On the EPR Parameters of Divalent Cobalt in ZnX (X = S, Se, Te) and CdTe

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The electron paramagnetic resonance (EPR) parameters g and the hyperfine structure constants A of Co^{2+} in ZnX (X = S, Se, Te) and CdTe are studied, using the perturbation formulas of the EPR parameters for a $3d^7$ ion in tetrahedra based on two mechanism models. In these formulas, both the contributions from the conventional crystal-field (CF) mechanism and those from the charge-transfer (CT) mechanism are taken into account. According to the investigations, the sign of the g-shift Δg_{CT} from the CT mechanism is the same as Δg_{CF} from the CF mechanism, whereas the contributions to the A value from the CF and CT mechanisms have opposite signs. Particularly, the contributions to the EPR parameters from the CT mechanism increase rapidly with increase of the spin-orbit coupling coefficient of the ligand and the covalency effect of the systems, i. e. $S^{2-} < Se^{2-} < Te^{2-}$.

Key words: Crystal-fields and Spin Hamiltonians; EPR; Co^{2+}; ZnX (X = S, Se, Te); CdTe.

1. Introduction

The II-VI semiconductors ZnX (X = S, Se, Te) and CdTe have attracted attention due to their magneto-optical, electronic, optical and laser properties as pure and transition-metal (TM) doped materials [1 – 6]. Usually, the TM impurity ions play an important role in the above properties. For example, optical and electron paramagnetic resonance (EPR) investigations have been carried out on these systems doped with Co^{2+} ($3d^7$) [7, 8]. The EPR g factors and the hyperfine structure constants of the cubic Co^{2+} centers have also been measured [8].

In theoretical investigations on the g factors, the two-spin-orbit (S. O.)-coupling coefficient model of the g factor for a $3d^7$ ion in tetrahedra may be adopted, because (i) the S. O. coupling coefficients of the ligands (particularly, Se^{2-} and Te^{2-}) are much larger than that of the central ion, and (ii) the covalency of these systems is significant, and so the contributions of p orbitals of the ligands should be taken into account [9, 10]. In the studies of d-d transitions of these systems, due to the different modifications of the e and t_2 orbitals (characterized by the factors N_t and N_e) and the contributions of the Racah parameter A (characterized by the effective cubic field parameter Δ_{eff}) [11 – 13], the "N_t, N_e and Δ_{eff}" scheme can be applied.

In the above two-S. O.-coupling-coefficient model, however, only the crystal-field (CF) mechanism related to the anti-bonding orbitals is included. In fact, another mechanism, i.e. the charge-transfer (CT) mechanism, related to the bonding (and non-bonding) orbitals, can also influence the EPR parameters of the ground state, as mentioned in [14, 15]. Most importantly, since the energies of the CT bands lower with increasing covalence and hence with increasing atomic number of the ligand ion in the same group of the periodic table [16], the contributions of the CT mechanism to the EPR parameters should be considered, especially for $3d^n$ ions in strong covalence crystals (e.g., II-VI semiconductors). In this paper, the complete perturbation formulas of the EPR parameters, based on the two mechanism model are established, where both the CF and CT contributions are taken into account. Based on this model, the g factors and the hyperfine structure constants for Co^{2+} ions in ZnX (X = S, Se, Te) and CdTe are investigated.

2. Calculations

For $3d^n$ ions in cubic tetrahedral clusters, the perturbation Hamiltonian containing the CF and CT mechanisms may be expressed as

$$\begin{aligned} H' = {} & H_b + H_{SO}^{CF} + H_{Ze}^{CF} + H_{hf}^{CF} + H_{SO}^{CT} \\ & + H_{Ze}^{CT} + H_{hf}^{CT}, \end{aligned} \tag{1}$$

where H_b, H_{SO}, H_{Ze} and H_{hf} are, respectively, the off-diagonal terms of the electrostatic Coulombic interaction, the S. O. coupling, the Zeeman term and the hyperfine interactions. The superscripts CF and CT denote the related terms in the CF and CT mechanisms, with the corresponding S. O. coupling coefficients ζ_{CF}, ζ'_{CF} and ζ_{CT}, ζ'_{CT}, the orbital reduction factors k_{CF}, k'_{CF} and k_{CT}, k'_{CT} and the dipole hyperfine structure parameters P_{CF}, P'_{CF} and P_{CT}, P'_{CT}.

Considering the contributions of the CT bands to the EPR parameters, one can write the many- electron wave-functions of the CT configurations in terms of seven-electron wave-functions out of t_2^a, t_2^b and e^n, where the superscripts a, b and n denote the anti-bonding orbitals (corresponding to the CF mechanism), bonding orbitals (corresponding to the CT mechanism) and non-bonding orbitals, respectively. So, the ground state $^4A_2$ can be written as

$$\begin{aligned} |^4A_2 \tfrac{3}{2} a_2\rangle = {} & [\theta^+\theta^-\varepsilon^+\varepsilon^-\xi^+\eta^+\zeta^+ \\ & |\xi^+\xi^-\eta^+\eta^-\zeta^+\zeta^-]. \end{aligned} \tag{2}$$

In the above square bracket, the letters on the left column are e^n and t_2^a orbitals and those on the right column are t_2^b orbitals. Since only one excited configuration $(e^n)^4(t_2^a)^4(t_2^b)^5$ (or $^4T_2^n$) has non-zero S. O. coupling interaction with the ground $^4A_2$ state, the ζ-component of the $^4T_2^n$ state with $M_S = 3/2$ can be given as

$$\begin{aligned} & |^4T_2^n \zeta\rangle = \\ & \{[\theta^+\theta^-\varepsilon^+\varepsilon^-\xi^+\eta^+\eta^-\zeta^+|\xi^+\xi^-\eta^+\eta^-\zeta^+] \\ & + [\theta^+\theta^-\varepsilon^+\varepsilon^-\xi^+\xi^-\eta^+\zeta^+|\xi^+\xi^-\eta^+\eta^-\zeta^+]\}/\sqrt{2}. \end{aligned} \tag{3}$$

According to the LCAO-MO (molecular orbital) model, the one-electron basic functions for the tetrahedral $3d^n$ clusters may be expressed as

$$\begin{aligned} \psi_t^x &= N_t^x(|d_t\rangle + \lambda_\sigma^x|\sigma_t\rangle + \lambda_\pi^x|\pi_t\rangle), \\ \psi_e^x &= N_e^x(|d_e\rangle + \sqrt{3}\lambda_\pi^x|\pi_e\rangle). \end{aligned} \tag{4}$$

Here the superscript x (= a or b) denotes the antibonding or bonding orbitals. $|d_e\rangle$ and $|d_t\rangle$ are the d orbitals of the $3d^n$ ion, and $|\pi_t\rangle$, $|\pi_e\rangle$ and $|\sigma_t\rangle$ are the p orbitals of the ligands. N_t^x and N_e^x are the normalization coefficients, and λ_σ and λ_π are the orbital mixing coefficients. From (4) we have the normalization relations

$$\begin{aligned} (N_t^x)^2[1 + (\lambda_\sigma^x)^2 + (\lambda_\pi^x)^2 + 2\lambda_\sigma^x S_\sigma + 2\lambda_\pi^x S_\pi] = 1, \\ (N_e^x)^2[1 + 3(\lambda_\pi^x)^2 + 6\lambda_\pi^x S_\pi] = 1, \end{aligned} \tag{5}$$

and the orthogonality relationships

$$\begin{aligned} \lambda_\pi^b &= -\frac{1 + 3\lambda_\pi^a S_\pi}{9(\lambda_\pi^a + S_\pi)}, \\ \lambda_\sigma^b &= -\frac{1 + \lambda_\pi^a\lambda_\pi^b + (\lambda_\pi^a + \lambda_\pi^b)S_\pi - \lambda_\sigma^a S_\sigma}{3(\lambda_\sigma^a + S_\sigma)}. \end{aligned} \tag{6}$$

Here S_π and S_σ are the group overlap integrals.

From Macfarlane's perturbation-loop method [17], by applying the perturbation Hamiltonian in (1) to the wave-function of the ground state $^4A_2$, the complete perturbation formulas of the g-shift and the hyperfine structure constant, including both the CF and CT mechanisms for a $3d^7$ ion in tetrahedra, can be derived, i. e.

$$\begin{aligned} \Delta g &= g - g_s = \Delta g_{CF} + \Delta g_{CT}, \\ \Delta g_{CF} &= 8k'_{CF}\zeta'_{CF}/(3E_1) \\ &\quad - 2\zeta'_{CF}(2k'_{CF}\zeta_{CF} - k_{CF}\zeta'_{CF} + 2g_s\zeta'_{CF})/(9E_1^2) \\ &\quad + 4\zeta'^2_{CF}(k_{CF} - 2g_s)/(9E_3^2) \\ &\quad - 2\zeta_{CF}^2(k_{CF} + g_s)/(3E_2^2) \\ &\quad + 4k'_{CF}\zeta_{CF}\zeta'_{CF} \\ &\quad \cdot [1/(9E_1E_3) - 1/(3E_1E_2) + 1/(3E_2E_3)], \\ \Delta g_{CT} &= 8k'_{CT}\zeta'_{CT}/(3E_n), \\ A &= A_{CF} + A_{CT}, \\ A_{CF} &= -P'_{CF}[8k'_{CF}\zeta'_{CF}/3E_1 + 2\zeta'_{CF}(2k'_{CF}\zeta_{CF} \\ &\quad - k_{CF}\zeta'_{CF} + 2g_S\zeta'_{CF})/9E_1^2 \\ &\quad - 4\zeta'^2_{CF}(k_{CF} - 2g_S)/9E_3^2 \\ &\quad + 2\zeta_{CF}^2(k_{CF} + g_s)/3E_2^2 \\ &\quad - 4k'_{CF}\zeta'_{CF}\zeta_{CF} \\ &\quad \cdot (1/9E_1E_3 - 1/3E_1E_2 + 1/3E_2E_3)] \\ &\quad - \kappa P_{CF}, \\ A_{CT} &= 8P'_{CT}k'_{CT}\zeta'_{CT}/(3E_n) + (\kappa/2)P_{CT}, \end{aligned} \tag{7}$$

where $g_s \approx 2.0023$ is the spin-only value. E_1, E_2, E_3 and E_n are, respectively, the energy differences between the CF excited states $^4T_2(t_2^4e^3)$, $^2T_{2a}$ $(t_2^3e^4)$ and $^2T_{2b}$ $(t_2^4e^3)$, the CT excited state $^4T_2^n$ and the ground state $^4A_2(t_2^3e^4)$. $B_4 = (N_t^a)^3\, N_e^a\, B_0$ (where B_0 and C_0 are the Racah parameters of the free $3d^7$ ion). The corresponding parameters in the CF mechanism are

$$\begin{aligned}
\zeta_{CF} &= (N_t^a)^2\{\zeta_d^0 + [\sqrt{2}\lambda_\pi^a\lambda_\sigma^a - (\lambda_\pi^a)^2/2]\zeta_p^0\},\\
\zeta'_{CF} &= N_t^a N_e^a\{\zeta_d^0 + [\lambda_\pi^a\lambda_\sigma^a/\sqrt{2} + (\lambda_\pi^a)^2/2]\zeta_p^0\},\\
k_{CF} &= (N_t^a)^2\{1 - (\lambda_\pi^a)^2/2 + \sqrt{2}\lambda_\pi^a\lambda_\sigma^a\\
&\qquad + 2\lambda_\sigma^a S_\sigma + 2\lambda_\pi^a S_\pi\},\\
k'_{CF} &= N_t^a N_e^a\{1 + (\lambda_\pi^a)^2/2 + \lambda_\pi^a\lambda_\sigma^a/\sqrt{2}\\
&\qquad + 4\lambda_\pi^a S_\pi + \lambda_\sigma^a S_\sigma\},\\
P_{CF} &= (N_t^a)^2 P_0,\\
P'_{CF} &= N_t^a N_e^a P_0,
\end{aligned} \tag{8}$$

and those in the CT mechanism are

$$\begin{aligned}
\zeta_{CT} &= N_t^b N_t^a\Big\{\zeta_d^0 + \Big[\frac{\lambda_\pi^a\lambda_\sigma^b + \lambda_\pi^b\lambda_\sigma^a}{\sqrt{2}} - \frac{\lambda_\pi^a\lambda_\pi^b}{2}\Big]\zeta_p^0\Big\},\\
\zeta'_{CT} &= N_e^b N_t^b\Big[\zeta_d^0 + \Big(\frac{\lambda_\pi^a\lambda_\sigma^b}{\sqrt{2}} + \frac{\lambda_\pi^a\lambda_\pi^b}{2}\Big)\zeta_p^0\Big],\\
k_{CT} &= N_t^a N_t^b\Big[-\frac{\lambda_\pi^a\lambda_\pi^b}{2} + \frac{\lambda_\pi^a\lambda_\sigma^b + \lambda_\pi^b\lambda_\sigma^a}{\sqrt{2}}\\
&\qquad + (\lambda_\sigma^a + \lambda_\sigma^b)S_\sigma + (\lambda_\pi^a + \lambda_\pi^b)S_\pi\Big],\\
k'_{CT} &= N_t^b N_e^a\Big[1 + \Big(\frac{\lambda_\pi^a\lambda_\pi^b}{2} + \frac{\lambda_\pi^a\lambda_\sigma^b}{\sqrt{2}}\Big)\\
&\qquad + 3\lambda_\pi^a S_\pi + \lambda_\pi^b S_\pi + \lambda_\sigma^b S_\sigma\Big],\\
P_{CT} &= N_t^b N_t^a P_0,\\
P'_{CT} &= N_e^a N_t^b P_0.
\end{aligned} \tag{9}$$

Here ζ_d^0 and ζ_p^0 are the S. O. coupling coefficients of the $3d^7$ ion and the ligand in free states, respectively. P_0 is the dipolar hyperfine structure parameter of the free $3d^7$ ion.

Now these formulas are utilized in studies of the EPR parameters for cubic Co^{2+} centers in ZnX and CdTe. When a Co^{2+} ion enters the lattice of the II-VI crystals, it will replace the host divalent cations and conserve the cubic symmetry, because no charge compensation is needed. Usually, the impurity-ligand distance R may differ from the host cation-anion distance R_H due to the difference in the ionic radii of the impurity and host ions. However, the distance R can be estimated from the empirical formula $R \approx R_H + (r_i - r_h)/2$ [18, 19]. Here, the radius of the impurity is $r_i(Co^{2+}) \approx 0.72$ Å [20], the radii of the host ions are $r_h(Zn^{2+}) \approx 0.74$ Å and $r_h(Cd^{2+}) \approx 0.97$ Å [20], and the distances R_H are 2.342, 2.454, 2.637 and 2.806 Å for ZnS, ZnSe, Zn Te and CdTe, respectively [21]. The distances R for these systems are shown in Table 1. Thus, the group overlap integrals S_π and S_σ are calculated from the R values and the Slater-type SCF wavefunctions [22, 23].

By fitting the optical spectra of the studied systems [7], the parameters N_t, N_e and Δ_{eff} are determined and collected in Table 1. Utilizing (7) and (8), as well as the free-ion values ζ_d^0 (≈ 533 cm^{-1} [24]) and P_0 ($\approx 254 \cdot 10^{-4}$ cm^{-1} [25]) of Co^{2+}, and ζ_p^0 (≈ 365, 1596 and 3384 cm^{-1} for S^{2-}, Se^{2-} and Te^{2-}, respectively [26]) of the ligands, the S. O. coupling coefficients, the orbital reduction factors and the dipole hyperfine structure parameters related to the CF and CT mechanisms are calculated and shown in Table 1.

The CT energy level E_n for the ligand to metal charge transfer (LMCT) can be obtained from the approximate relationship [16]

$$E_n \approx 30000[\chi(L) - \chi(M)]\ \text{cm}^{-1}, \tag{10}$$

where $\chi(L)$ and $\chi(M)$ are, respectively, the optical electronegativities of the ligand and metal ions. For the $(CoS_4)^{6-}$ cluster, $\chi(Co^{2+}) \approx 1.9$ and $\chi(S^{2-}) \approx 2.5$ [16], Thus we have $E_n \approx 18000$ cm^{-1}. The values of $\chi(Se^{2-})$ and $\chi(Te^{2-})$ were not reported. Considering that $\chi(L)$ in the same group of periodic table decreases with increasing atomic number of the ligand [e.g., $\chi(L)$ in VI group [16] is in the order $O^{2-}(3.2) > S^{2-}(2.5)$], one can approximately estimate $\chi(Se^{2-}) \approx 2.3$ and $\chi(Te^{2-}) \approx 2.1$. Thus, we have $E_n \approx 12000$ and 6000 cm^{-1} for ZnSe:Co^{2+} and ZnTe (or CdTe):Co^{2+}.

The core polarization constant in the formula of the A factor can be expressed as $\kappa \approx -2\xi/(3\langle r^{-3}\rangle)$, where ξ is characteristic of the density of unpaired spins at the nucleus of the central metal ion, and $\langle r^{-3}\rangle$ the expectation value of the inverse cube of the radial wavefunction of the 3d orbital [27] according to the values of $\langle r^{-3}\rangle$ (≈ 6.035 [27]) for Co^{2+} and ξ for Co^{2+} doped in ZnX and CdTe (note: the χ for ZnSe:Co^{2+} is taken as the average of those for ZnS:Co^{2+} and Zn Te:Co^{2+}).

Table 1. The effective cubic field parameter $\Delta_{\rm eff}$ (in $\rm cm^{-1}$), the normalization coefficients $N_{\rm t}^{\rm a}$ and $N_{\rm e}^{\rm a}$, the impurity-ligand distance R (in Å), the group overlap integrals, and the S. O. coupling coefficients (in $\rm cm^{-1}$), the orbital reduction factors and the dipole hyperfine structure parameters (in 10^{-4} $\rm cm^{-1}$) in the CF and CT mechanisms, as well as the core polarization constant κ for Co^{2+} in ZnX (X = S, Se, Te) and CdTe.

Hosts	$\Delta_{\rm eff}$	$N_{\rm t}^{\rm a}$	$N_{\rm e}^{\rm a}$	R	S_π	S_σ	$\zeta_{\rm CF}$	$\zeta'_{\rm CF}$	$\zeta_{\rm CT}$	$\zeta'_{\rm CT}$	$k_{\rm CF}$	$k'_{\rm CF}$	$k_{\rm CT}$	$k'_{\rm CT}$	$P_{\rm CF}$	$P'_{\rm CF}$	$P_{\rm CT}$	$P'_{\rm CT}$	κ
ZnS	4680	0.904	0.933	2.332	0.0098	0.0291	389	432	435	406	0.652	0.772	0.855	0.783	230	214	173	178	0.238
ZnSe	4420	0.897	0.927	2.444	0.0092	0.0287	234	368	686	507	0.653	0.765	0.841	0.762	228	211	168	174	0.230
ZnTe	4280	0.878	0.867	2.627	0.0084	0.0262	195	308	967	583	0.650	0.711	0.788	0.680	223	193	157	155	0.221
CdTe	4190	0.879	0.886	2.681	0.0074	0.0240	157	316	929	556	0.674	0.737	0.750	0.653	223	198	148	150	0.215

Table 2. The g-shifts and hyperfine structure constants A (in 10^{-4} $\rm cm^{-1}$) for Co^{2+} in ZnX (X = S, Se, Te) and CdTe.

Hosts	$\Delta g_{\rm CF}$	$\Delta g_{\rm CT}$	$\Delta g_{\rm CT}/\Delta g_{\rm CF}$	$\Delta g_{\rm tot}$	$\Delta g_{\rm expt}$ [8]	$A_{\rm CF}$	$A_{\rm CT}$	$A_{\rm CT}/A_{\rm CF}$	$A_{\rm tot}$	$A_{\rm expt}$ [8]
ZnS	0.1983	0.0472	0.24	0.2454	0.2457	−10.9	15.4	−1.41	4.5	1.8
ZnSe	0.1813	0.0858	0.47	0.2671	0.2677	−14.1	22.7	−1.61	8.6	
ZnTe	0.1290	0.1663	1.29	0.2953	0.2949	−26.3	44.8	−1.70	18.5	17.5
CdTe	0.1465	0.1614	1.10	0.3079	0.3070	−22.2	43.3	−1.95	21.1	24.3

This way the values of κ for various systems are obtained as shown in Table 1. Substituting the above values into (7), the EPR parameters for these Co^{2+} centers are obtained and given in Table 2. The results (i. e. $\Delta g_{\rm CF}$ and $A_{\rm CF}$) on neglecting the contributions from CT mechanism are also collected in Table 2.

3. Discussion

Table 2 shows that by considering both the CF and CT mechanisms the theoretical EPR parameters agree better with the observed values than those including only the conventional CF mechanism. This reveals that for systems with strong covalency and a large S. O. coupling coefficient of the ligands the two mechanism model containing both the CF and CT contributions should be adopted.

Based on these studies, the contributions $\Delta g_{\rm CT}$ from the CT mechanism have the same sign as $\Delta g_{\rm CF}$ from the CF mechanism. Moreover, the importance of the CT mechanism (which can be characterized by $\Delta g_{\rm CT}/\Delta g_{\rm CF}$) increases rapidly with the increase of the covalency (or decease of the denominator E_n) and the magnitude of $\zeta_{\rm p}^0$, i.e. $S^{2-} < Se^{2-} < Te^{2-}$. For Co^{2+} in Zn Te or CdTe, the magnitude of $\Delta g_{\rm CT}$ even exceeds that of $\Delta g_{\rm CF}$. So, for the ligands Se^{2-} and Te^{2-} the contributions to Δg due to the CT mechanism should be taken into account. As regards the hyperfine structure constant, the signs of $A_{\rm CF}$ and $A_{\rm CT}$ are opposite and the ratio $|A_{\rm CT}/A_{\rm CF}|$) is about $1.4 \sim 2.0$ for various systems, which is more significant than in case of the g factor. For the studied II-VI semiconductors, the covalency effect is strong and the mixture of the 3d orbitals of the central Co^{2+} with the np ($n = 3, 4, 5$) orbitals of the ligands as well as the CT contributions can be expected to be obvious. This would lead to a significant perturbation of the electronic states in the $[CoX_4]^{6-}$ tetrahedra and hence of the hyperfine structure constants, which are usually regarded as indication of covalency for TM ion complexes [28]. Thus, the large contribution $A_{\rm CT}$ to the hyperfine structure constant as well as the increase of the importance of $A_{\rm CT}$ with respect to $A_{\rm CF}$ can be understood.

In the above calculations the contributions arising from the s orbitals of the ligands are neglected, which may be explained the discrepancies between the calculated and experimental A values, particularly for ZnS:Co^{2+}. This neglect is supported by studies on some $3d^n$ ions in octahedral environments, where the contributions of the s orbitals of the ligands are believed to be very small [29, 30]. However, the above contributions may not be always negligible for the systems with strong covalency. This problem remains to be further investigated.

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