2+}$  in the PVA capped ZnSe nanocrystals occupies the interstitial octahedral site rather than the substitutional tetrahedral site. The latter is more frequently found for  $3d^n$  impurities in ZnSe bulk crystals [24, 25] (with the tetragonal symmetry due to the Jahn–Teller effect) and some ZnSe nanocrystals synthesized by other methods [19, 26, 27] (note: the different  $3d^n$  impurity sites in ZnSe nanocrystals may be caused by the different synthesized methods. In fact, similar to  $\text{Cu}^{2+}$ , for  $\text{Fe}^{3+}$ - and  $\text{Mn}^{2+}$ -doped PVA capped ZnSe nanocrystals,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  were found to be on the interstitial octahedral sites by Begum et al. [13, 14]). Until now, no theoretical calculations with the above defect model (i.e.,  $\text{Cu}^{2+}$  site) have been made for the optical and EPR data of the tetragonal  $\text{Cu}^{2+}$  center in  $\text{Cu}^{2+}$ -doped PVA capped ZnSe nanocrystals. In this paper, we calculate these optical and EPR data together by using the complete diagonalization (of energy matrix) method. The results (including the tetragonal distortion of  $\text{Cu}^{2+}$  center due to the Jahn–Teller effect) are discussed.

## 2. Calculation

In consideration of the strong covalence of ZnSe, the complete diagonalization method should be based on the cluster approach, where the admixture between the  $d$  orbitals  $|d_{\gamma}\rangle$  of central  $3d^n$  ion and  $p$  orbitals  $|p_{\gamma}\rangle$  of ligand is taken into account. Thus, the one-electron basis functions for a  $d^n$  octahedral cluster in crystals should take the form [28]:

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$$|\psi_y\rangle = N_y^{1/2} (|d_y\rangle - \lambda_y |p_y\rangle), \quad (1)$$

where  $\gamma = t$  or  $e$  stands for the irreducible representation of  $O_h$  group. The normalization coefficient  $N_\gamma$  and orbital mixing coefficient  $\lambda_\gamma$  are the molecular orbital (MO) coefficients. The one-electron basis functions can lead to two spin-orbit parameters  $\zeta$ ,  $\zeta'$ , two orbital reduction factors  $k$ ,  $k'$  and three dipolar hyperfine structure constants  $P$ ,  $P'$ ,  $P''$ , i.e.

$$\begin{aligned} \zeta &= \zeta_{tt} = N_t (\zeta_d^0 + \lambda_t^2 \zeta_p^0 / 2), \\ \zeta' &= \zeta'_{te} = (N_t N_e)^{1/2} (\zeta_d^0 - \lambda_t \lambda_e \zeta_p^0 / 2), \\ k &= k_{tt} = N_t [1 - 2\lambda_t S_{dp}(t_{2g}) + \lambda_t^2 / 2], \\ k' &= k'_{te} = \\ & (N_t N_e)^{1/2} [1 - \lambda_t S_{dp}(t_{2g}) - \lambda_e S_{dp}(e_g) - \lambda_t \lambda_e / 2], \\ P &= P_{tt} = N_t P_0, \\ P' &= P'_{te} = \sqrt{N_t N_e} P_0, \quad P'' = P''_{ee} = N_e P_0, \end{aligned} \quad (2)$$

where the subscripts  $tt$ ,  $te$ , and  $ee$  indicate the interactions within  $t$  states, between  $t$  and  $e$  states and within  $e$  states, respectively.  $\zeta_d^0$  and  $P_0$  are the corresponding parameters of free  $d^n$  ion.  $\zeta_p^0$  is the spin-orbit parameter of free ligand. For ZnSe:  $\text{Cu}^{2+}$  under consideration, we have  $\zeta_d^0(\text{Cu}^{2+}) \approx 829 \text{ cm}^{-1}$  [29],  $P_0(\text{Cu}^{2+}) \approx 388 \times 10^{-4} \text{ cm}^{-1}$  [30] and  $\zeta_p^0(\text{Se}^{2-}) \approx 1659 \text{ cm}^{-1}$  [31].  $S_{dp}(\gamma)$  are the group overlap integrals which can be calculated from the Slater-type self-consistent field (SCF) functions [32, 33] with the mean metal-ligand distance  $R_0$ . In the host ZnSe crystal, the distance  $R_h$  between the interstitial site and  $\text{Se}^{2-}$  ion is  $2.835 \text{ \AA}$  [34]. When  $\text{Cu}^{2+}$  occupies the interstitial site, the  $\text{Cu}^{2+}$ - $\text{Se}^{2-}$  distance  $R_0$  should be smaller than the distance  $R_h$  because of the electrostatic attraction between  $\text{Cu}^{2+}$  and  $\text{Se}^{2-}$  ions. We assume the distances  $R_0 \approx 2.63 \text{ \AA}$ , the sum of ionic radii of  $\text{Cu}^{2+}$  and  $\text{Se}^{2-}$  ions [34]. Thus, we have  $S_{dp}(t) \approx 0.0075$  and  $S_{dp}(e) \approx 0.0238$ .

Based on the cluster approach, the complete Hamiltonian for calculating the optical and EPR data of a  $d^9$  ion in tetragonal crystal field and under an external magnetic field  $H_M$  (required by the EPR measurement) is written as

$$\begin{aligned} H &= H_f + H_{\text{SO}}(\zeta, \zeta') + H_{\text{CF}}(Dq, Ds, Dt) \\ &+ H_{\text{Ze}}(k, k') + H_{\text{hf}}(P, P', P'') \end{aligned} \quad (3)$$

with

$$H_{\text{Ze}} = \mu_B [(k, k') \mathbf{L} + g_s \mathbf{S}] \cdot \mathbf{H}_M, \quad (4)$$

$$\begin{aligned} H_{\text{hf}} &= (P, P', P'') \left\{ \mathbf{L} + \left( \frac{4}{7} N(E) - \kappa \right) \mathbf{S} \right. \\ &\left. - \frac{1}{7} [(\mathbf{L} \cdot \mathbf{S}) \mathbf{L} + \mathbf{L} (\mathbf{L} \cdot \mathbf{S})] \right\} \cdot \mathbf{I}. \end{aligned} \quad (5)$$

The five terms in Eq. (3) are, respectively, free ion, spin-orbit interaction, crystal field interaction, magnetic

(or Zeeman) interaction and hyperfine interaction terms.  $\mu_B$  is the Bohr magneton.  $g_s \approx 2.0023$  is the free-electron  $g$  value.  $\mathbf{L}$ ,  $\mathbf{S}$  and  $\mathbf{I}$  are, respectively, the orbit, spin, and nuclear spin momenta.  $N(E) (\leq 1)$  is a parameter indicating the effective Jahn-Teller reduction in the hyperfine structure constants [28, 35] and  $\kappa$  is the core polarization constant.

The  $10 \times 10$  energy matrix of the Hamiltonian in Eq. (3) is founded in terms of the strong field basis functions [36]. Diagonalizing the energy matrix, the eigenvalues corresponding to the crystal field energy levels and hence the optical band positions, the Zeeman splittings  $\Delta E_{\text{Ze}}(j)$  (under the external magnetic field along the  $j$  direction) and hyperfine splittings  $\Delta E_{\text{hf}}(j)$  (with the operators in Eq. (5) along  $j$  direction) can be obtained. The spin-Hamiltonian parameters are calculated by using the following formulae:

$$g_{\parallel} = g_z = \frac{\Delta E_{\text{Ze}}(z)}{\mu_B H_z}, \quad g_{\perp} = g_x = \frac{\Delta E_{\text{Ze}}(x)}{\mu_B H_z},$$

$$A_{\parallel} = A_z = \Delta E_{\text{hf}}(z), \quad A_{\perp} = A_x = \Delta E_{\text{hf}}(x). \quad (6)$$

The energy matrix contains the parameters in Eq. (2), the crystal-field parameters  $Dq$ ,  $Ds$ ,  $Dt$ , and the parameters  $N(E)$  and  $\kappa$ . The calculations of parameters in Eq. (2) need the values of MO coefficients. They can be connected by the normalization relationships obtained from Eq. (1):

$$N_\gamma [1 - 2\lambda_\gamma S_{dp}(\gamma) + (\lambda_\gamma)^2] = 1. \quad (7)$$

Thus, the coefficients  $N_\gamma$  can be calculated from the values of  $\lambda_\gamma$ . The coefficients  $\lambda_t$  and  $\lambda_e$  are taken as the adjustable parameters. For decreasing the number of adjustable parameter, we assume  $\lambda_t \approx \lambda_e \approx \lambda_\gamma$  because the studies for  $3d^n$  octahedral clusters in crystals show that the value of  $\lambda_t$  is close to that of  $\lambda_e$  [37–39]. The parameters  $Dq$ ,  $Ds$ , and  $Dt$  are generally calculated from the superposition model [40]. According to the model [40], we have

$$\begin{aligned} Dq &\approx \frac{4}{3} \bar{A}_4(R_0), \\ Ds &= \frac{4}{7} \bar{A}_2(R_0) \left[ \left( \frac{R_0}{R_{\perp}} \right)^{t_2} - \left( \frac{R_0}{R_{\parallel}} \right)^{t_2} \right], \\ Dt &= \frac{16}{21} \bar{A}_4(R_0) \left[ \left( \frac{R_0}{R_{\perp}} \right)^{t_4} - \left( \frac{R_0}{R_{\parallel}} \right)^{t_4} \right], \end{aligned} \quad (8)$$

where  $t_k$  ( $k = 2, 4$ ) and  $\bar{A}_k(R_0)$  are the power-law exponents and intrinsic parameters (with the reference distance  $R_0$ ), respectively. We take  $t_2 \approx 3$  and  $t_4 \approx 5$  [28, 40–42] here. By means of the studies of the crystal field parameters with superposition model in the optical and EPR data for  $3d^n$  ions in a number of crystals, the ratio  $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 8$ – $12$  was found [28, 41–44]. We take  $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 11$  here.  $R_{\parallel}$  and  $R_{\perp}$  are the metal-ligand distances along and normal to  $C_4$  axis in the studied octahedral cluster. The site symmetry of interstitial site in ZnSe is cubic. When a  $\text{Cu}^{2+}$  ion occupies

this site, the ground state of  $\text{Cu}^{2+}$  ( $d^9$ ) ion in cubic octahedron is orbit doublet  ${}^2E$ . The degenerated ground orbit state is unstable and the static Jahn–Teller effect leads the cubic octahedron to become tetragonal one because the  ${}^2E$  state can be split by the tetragonal crystal field into two-orbit singlets  ${}^2B_1(|d_{x^2-y^2}\rangle)$  and  ${}^2A_1(|d_{z^2}\rangle)$ . Thus, the ground orbit state of  $\text{Cu}^{2+}$  ( $d^9$ ) ion in tetragonal octahedron may be  ${}^2B_1$  or  ${}^2A_1$ , corresponding to the tetragonally-elongated or tetragonally-compressed octahedron. The considered  $(\text{CuSe}_6)^{10-}$  octahedron in ZnSe nanocrystals is tetragonally-elongated because the observed  $g$  factors  $g_{\parallel} > g_{\perp}$  [15]. So,  $R_{\parallel}$  and  $R_{\perp}$  due to the Jahn–Teller effect can be given as

$$R_{\parallel} = R_0 + 2a, \quad R_{\perp} = R_0 - a, \quad (9)$$

where  $a$  indicates the tetragonal distortion. Thus, in the energy matrix, five parameters  $\lambda_{\gamma}$ ,  $\bar{A}_4(R_0)$ ,  $a$ ,  $N(E)$  and  $\kappa$  are unknown and left as the adjustable parameters. By changing these adjustable parameters systematically with a fitting routine until the best matches between the calculated (with the complete diagonalization method) and experimental optical and EPR data are obtained, we find for  $(\text{CuSe}_6)^{10-}$  octahedron in ZnSe nanocrystals

$$\lambda_{\gamma} \approx 0.366, \quad \bar{A}_4(R_0) \approx 900 \text{ cm}^{-1}, \quad a \approx 0.1 \text{ \AA},$$

$$N(E) \approx 0.8, \quad \kappa \approx 0.43. \quad (10)$$

The MO coefficients  $N_{\gamma}$  obtained from  $\lambda_{\gamma}$  and hence the parameters in Eq. (2) are collected in Table I. The calculated optical and EPR data are compared with the experimental values in Table II.

TABLE I

MO coefficients, spin-orbit parameters (in  $\text{cm}^{-1}$ ), orbital reduction factors and dipolar hyperfine structure constants (in  $10^{-4} \text{ cm}^{-1}$ ) of  $\text{Cu}^{2+}$  center in  $\text{Cu}^{2+}$ -doped PVA ZnSe nanocrystals.

$N_t$	$N_e$	$\zeta$	$\zeta'$	$k$	$k'$	$P$	$P'$	$P''$
0.8862	0.8956	833	640	0.9406	0.8210	344	346	347

TABLE II

Optical band positions (in  $\text{cm}^{-1}$ ) and spin Hamiltonian parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$  and  $A_{\perp}$  ( $A_i$  are in units of  $10^{-4} \text{ cm}^{-1}$ ) of the tetragonal  $\text{Cu}^{2+}$  center in  $\text{Cu}^{2+}$ -doped PVA ZnSe nanocrystals.

${}^2B_1 \rightarrow$	${}^2A_{1g}$	${}^2B_{2g}$	${}^2E$	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$
Calc.	7413	11992	14730, 15585	2.3357	2.0610	155	47
Expt.[15]	8345	12192	14573	2.3347	2.1225	150	48

### 3. Discussion

The core polarization constant  $\kappa$  ( $\approx 0.43$ ) obtained from the above calculations is within the range 0.2–0.8 found from the studies for the hyperfine structure constants of  $\text{Cu}^{2+}$  ions in many crystals [28, 45–48] and seems to be reasonable.

The tetragonal elongation  $R_{\parallel} - R_{\perp}$  ( $= 3a$ ) due to the Jahn–Teller effect acquired for  $\text{Cu}^{2+}$  center in ZnSe nanocrystals is about 0.3  $\text{\AA}$ . The elongation is close to those ( $\approx 0.1$ – $0.3 \text{ \AA}$ ) of the tetragonal or approximately tetragonal  $\text{Cu}^{2+}$  octahedral clusters in some pure crystals containing  $\text{Cu}^{2+}$  (i.e.,  $\text{Cu}^{2+}$  ion is the host ion rather than an impurity) [49–52]. In these pure crystals, the structures of crystals and hence the tetragonal elongations of  $\text{Cu}^{2+}$  octahedra are exactly measured by X-ray diffraction, so the tetragonal elongation obtained in our calculation can be regarded as rational.

By using the above suitable parameters and with the defect model of  $\text{Cu}^{2+}$  on the interstitial octahedral site with tetragonal symmetry due to the Jahn–Teller effect, the calculated three optical band positions and four spin-Hamiltonian parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$ ,  $A_{\perp}$  from the complete diagonalization method are close to the experimental values (see Table II). So, the defect model suggested in Ref. [15] is confirmed, the defect structure (i.e., tetragonal elongation  $R_{\parallel} - R_{\perp}$ ) is obtained and the optical and EPR data for  $\text{Cu}^{2+}$  center in  $\text{Cu}^{2+}$ -doped PVA capped ZnSe nanocrystals are explained reasonably.

It is noted that there are small disparities between the calculated and observed optical and EPR data for  $\text{Cu}^{2+}$  center in ZnSe nanocrystals (see Table II). An important cause is, in our opinion, that the observed optical and EPR data of  $d^n$  ion in crystals at various temperatures come from two contributions, the static or implicit contribution due to the crystal field acting the central  $\text{Cu}^{2+}$  (or other  $d^n$ ) ions and the vibrational or explicit one caused by the electron–phonon interaction [53–58]. In the above calculations, we take into account only the important static contribution. So, the small disparities seem to be comprehensible.

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