Defect model of a Cu^{2+} center in CdSe nanocrystals

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ABSTRACT

By using the defect model of Cu^{2+} at the substitutional tetrahedral site with tetragonal symmetry, the spin-Hamiltonian parameters $g_{//}, g_{\perp}, A_{//}$ and $A_{\perp}$ of a Cu^{2+} center in CdSe nanocrystals are calculated from the high-order perturbation formulas based on the cluster approach. The calculated results are in reasonable agreement with the experimental values. However, in a previous paper, these spin-Hamiltonian parameters were also explained from the high-order perturbation formulas based on the cluster approach by using another defect model of the Cu^{2+} ion at the interstitial octahedral site with tetragonal symmetry in CdSe nanocrystals. So it may be impossible to determine the defect model of the Cu^{2+} center in CdSe nanocrystals by analyzing only the spin-Hamiltonian parameters obtained from EPR spectra. A possible method of absorption spectra in the range $4000–15{,}000\ cm^{-1}$ is suggested to determine the defect model of the Cu^{2+} center in CdSe nanocrystals.

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1. Introduction

Impurities in crystals and nanocrystals can strongly influence their properties. So studies of the defect model of impurity centers in crystals and nanocrystals are of interest. Since spectroscopic methods are powerful tools to study the defect model of a transition metal or rare earth impurity in crystals and nanocrystals, many spectroscopic measurements on crystals and nanocrystals doped with these impurities were carried out [1,2]. For example, the optical and electron paramagnetic resonance (EPR) spectra for Cu^{2+}-doped CdSe nanocrystals were measured [3]. From these measurements, a broad emission band peaking at $17{,}745\ cm^{-1}$ and a strong anisotropic EPR signal corresponding to the anisotropic g factors $g_{//} \approx 2.321(6)$, $g_{\perp} \approx 2.053(6)$ and hyperfine structure constants $|A_{//}| = 225(18) \times 10^{-4}\ cm^{-1}$, $|A_{\perp}| = 63(18) \times 10^{-4}\ cm^{-1}$ were found [3]. The broad emission band is attributed to an unidentical defect structure because it can be found in the undoped CdSe nanocrystals [4]. For the anisotropic EPR data, the authors [3] thought that they are due to a Cu^{2+} impurity center caused by the substitutional Cu^{2+} at the trigonally-distorted tetrahedral Cd^{2+} site in CdSe nanocrystals. Recently, Wu et al. [5] pointed out that, since the spin-Hamiltonian parameters of the conventional trigonally-distorted tetrahedral Cu^{2+} centers in bulk II–VI semiconductors generally yield small average values 0.2–1.9 for the g factors (with either $g_{//}$ or $g_{\perp}$ significantly smaller than 2) and the anisotropy $|A_{//}| < |A_{\perp}|$ for the hyperfine structure constants, the studied Cu^{2+} center in CdSe nanocrystals with the large average g value 2.14 ($g_{//} > g_{\perp} > 2$) and the anisotropy |

$A_{//}| > |A_{\perp}|$ means that the defect model of Cu^{2+} center may not be for Cu^{2+} substituted at the trigonally-distorted tetrahedral Cd^{2+} site. Considering that the observed spin-Hamiltonian parameters for Cu^{2+} in CdSe nanocrystals are quite similar to those of Cu^{2+} ions in various tetragonally-elongated octahedra, Wu et al. suggested that the observed Cu^{2+} center in CdSe nanocrystals is due to Cu^{2+} surrounded by a tetragonally-elongated octahedron (e.g., at an interstitial octahedral site). Based on the defect model suggested, Wu et al. calculated the spin-Hamiltonian parameters of Cu^{2+} in CdSe nanocrystals by using high-order perturbation formulas based on the cluster approach. The results are in agreement with the experimental values [5].

However, the above observed spin-Hamiltonian parameters of Cu^{2+} in CdSe nanocrystals are also similar to those of Cu^{2+} in tetragonally-compressed tetrahedra. For example, in the approximate tetragonal Cu^{2+} center due to the substitutional Cu^{2+} at the tetragonally-compressed tetrahedral Cu^{+} site in $CuGaSe_2$ crystals [6,7], the g factors $g_{//}(=g_z \approx 2.40(5))$ and $g_{\perp}$ ($\approx (g_x + g_y)/2 \approx 2.12(2)$) and the anisotropy $|A_{//}|$ ($\approx 131 \times 10^{-4}\ cm^{-1}$) $> |A_{\perp}|$ ($\approx 28 \times 10^{-4}\ cm^{-1}$) are analogous to those of Cu^{2+} in CdSe nanocrystals. So, another defect model of substitutional Cu^{2+} in a tetragonally-compressed tetrahedron may be possible. In fact, in some II–VI semiconductors doped with transition-metal ($3d^n$) ions, the tetragonally-distorted tetrahedral impurity centers (possibly due to the Jahn–Teller effect [8–11]) were found. For instance, the tetragonal tetrahedral Ti^{3+} centers in ZnSe [8] and $CdS_{0.75}Se_{0.25}$ semiconductors [9] and the tetragonal tetrahedral Cu^{2+} center in ZnS nanocrystals (note: its g factors $g_{//} \approx 2.34$ and $g_{\perp} \approx 2.05$ are very similar to those of the studied Cu^{2+} center in CdSe nanocrystals [10]) were reported. In order to confirm further the possible defect model for Cu^{2+} ion in CdSe nanocrystals suggested in the paper,

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we calculate the spin-Hamiltonian parameters of Cu^{2+} in CdSe nanocrystals from the high-order perturbation formulas based on the cluster approach for d^9 ions in tetragonally-compressed tetrahedral clusters. The results are discussed.

2. Calculation

The one-electron basis functions in the cluster approach for a d^n tetrahedral cluster are the molecular orbitals (MO) containing the d orbitals $|d_\gamma>$ of d^n ion and p orbitals $|\pi_\gamma>$, $|\sigma_\gamma>$ of ligand ions [11,12]

$$|\varphi_e\rangle = N_e(|d_e\rangle + \sqrt{3}\lambda_\pi|\pi_e\rangle)$$
$$|\varphi_t\rangle = N_t(|d_t\rangle + \lambda_\sigma|\sigma_t\rangle + \lambda_\pi|\pi_t\rangle) \qquad (1)$$

where the subscript $\gamma=t$ or e stands for the irreducible representations of the T_d group. N_γ (the normalization coefficient) and λ_β ($\beta=\sigma$ or π, the orbital mixing coefficient) are the MO coefficients.

Eq. (1) results in two spin–orbit parameters ζ, ζ', two orbit reduction factors k, k' and two dipolar hyperfine structure constants P, P' (where ζ, k and P are connected with the interaction within t states, and ζ', k' and P' with that between t and e states). They are [11,12]

$$\zeta = N_t^2\left(\zeta_d^0 + \left(\sqrt{2}\lambda_\pi\lambda_\sigma - \frac{(\lambda_\pi)^2}{2}\right)\zeta_p^0\right)$$

$$\zeta' = N_t N_e\left(\zeta_d^0 + \left(\frac{\lambda_\pi\lambda_\sigma}{\sqrt{2}} - \frac{(\lambda_\pi)^2}{2}\right)\zeta_p^0\right)$$

$$k = N_t^2\left(1 - \frac{(\lambda_\pi)^2}{2} + \sqrt{2}\lambda_\pi\lambda_\sigma + 2\lambda_\pi S_{dp}(\pi) + 2\lambda_\sigma S_{dp}(\sigma)\right)$$

$$k' = N_t N_e\left(1 + \frac{(\lambda_\pi)^2}{2} + \frac{\lambda_\pi\lambda_\sigma}{\sqrt{2}} + 4\lambda_\pi S_{dp}(\pi) + \lambda_\sigma S_{dp}(\sigma)\right)$$

$$PN_t^2 P_0, \quad P' = N_t N_e P_0 \qquad (2)$$

in which ζ_d^0 and ζ_p^0 are the spin–orbit parameters of free d^n ion and the free ligand ion, respectively. P_0 is the dipolar hyperfine structure constant of free d^n ion. For CdSe:Cu^{2+} considered, we have $\zeta_d^0(Cu^{2+}) \approx 829\ cm^{-1}$ [13], $\zeta_p^0(Se^{2-}) \approx 1659\ cm^{-1}$ [14] and $P_0(Cu^{2+}) \approx 388 \times 10^{-4}\ cm^{-1}$ [15]. The group overlap integrals $S_{dp}(\beta)$ are calculated from the Slater-type self-consistent field (SCF) functions [16,17] with the mean metal–ligand distance R in the studied cluster. The distance R in an impurity center in crystals may differ from the corresponding distance R_h in the host crystal because the ionic radius r_i of an impurity is different from the radius r_h of the replaced host ion [18,19]. An approximate formula $R=R_h+(r_i-r_h)/2$ [19] is often used to estimate the distance R. For CdSe:Cu^{2+} considered, from $r_i(Cu^{2+}) \approx 0.72$ Å and r_h (Cd^{2+}) ≈ 0.97 Å [20] and $R_h \approx 2.631$ Å [21], we yield $R=2.506$ Å. Thus, we have the group overlap integrals $S_{dp}(\sigma) \approx -0.02050$ and $S_{dp}(\pi) \approx 0.00498$.

For a d^9 ion in a tetragonally-compressed tetrahedron, the ground state should be $|d_{xy}>$ [11]. By means of the above one-electron basis functions and the perturbation method [11,13,22], the high-order perturbation formulas of spin-Hamiltonian parameters based on the cluster approach for d^9 ion in tetragonal tetrahedra with ground state $|d_{xy}>$ are derived as

$$g_{//} = g_e + \frac{8k'\zeta'}{E_1} - \frac{(g_e+k)\zeta^2}{2E_2^2}\frac{4k'\zeta\zeta'}{E_1 E_2}$$

$$g_\perp = g_e + \frac{2k\zeta}{E_2} - \frac{2k\zeta'^2 - 2k'\zeta\zeta'}{E_1 E_2} - \frac{g_e\zeta^2/2 - \zeta^2 k}{E_2^2} - \frac{2g_e\zeta'^2}{E_1^2}$$

$$A_{//} = P\left(-\kappa - \frac{4}{7}\right) + P'[(g_{//}-g_e) + \frac{3}{7}(g_\perp - g_e)]$$

$$A_\perp = P\left(-\kappa + \frac{2}{7}\right) + \frac{11}{14}P'(g_\perp - g_e) \qquad (3)$$

where g_e (≈ 2.0023) is the g value of the free electron. κ is the core polarization constant. The crystal field energy levels E_1 and E_2 are written as

$$E_1 = 10Dq, \quad E_2 = -3Ds + 5Dt \qquad (4)$$

in which the tetragonal field parameters Ds and Dt are frequently calculated from the superposition model [23]. For a tetragonal tetrahedron, their expressions in superposition model are

$$Ds = \frac{4}{7}\overline{A}_2(R)(3\cos^2\theta - 1),$$

$$Dt = \frac{4}{21}\overline{A}_4(R)(35\cos^4\theta - 30\cos^2\theta + 3 + 7\sin^4\theta) \qquad (5)$$

where $\overline{A}_2(R)$ and $\overline{A}_4(R)$ are the intrinsic parameters. For d^n tetrahedral clusters in many crystals, $\overline{A}_4(R) \approx (27/16)Dq$ [11,23,24], and the relation $\overline{A}_2(R) \approx 10\overline{A}_4(R)$ [11,24,25] has been found valid. They are applied here. The cubic field parameter Dq is often obtained from the optical spectra (in particular, the absorption spectra) due to d–d transitions of the studied system. For Cu^{2+} in CdSe nanocrystals and crystals, no d–d transition spectra were reported, we estimate the value of Dq from the observed Dq values of similar systems. The $Dq \approx 556\ cm^{-1}$ for Cu^{2+} in CdS [26] and $Dq \approx 353$ and $329\ cm^{-1}$ for the isoelectronic $3d^9$ ion Ni^+ in ZnS and ZnSe crystals [27] were reported. Thus, the value $Dq \approx 520\ cm^{-1}$ for Cu^{2+} in CdSe is estimated from the approximate relationship $Dq(ZnS: Ni^+)/Dq(ZnSe: Ni^+) \approx Dq(CdS: Cu^{2+})/Dq(CdSe:Cu^{2+})$. In Eq. (5), θ is the angle between the metal–ligand distance R and C_4 axis. θ is taken as an adjustable parameter.

The MO coefficients used in the calculations of the parameters in Eq. (2) can be related by the normalization relationships [11,12]

$$N_e = [1 + 3\lambda_\pi^2 + 6\lambda_\pi S_{dp}(\pi)]^{-1/2}$$

$$N_t = [1 + \lambda_\sigma^2 + \lambda_\pi^2 + 2\lambda_\sigma S_{dp}(\sigma) + 2\lambda_\pi S_{dp}(\pi)]^{-1/2}, \qquad (6)$$

and the approximate correlations [11,12]

$$f_e = N_e^4[1 + 6\lambda_\pi S_{dp}(\pi) + 9\lambda_\pi^2 S_{dp}^2(\pi)]$$

$$f_t = N_t^4[1 + 2\lambda_\sigma S_{dp}(\sigma) + 2\lambda_\pi S_{dp}(\pi) + 2\lambda_\sigma S_{dp}(\sigma)\lambda_\pi S_{dp}(\pi)$$
$$+ \lambda_\sigma^2 S_{dp}^2(\sigma) + \lambda_\pi^2 S_{dp}^2(\pi)] \qquad (7)$$

where $f_t \approx f_e \approx f_\gamma$ is a parameter concerning the covalence of d^n cluster and is also taken as an adjustable parameter [11,12]. Thus, in the above formulas, three parameters f_γ, θ and κ are treated as adjustable parameters to get the best fit to the observed spin-Hamiltonian parameters. The good match between the calculated (using the above high-order perturbation formulas) and experimental spin-Hamiltonian parameters of Cu^{2+} in CdSe nanocrystals requires

$$f_\gamma \approx 0.47, \quad \theta \approx 55.40^\circ, \quad \kappa \approx 0.61 \qquad (8)$$

The MO coefficients from the above f_γ and the parameters in Eq. (2) based on the MO coefficients are given in Tables 1 and 2, respectively. The calculated spin-Hamiltonian parameters are compared with the experimental values in Table 3.

Table 1
Molecular orbital coefficients of the Cu^{2+} tetrahedral cluster in CdSe: Cu^{2+} nanocrystals.

Nt	Ne	$\lambda\pi$	$\lambda\sigma$
0.8336	0.8304	−0.3924	0.5585

Table 2
The spin–orbit parameters, orbit reduction factors and dipolar hyperfine structure constants of the Cu^{2+} tetrahedral clusters in CdSe: Cu^{2+} nanocrystals.

ξ (cm^{-1})	ξ' (cm^{-1})	k	k'	$P(10^{-4}$ cm$^{-1})$	$P'(10^{-4}$ cm$^{-1})$
130	484	0.4074	0.6249	270	269

Table 3
Spin-Hamiltonian parameters for Cu^{2+} ion in CdSe nanocrystals.

	$g_{//}$	$g_\perp$	$A_{//}$ (10^{-4} cm^{-1})	$A_\perp$ (10^{-4} cm^{-1})
Calc. [a]	2.322	2.053	−227	−77
Calc. [b]	2.320	2.056	−234	−52
Expt. [3]	2.321(6)	2.053(6)	225(18)[c]	63(18)[c]

[a] Calculated with the defect model of Cu^{2+} on the substitutional tetrahedral site in this work.
[b] Calculated with the defect model of Cu^{2+} on the interstitial octahedral site in Ref. [5].
[c] The absolute value, see the text.

3. Discussion

The signs of hyperfine structure constants A_i for d^n and f^n ions in crystals are difficult to be determined solely by EPR experiments [15,22,28], so the constants A_i obtained in EPR experiments for these ions in crystals are practically the absolute values although they (containing those of Cu^{2+} in CdSe nanocrystals considered) are often written as positive. Our calculations, similar to those calculated with the defect model of tetragonally-elongated Cu^{2+} octahedron in Ref. [5] (see Table 3), suggest that $A_{//}$ and $A_\perp$ are negative for Cu^{2+} in CdSe nanocrystals. Negative signs of hyperfine structure constants for Cu^{2+} clusters were suggested for many systems [15].

From investigations of hyperfine structure constants for Cu^{2+} in many crystals, one can find the core polarization constant $\kappa \approx 0.2$–0.8 [25,29–33]. Our value of $\kappa \approx 0.61$ obtained for CdSe: Cu^{2+} nanocrystals is in this range and can be regarded as reasonable.

For a tetragonal tetrahedron, when the angle $\theta > \theta_0 (\approx 54.74°$, the same angle in cubic tetrahedron), the tetrahedron is compressed, whereas if $\theta < \theta_0$, it is elongated. The angle θ ($\approx 55.40°$) $> \theta_0$ obtained for Cu^{2+} in CdSe nanocrystals suggests that the Cu^{2+} tetrahedron in CdSe is, as mentioned above, tetragonally-compressed. So, the angle θ seems to be suitable.

Table 3 shows that by using the above defect model, the calculated spin-Hamiltonian parameters $g_{//}$, $g_\perp$, $A_{//}$ and $A_\perp$ from the high-order perturbation formulas based on the cluster approach with the suitable parameters are in reasonable agreement with the observed values. This suggests that the defect model of Cu^{2+} substituted at the tetrahedral site in CdSe nanocrystals seems to be possible.

However, since the calculated spin-Hamiltonian parameters with the defect model of Cu^{2+} at the interstitial octahedral site suggested in Ref. [5] are also in agreement with the experimental values (see Table 3), it is difficult to determine the defect model of Cu^{2+} center in CdSe nanocrystals by only analyzing the EPR data. The cubic field parameters Dq for Cu^{2+} tetrahedral clusters in II–VI semiconductors [26,34] are about half of those for Cu^{2+} octahedral clusters in crystals. For example, the Dq for $(CuO_4)^{6-}$ tetrahedron in ZnO is about 572 cm^{-1} [34], and those for $(CuO_6)^{10-}$ octahedral clusters in crystals are about 1000–1250 cm^{-1} [25,35]. So, the absorption bands of Cu^{2+} tetrahedral clusters in crystals should be below 8000 cm^{-1} [26,34], whereas those of Cu^{2+} octahedral clusters in crystals may be in the range

8000–17,000 cm^{-1} [25,35,36]. Thus, the absorption spectrum is a useful tool to determine the defect model of Cu^{2+} (at the substitutional tetrahedral site or at the interstitial octahedral site) in CdSe and other II–VI semiconductors. For example, for Cu^{2+} in similar ZnSe nanocrystals, three absorption bands at about 8345, 12,192 and 14,573 cm^{-1} were found in the absorption spectra from 7500 to 22,000 cm^{-1} [36]. This allows us to conclude that Cu^{2+} ion is on the interstitial octahedral site in ZnSe nanocrystals [36]. However, for Cu^{2+} in CdSe nanocrystals, only the absorption spectra from 14,500 to 20,000 cm^{-1} were measured in which no absorption bands were found [3]. So the defect model of the studied Cu^{2+} center in CdSe nanocrystals should be further studied by experimental determination of the absorption spectrum in the range 4000–14,500 cm^{-1}.

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