EPR Parameters and Local Atom-position Parameters for Co^{2+} Ions in CdS and CdSe Semiconductors

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The EPR parameters (zero-field splitting D and g factors $g_\parallel$, $g_\perp$) of Co^{2+} ions in CdS and CdSe semiconductors are calculated from the high-order perturbation formulas based on the cluster approach for a $3d^7$ ion in trigonal symmetry. These formulas include the contribution to the EPR parameters from both the spin-orbit coupling parameter of the $3d^7$ ion and that of the ligand. From the calculations, the local atom-position parameters u (which are different from the corresponding values in the host crystals) for the Co^{2+} impurity centers in both semiconductors are estimated. The results are discussed.

Key words: Electron Paramagnetic Resonance; Local Atom-Position Parameter; Crystal- and Ligand- Field Theory; Co^{2+}; CdS; CdSe.

1. Introduction

Transition medal impurities strongly influence the optical, electric and magnetic properties of semiconductor devices [1, 2]. Therefore it is important to get information about the local structure of these impurity centers in semiconductors. As is known, the EPR parameters (zero-field splitting and g factors) of a paramagnetic impurity in crystals are sensitive to its immediate environment. Therefore one can obtain useful information on the local or defect structures of transition metal impurity centers in semiconductors. The zero-field splitting D and g factors $g_\parallel$, $g_\perp$ of Co^{2+} in CdS and CdSe crystals were reported [3, 4], however the defect structures of these Co^{2+} impurity centers in both crystals have not been estimated by analyzing these EPR parameters. Co^{2+} ions in CdS and CdSe replace the Cd^{2+} ions and occupy the trigonal symmetry sites [3, 4]. The trigonal distortion of the tetrahedral MX_4 clusters in the wurtzite structure is sensitive to the atom-position parameter u. Since the nature and size of the Co^{2+} impurity are unlike those of the replaced Cd^{2+} ion, the local trigonal distortion and hence the local atom-position parameter u_{loc} may be different from the corresponding values in the host or pure crystals. In this paper, we study the local atom-position parameters u_{loc} and hence the local structures for Co^{2+} in CdS and CdSe semiconductors by calculating their EPR parameters. The results are discussed.

2. Calculation

For $3d^n$ ions in semiconductors, such as Co^{2+} in CdS, and CdSe, the conventional one spin-orbit (SO) parameter model (where only the contribution of the SO coupling parameter ζ_d of the central $3d^n$ ion is included) based on the classical crystal-field theory is not suitable, because of the strong covalence of these semiconductors, and the admixture of the SO coupling parameters between the d electrons of the $3d^n$ ion and the p electrons of the ligands via the covalence effects should be considered [5, 6]. Therefore, a two-SO-parameter model (where the contributions of both the SO coupling parameter of $3d^n$ ion and that of the ligand are included) based on the cluster approach must be used here [6–8]. According to this model, the one-electron basis functions of a $3d^n$ MX_4 cluster can be expressed as

$$\Psi_t = N_t(|d_t\rangle + \lambda_\sigma|\sigma_t\rangle + \lambda_\pi|\pi_t\rangle),$$
$$\Psi_e = N_e(|d_e\rangle + \sqrt{3}\lambda_\pi|\pi_e\rangle), \tag{1}$$

where the subscript e or t stands for the irreducible representation of the T_d group. $|d_e\rangle$ and $|d_t\rangle$ are the d orbitals of the 3d^n ion. $|\pi_e\rangle$, $|\pi_t\rangle$ and $|\sigma_t\rangle$ are the p orbitals of the ligands. N_t and N_e are the normalization coefficients, and λ_σ and λ_π are the orbital mixing coefficients.

From these basis functions and Macfarlane's perturbation-loop method [9, 10], the high-order perturbation formulas of the EPR parameters D, $g_\parallel$ and $g_\perp$, based on the cluster approach for the 3d^7 ion in a trigonal MX$_4$ cluster can be derived as

$$D = 2\zeta'^2(1/E_1^2 - 1/E_2^2)v/9 - \sqrt{2}v'\zeta\zeta'\left[2/(3E_1E_4) + 1/(E_2E_3) + 1/(3E_3E_4) + 1/(E_2E_4) + \sqrt{2}B_4/(E_1E_4E_5)\right]$$
$$- \sqrt{2}v'B_4\zeta'^2\left[4/(E_3E_4E_5) + 9/(E_2^2E_3)\right], \tag{2}$$

$$g_\parallel = g_s + 8k'\zeta'/(3E_1) - 2\zeta'(2k'\zeta - k\zeta' + 2g_s\zeta')/(9E_1^2) + 4\zeta'^2(k - 2g_s)/(9E_3^2) - 2\zeta^2(k + g_s)/(3E_2^2)$$
$$+ 4k'\zeta\zeta\left[1/(9E_1E_3) - 1/(3E_1E_2) + 1/(3E_2E_3)\right] - 8k'\zeta'v/(9E_1^2) + 4\sqrt{2}v'(k'\zeta + k\zeta')/(eE_1E_4), \tag{3}$$

$$g_\perp = g_\parallel + 4k'\zeta'v/(3E_1^2) - 4\sqrt{2}v'(k'\zeta + 2k\zeta')/(3E_1E_4),$$

where E_1, E_2, E_3, E_4 and E_5 are the zero-order energy separations between the ground state $^4A_2(t_2^3e^4)$ and the excited states $^4T_2$ $(t_2^4e^3)$, $^2T_{2a}(t_2^3e^4)$, $^2T_{2b}(t_2^4e^3)$, $^4T_{1a}$ $(t_2^3e^4)$ and $^4T_{1b}$ $(t_2^4e^3)$, respectively. g_s ($\approx$ 2.0023) is the free-ion value. $B_4 = N_t^3N_eB_0$ [B_0 (and C_0) are the Racah parameters of a free 3d^7 ion]. v and v' are the trigonal field parameters. The SO coupling parameters ζ, ζ' and the orbital reduction factors k, k' are

$$\zeta = (N_t)^2\left\{\zeta_d^0 + \left[\sqrt{2}\lambda_\pi\lambda_\sigma - (\lambda_\pi)^2/2\right]\zeta_p^0\right\},$$
$$\zeta' = N_t \cdot N_e\left\{\zeta_d^0 + \left[\lambda_\pi\lambda_\sigma/\sqrt{2} + (\lambda_\pi)^2/2\right]\zeta_p^0\right\},$$
$$k = (N_t)^2\left[1 - (\lambda_\pi)^2/2 + \sqrt{2}\lambda_\pi\lambda_\sigma + 2\lambda_\sigma S_{dp}(\sigma)\right.$$
$$\left. + 2\lambda_\pi S_{dp}(\pi)\right], \tag{4}$$
$$k' = N_t \cdot N_e\left[1 + (\lambda_\pi)^2/2 + \lambda_\pi\lambda_\sigma/\sqrt{2}\right.$$
$$\left. + 4\lambda_\pi S_{dp}(\pi) + \lambda_\sigma S_{dp}(\sigma)\right],$$

where ζ_d^0 and ζ_p^0 are, respectively, the SO coupling parameter of the 3d^7 ion and that of the ligands in free state. $S_{dp}(\pi) = \langle d_t|\pi_t\rangle = \langle d_e|\pi_e\rangle/\sqrt{3}$ and $S_{dp}(\sigma) = \langle d_t|\sigma_t\rangle$ are the group overlap integrals. From the Slater-type SCF functions [11, 12] and the average metal-ligand distances in CdS and CdSe [13], we calculate $S_{dp}(\pi) \approx 0.0054$ and $S_{dp}(\sigma) \approx -0.0226$ for CdS: Co^{2+} and $S_{dp}(\pi) \approx 0.0053$ and $S_{dp}(\sigma) \approx -0.0230$ for CdSe: Co^{2+}.

According to the one-electron basis functions, we have the normalization relationships

$$N_t = \left[1 + (\lambda_\sigma)^2 + (\lambda_\pi)^2 + 2\lambda_\sigma S_{dp}(\sigma) + 2\lambda_\pi S_{dp}(\pi)\right]^{-\frac{1}{2}},$$
$$N_e = \left[1 + 3(\lambda_\sigma)^2 + 6\lambda_\pi S_{dp}(\pi)\right]^{-\frac{1}{2}}. \tag{5}$$

The parameters N_t and N_e can be obtained by analyzing the optical spectra of the studied system. For 3d^n ions in II-VI and III-V semiconductors, the conventional B, C and Δ crystal-field scheme is not suitable for the analysis of d-d transition optical spectra because of the strong covalence [5, 14, 15], and so a modified N_t, N_e and Δ_{eff} scheme [6–8] should be used here. Thus, according to the optical spectra of CdS: Co^{2+} [16, 17] and CdSe: Co^{2+} [17, 18] and the Racah parameters $B_0 \approx 1115$ cm^{-1} and $C_0 \approx 4366$ cm^{-1} of free Co^{2+} ion [19], we obtain for CdS: Co^{2+}

$$N_t \approx 0.884, \; N_e \approx 0.923, \; \Delta_{eff} \approx 3600 \text{ cm}^{-1}, \tag{6}$$

and for CdSe: Co^{2+}

$$N_t \approx 0.886, \; N_e \approx 0.925, \; \Delta_{eff} \approx 3300 \text{ cm}^{-1}. \tag{7}$$

Substituting the parameters $S_{dp}(\pi)$, $S_{dp}(\sigma)$, N_t and N_e into (5), we obtain for CdS: Co^{2+}, $\lambda_\pi \approx -0.246159$, $\lambda_\sigma \approx 0.494021$, and for CdSe: Co^{2+}, $\lambda_\pi \approx -0.24252$, $\lambda_\sigma \approx 0.490093$. Thus, from the above parameters and the free-ion values of ζ_d^0 (Co^{2+}) ≈ 533 cm^{-1} [19], ζ_p^0 (S^{2-}) ≈ 365 cm^{-1} and $\zeta_p^0(Se^{2-}) \approx 1659$ cm^{-1} [20], the SO coupling parameters and the orbital reduction factors in (4) for Co^{2+} in both crystals can be calculated easily.

The trigonal field parameters in the superposition model [21]

$$v = 3/7\bar{A}_2(R_0)\left[2(R_0/R_1)^{t2}\right.$$
$$+ 3(3\cos^2\theta - 1)(R_0/R_2)^{t2}\right]$$
$$+ 20/63\bar{A}_4(R_0)\left[8(R_0/R_1)^{t4}\right.$$
$$+ 3(35\cos^4\theta - 30\cos^2\theta - 1)(R_0/R_2)^{t4}\right]$$
$$+ 20\sqrt{2}/3\bar{A}_4(R_0)\sin^3\theta\cos\theta(R_0/R_2)^{t4},$$

$$v' = -\sqrt{2}/7\bar{A}_2(R_0)\big[2(R_0/R_1)^{t_2}$$
$$+ 3(3\cos^2\theta - 1)(R_0/R_2)^{t_2}\big]$$
$$+ 5\sqrt{2}/63\bar{A}_4(R_0)\big[8(R_0/R_1)^{t_4} \qquad (8)$$
$$+ 3(35\cos^4\theta - 30\cos^2\theta + 3)(R_0/R_2)^{t_4}\big]$$
$$+ 10/3\bar{A}_4(R_0)\sin^3\theta\cos\theta(R_0/R_2)^{t_4},$$

where t_2 and t_4 are the power-law exponents. For the 3d^n ions in many crystals we take $t_2 \approx 3$ and $t_4 \approx 5$ [8, 22, 23]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference distance $R_0 \approx \bar{R} \approx (R_1 + 3R_2)/4$. For 3d^n MX$_4$ clusters, $\bar{A}_4(R_0) = 27D_q/16$ [8, 21, 23]. The ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 9 \sim 12$ [8, 22–24] is obtained for 3d^n ions in many crystals. We take the average value $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 10.5$ here. R_1 is the bonding length along C_3 axis, and θ is the angle between the directions of R_1 and R_2. The structural parameters R_1, R_2 and θ in wurtzite structure can be calculated from the lattice constants a, c and the atom-position parameter u (note: the trigonal distortion of the MX$_4$ cluster is sensitive to the parameter u). For CdS [3], $a \approx 4.137$ Å, $c \approx 6.7144$ Å, $u \approx 0.378$, and for CdSe [13], $a \approx 4.30$ Å, $c \approx 7.0133$ Å, $u \approx 0.377$. Applying the structure data of the host crystals to the above formulas, the EPR parameters of CdS: Co^{2+} and CdSe: Co^{2+} have been calculated. The calculated zero-field splittings D agree poorly in sign and magnitude with the observed values (see Table 1), suggesting that the local structural parameters in the vicinity of the Co^{2+} ions in CdS and CdSe are unlike the corresponding structural parameters in the pure host crystals. Since the zero-field splitting D is very sensitive to the trigonal distortion of impurity centers and hence to the local atom-position parameter u_{loc}, we mainly study the change of the atom-position parameter u caused by the impurity (i.e., the local parameter u_{loc}) for Co^{2+} in both crystals. By fitting the calculated EPR parameters (in particular, the zero-fields splitting D) to the observed values, we obtain for CdS: Co^{2+}

$$u_{\text{loc}} \approx 0.3747, \qquad (9)$$

and for CdSe: Co^{2+}

$$u_{\text{loc}} \approx 0.3741. \qquad (10)$$

The comparisons between the calculated and experimental EPR parameters are shown in Table 1.

Table 1. EPR parameters (zero-field splitting and g factors) for Co^{2+} in CdS and CdSe semiconductors.

	CdS: Co^{2+}			CdSe: Co^{2+}		
	Cal.[a]	Cal.[b]	Expt. [3]	Cal.[a]	Cal.[b]	Expt. [4]
D (cm^{-1})	−1.2255	0.6637	0.66(2)	−0.7981	0.4827	0.475(10)
$g_\parallel$	2.2691	2.2580	2.269	2.2655	2.2552	2.295(10)
$g_\perp$	2.2593	2.2648	2.286	2.2558	2.2612	2.294(20)

[a] calculated by using the atom-position parameter u in the pure crystal. [b] calculated by using the local atom-position parameter u_{oc} in the impurity center.

3. Discussion

From Table 1 it can be seen that by applying suitable local atom-position parameters u_{loc}, the calculated EPR parameters for CdS: Co^{2+} and CdSe: Co^{2+} are consistent with the observed values. The local parameter u_{loc}, differing from the host parameter u, suggests that the impurity ions Co^{2+} in CdS and CdSe do not occupy the exact Cd^{2+} sites, but are displaced by $\Delta R = (u - u_{\text{loc}})c \approx 0.022$ Å along the C_3 axis for CdS: Co^{2+}, and $\Delta R \approx 0.020$ Å for CdSe: Co^{2+}. Similar displacements of 3d^n impurities in wurtzite-type semiconductors have also been found for Ti^{2+} and V^{3+} in CdS [8] and Fe^{3+}, Mn^{2+} and Ni^{3+} in GaN [23]. So, the local atom-position parameters u_{loc}, and hence the displacements of Co^{2+} in CdS: Co^{2+} and CdSe: Co^{2+} crystals can be regarded as reasonable. Evidently the local structure of 3d^n impurity centers in crystals can be estimated by studying their EPR parameters.

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