Theoretical Explanation of the EPR Parameters of Tetragonal Ti^{3+} Centers in ZnSe and $CdS_{0.75}Se_{0.25}$ Semiconductors

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The electron paramagnetic resonance (EPR) parameters (g factors $g_{\|}$, $g_{\perp}$ and hyperfine structure constants $A_{\|}$, $A_{\perp}$) of the tetragonal Ti^{3+} centers in ZnSe and $CdS_{0.75}Se_{0.25}$ semiconductors are calculated from high-order perturbation formulas based on the cluster approach. In these formulas, both the contribution from the spin-orbit coupling parameters of the central $3d^n$ ion and that of ligands are considered. The calculated results show reasonable agreement with the observed values. The defect structures of the tetragonal Ti^{3+} centers in both semiconductors caused by the static Jahn-Teller effect are suggested.

Key words: Crystal- and Ligand-Field Theory; Electron Paramagnetic Resonance; Local Lattice Distortion; II-VI Semiconductors; Ti^{3+}.

1. Introduction

Transition metal ($3d^n$) impurities in II-VI and III-V semiconductors have attracted attention because of their technological importance. For example, V- or Ti-induced midgap donors in CdTe are assumed to be responsible for the photorefractive process [1, 2]. Fe, Ti, Cr or V in III-V compounds can lead to thermally stable semi-insulating materials which can be used in high-speed metal-semi-insulating-metal (MSIM) photodetectors [3, 4]. Thus, many spectroscopic studies of these compound semiconductors doped with $3d^n$ impurities have been made [5 – 11]. Among them, the EPR and optical spectra of Ti in ZnSe and $CdS_{0.75}Se_{0.25}$ were measured [10, 11]. From the measurements, a tetragonal Ti^{3+} center caused by a static Jahn-Teller effect was found in both crystals, and their EPR parameters (g factors $g_{\|}$, $g_{\perp}$ and hyperfine structure constants $A_{\|}$, $A_{\perp}$) were reported [10, 11]. Note: For $CdS_{0.75}Se_{0.25} : Ti^{3+}$, $A_{\|}$ and $A_{\perp}$ were not given. No satisfactory theoretical explanation has yet been given for the EPR parameters of the tetragonal Ti^{3+} centers in ZnSe and $CdS_{0.75}Se_{0.25}$. In this paper, we study these by high-order perturbation formulas based on the cluster approach for the EPR parameters of $3d^1$ ions in tetragonal tetrahedra.

2. Calculation

Ti^{3+} in ZnSe replaces Zn^{2+} ions and is surrounded by four Se^{2-} ions. For Ti^{3+} in $CdS_{0.75}Se_{0.25}$ from the cubic field parameters $Dq \approx 4385$, 4010(5), and 4302(10) cm^{-1} for Ti^{3+} in CdS, CdSe and $CdS_{0.75}Se_{0.25}$, respectively [11], we can assume reasonably that in the tetragonal Ti^{3+} center, Ti^{3+} substitutes for Cd^{2+} and is surrounded by four S^{2-} ions (this may be due to the number of S^{2-} being much larger than that of Se^{2-} [11]). In both systems, since the spin-orbit coupling parameters of the ligands Se^{2-} ($\zeta_p^0 \approx 1659$ cm^{-1} [12]) and S^{2-} ($\zeta_p^0 \approx 365$ cm^{-1} [12]) are larger than these ($\zeta_d^0 \approx 154$ cm^{-1} [13]) of the central metal ion Ti^{3+}, the contribution to EPR parameters from the spin-orbit coupling parameter of ligands via covalence effects cannot be neglected. Therefore, the perturbation formulas of EPR parameters based on the conventional crystal-field theory [13, 14] (in which only the contribution from the spin-orbit coupling parameter of central $3d^n$ ion is considered) cannot be applied here. Thus, high-order perturbation formulas of EPR parameters used in the above systems should be based on the cluster approach [15], where the contributions to EPR parameters from both spin-orbit coupling parameters ζ_d^0 and ζ_p^0 are included, and consequently the one-electron molecular orbitals (MO) of $3d^n$ clusters are given as linear combinations of the d orbitals of $3d^n$ ions and the p orbitals of ligands. For a $3d^n$ ion in MX_4 tetrahedral clusters, the one-electron basis functions can be expressed as [16]

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

in which the subscript t or e denotes the irreducible representation of the T_d group. $|d_\gamma>$(where $\gamma =$ t or e) stands for the d orbital of the $3d^n$ ion and $|\pi_t>$, $|\pi_e>$ and $|\sigma_t>$ denote the p orbitals of ligands. N_γ is the normalization coefficient and λ_β (where $\beta = \pi$ or σ) is the orbital mixing coefficient. These MO coefficients can be related by the normalization relationship

$$\begin{aligned} N_t &= [1 + (\lambda_\sigma)^2 + (\lambda_\pi)^2 + 2\lambda_\sigma S_{dp}(\sigma) \\ &\quad + 2\lambda_\pi S_{dp}(\pi)]^{-1/2}, \\ N_e &= [1 + 3(\lambda_\sigma)^2 + 6\lambda_\pi S_{dp}(\pi)]^{-1/2}, \end{aligned} \tag{2}$$

where $S_{dp}(\sigma) = \langle d_t|\sigma_t\rangle$ and $S_{dp}(\pi) = \langle d_t|\pi_t\rangle = \langle d_e|\pi_e\rangle/\sqrt{3}$ are the group overlap integrals.

From the values of g factors in both systems one can conclude that the ground state is $^2B_1$, and that the $3d^1$ MX_4 tetrahedron is elongated. By use of the perturbation method and the one-electron basis functions, the high-order perturbation formulas of EPR parameters based on the cluster approach for a tetragonal $3d^1$ MX_4 cluster can be deduced as

$$\begin{aligned} g_\parallel &= g_s - \frac{8k'\zeta'}{E_1} - \frac{k'\zeta'^2}{E_2^2} - \frac{4k'\zeta\zeta'}{E_1E_2} - \frac{g_s\zeta'^2}{E_2^2}, \\ g_\perp &= g_s - \frac{2k'\zeta'}{E_2} + \frac{k'\zeta\zeta'}{E_2^2} + \frac{2k\zeta'^2}{E_1E_2} - \frac{2k'\zeta\zeta'}{E_1E_2} \\ &\quad - \frac{2g_s\zeta'^2}{E_1^2} - \frac{g_s\zeta'^2}{2E_2^2}, \\ A_\parallel &= P\left(-\kappa - \frac{4}{7}\right) + P(g_\parallel - g_s) + \frac{3}{7}P'(g_\perp - g_s), \\ A_\perp &= P\left(\frac{2}{7} - \kappa\right) + P'(2k' - \frac{3}{7})(g_\perp - g_s), \end{aligned} \tag{3}$$

with

$$\begin{aligned} \zeta &= (N_t)^2\left\{\zeta_d^0 + \left[\sqrt{2}\lambda_\pi\lambda_\sigma - (\lambda_\pi)^2/2\right]\zeta_p^0\right\}, \\ \zeta' &= N_t \cdot N_e\left\{\zeta_d^0 + \left[\lambda_\pi\lambda_\sigma/\sqrt{2} + (\lambda_\pi)^2/2\right]\zeta_p^0\right\}, \\ k &= (N_t)^2\left[1 - (\lambda_\pi)^2/2 + \sqrt{2}\lambda_\pi\lambda_\sigma \right. \\ &\quad \left. + 2\lambda_\sigma S_{dp}(\sigma) + 2\lambda_\pi S_{dp}(\pi)\right], \\ k' &= N_t \cdot N_e\left[1 - (\lambda_\pi)^2/2 \right. \\ &\quad \left. + \lambda_\pi\lambda_\sigma/\sqrt{2} + 4\lambda_\pi S_{dp}(\pi) + \lambda_\sigma S_{dp}(\sigma)\right], \\ P &= N_t^2 P_0, \quad P' = N_t N_e P_0, \\ E_1 &= E(^2B_2) - E(^2B_1) = 10Dq, \\ E_2 &= E(^2E) - E(^2B_1) = 10Dq + 3Ds - 5Dt, \end{aligned} \tag{4}$$

in which $g_s(\approx 2.0023)$ is the free-electron value. P_0 is the dipolar hyperfine structure parameter of a free $3d^1$ ion. For the free Ti^{3+} we have $P_0 \approx -25.7 \cdot 10^{-4}$ cm^{-1} [17]. κ is the core polarization constant, which is often taken as an adjustable parameter. Ds and Dt are the tetragonal field parameters. From the superposition model [18], these parameters can be expressed as

$$\begin{aligned} Ds &\approx \frac{4}{7}\bar{A}_2(R_0)\left[3\cos^2\theta - 1\right], \\ Dt &\approx \frac{4}{21}\bar{A}_4(R_0)\left[7(1 - \cos^2\theta)^2 \right. \\ &\quad \left. + (35\cos^4\theta - 30\cos^2\theta + 3)\right], \end{aligned} \tag{5}$$

where $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters. For a $3d^n$ MX_4 cluster, $\bar{A}_4(R_0) = 27/16Dq$ [15, 18]. $\bar{A}_2(R_0) \approx (9 \sim 12)\bar{A}_4(R_0)$ is obtained for $3d^n$ ions in many crystals [15, 19–21]. We take $\bar{A}_2(R_0) \approx 9\bar{A}_4(R_0)$ here. θ is the angle between the direction of metal-ligand distance and the C_4 axis, which is not equal to the angle θ_0 ($\approx 54.74°$), the value of the cubic tetrahedron, because of the static Jahn-Teller effect.

Now we apply the above formulas and parameters to calculate the EPR parameters of the tetragonal $[TiSe_4]^{5-}$ cluster in ZnSe. The group overlap integral $S_{dp}(\beta)$ depends upon the impurity-ligand distance R_0 in the doped crystal. Since the size and/or charge of the impurity ion are unlike those of the replaced host ion, the distance R_0 may be different from the corresponding cation-anion distance R_H in the host crystal. We can reasonably estimate the distance R_0 from the empirical formula $R_0 \approx R_H + \frac{1}{2}(r_i - r_h)$ [22, 23], where

Table 1. The group overlap integrals, spin-orbit coupling coefficients, orbital reduction factors and dipolar hyperfine structure parameters of Ti^{3+}centers in ZnSe and $CdS_{0.75}Se_{0.25}$ crystals.

	$S_{dp}(\pi)$	$S_{dp}(\sigma)$	ζ (cm^{-1})	ζ' (cm^{-1})	k	k'	P (10^{-4} cm^{-1})	P' (10^{-4} cm^{-1})
ZnSe : Ti^{3+}	0.0254	−0.0878	−11.9	85.6	0.7015	0.8311	−22.2	−23.4
$CdS_{0.75}Se_{0.25}$: Ti^{3+}	0.0281	−0.0915	66.1	109.9	0.5300	0.7231	−19.7	−21.6

Table 2. The EPR parameters of the tetragonal Ti^{3+} centers in ZnSe and $CdS_{0.75}Se_{0.25}$ crystals.

	$g_\parallel$		$g_\perp$		$A_\parallel$ (10^{-4} cm^{-1})		$A_\perp$ (10^{-4} cm^{-1})	
	Cal.	Expt.	Cal.	Expt.	Cal.	Expt.	Cal.	Expt.
ZnSe : Ti^{3+}	1.8804	1.8889(5) [10]	1.9710	1.9620(5) [10]	27	23.0(5) [10]	6	9 [10]
$CdS_{0.75}Se_{0.25}$: Ti^{3+}	1.8521	1.86 [11]	1.9628	1.95 [11]	25		5	

r_i and r_h are the ionic radius of the impurity and that of the replaced host ion, respectively. For ZnSe : Ti^{3+}, $\bar{R}_H \approx 2.454$ Å [24], $r_i \approx 0.76$ Å, $r_h \approx 0.74$ Å [25], thus we have $R_0 \approx 2.555$ Å. The integral $S_{dp}(\beta)$ can be calculated from the Slater-type SCF functions [26, 27] and the distance R_0. The results are shown in Table 1. According to the suggestion in [16], the orbital mixing coefficient λ_β can be taken as proportional to the negative of the corresponding integral $S_{dp}(\beta)$, i. e.,

$$\lambda_\pi \approx -k_0 S_{dp}(\pi), \quad \lambda_\sigma \approx -k_0 S_{dp}(\sigma), \tag{6}$$

in which k_0 is an adjustable parameter. Thus, there are three adjustable parameters θ, k_0 and κ in the above formulas. By fitting the calculated EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ to the observed values, we obtain for ZnSe : Ti^{3+}:

$$\theta \approx 54.71^\circ, \quad k_0 \approx 5.39, \quad \kappa \approx 0.5. \tag{7}$$

The calculated EPR parameters are compared with the observed values in Table 2. The spin-orbit coupling parameters ζ, ζ', the orbital reduction factors k, k' and the dipolar hyperfine constants P, P' in ZnSe : Ti^{3+}, obtained by the above formulas, are collected in Table 1.

For the $[TiS_4]^{5-}$ cluster in the $CdS_{0.75}Se_{0.25}$ mixed crystal, $\bar{R}_H \approx 2.528$ Å [24] and $r_h(Cd^{2+}) \approx 0.97$ Å [25], thus we have $R_0 \approx 2.423$ Å. The calculated values of $S_{dp}(\pi)$ and $S_{dp}(\sigma)$ from similar method are shown in Table 1. Similarly, by fitting the calculated g factors $g_\parallel$, $g_\perp$ to the observed values, we obtain for $CdS_{0.75}Se_{0.25}$: Ti^{3+}:

$$\theta \approx 54.71^\circ, \quad k_0 \approx 6.8. \tag{8}$$

The comparisons between the calculated g factors and the observed values are shown in Table 2 and the parameters used in the calculation are collected in Table 1.

No EPR parameters $A_\parallel$ and $A_\perp$ for the tetragonal $[TiS_4]^{5-}$ cluster in $CdS_{0.75}Se_{0.25}$ crystal were reported. If we assume $\kappa \approx 0.5$, as in the case of ZnSe : Ti^{3+}, the parameters $A_\parallel$ and $A_\perp$ can be calculated. They are also shown in Table 2.

3. Discussion

For the tetragonal $[TiS_4]^{5-}$ cluster in $CdS_{0.75}Se_{0.25}$, the above calculations suggest that the hyperfine structure constants $A_\parallel$ and $A_\perp$ may be close to those shown in Table 2, this point remains to be checked by further EPR experiment. The above calculations also show that by considering the tetragonal distortions of the impurity center caused by the static Jahn-Teller effect, the calculated EPR parameters from the high-order perturbation formulas based on the cluster approach for the tetragonal Ti^{3+} centers in ZnSe and $CdS_{0.75}Se_{0.25}$ crystals are close to the observed values (see Table 2). So, these perturbation formulas and the defect structures of impurity centers can be regard as reasonable.

There are small errors in the calculated EPR parameters. The causes may be as follows: (i) the vibrational contribution to the EPR parameters due to electron-phonon interaction is neglected [28, 29], and (ii) the contribution due to the dynamic Jahn-Teller effect is not taken into account. Considering these points, the EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for the tetragonal Ti^{3+} centers in both systems seem to be reasonably explained.

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