The Covalence Effect of the Electron States of ZnSe:Co^{2+}

Jia-Jun Chen[a], Mao-Lu Du[b], and Ti-Xian Zheng[a]

[a] Department of Physics and Electronic Information, China West Normal University,
Nanchong 637002, China
[b] Department of Physics, Southwest University for Nationalities, Chengdu 610041, China

Reprint requests to J.-J. C.; E-mail: chenjjnc@nc-public.sc.cninfo.net

Z. Naturforsch. **61a,** 357 – 363 (2006); received April 24, 2006

In the investigation of the optical and magnetic properties of 3d^N ion impurities in semiconductors, the contribution of the covalence must be considered. A modified d function (d*) and two covalent factors associated with the t$_2$ and e orbitals have been adopted for describing this covalence. We present the contribution of the covalent factors to the energy matrix of the d^{*7} electron and d^{*3} hole system. This suggests that the d^N electron system cannot be explained with the d^{10-N} hole system when the covalence is considered. The calculation of the energy levels by the d^{*7} energy matrix agrees with the experimental finding of ZnSe:Co^{2+}. – PACS numbers: 71.70.Ch, 71.55.Gs

Key words: Ligand-Fields; Covalence Effect; II-VI Semiconductors; Optical Spectra.

1. Introduction

Transition metal impurities in semiconductors have been the subject of many investigations, both experimental and theoretical. The optical and magnetic properties of cobalt ion impurities in II-VI and III-V semiconductor materials have been extensively studied [1 – 8]. The classical crystal-field theory has been extensively and successfully applied to the optical and magnetic properties of ionic compounds. The crystal-field theory describes d electrons in full d shell. When $N > 5$, the d^N electron system can be treated as a d^{10-N} hole system since the difference between the energy matrix elements of the $t_2^m e^n$ term of the d^N system $(n+m=N)$ and its complementary $t_2^{6-m}e^{4-n}$ term of the d^{10-N} system is the same. This simple relation has been widely used in the calculation of the energy levels of d^N ions $(N > 5)$ in crystals, such as crystal-field energy levels of Co^{2+}(d^7).

As the covalence in these semiconductors is strong, the classical crystal-field theory may be unsuitable to explain the optical and magnetic properties uniformly. There are quite a few works [2, 9 – 12] where two covalent factors, N_t and N_e, are introduced to describe the covalence. Because a semiconductor has a stronger covalence than an ionic crystal, it is necessary to consider a mixed orbital instead of a pure d orbital in calculating the energy levels. This requires the use of linear combination of atomic orbitals (LCAO) with a modified d function (d*). Because the t$_{2g}$ and e$_g$ orbitals do not have the same values, two covalent factors should be introduced. Thus the energy matrices of the d^{*N} system differ from those of the pure d^N system.

In this paper we present the energy matrices of the modified d^{*7} and d^{*3} systems for strongly covalent host materials. It is shown that the energy levels of the d^{*7} electron system are different from those of the d^{*3} hole system when the difference between the t$_{2g}$ and e$_g$ orbitals is taken into account. The energy matrix of the modified d^{*7} systems is applied to calculate the energy levels of Co^{2+} ions in a ZnSe semiconductor. The calculated energy levels agree with the experimental finding for Co^{2+} in ZnSe:Co^{2+}.

2. Energy Matrices

2.1. The Energy Matrix of the d^{*3} System

In a cubic crystal-field, the one-electron orbit is split into two parts transforming as the t$_{2g}$ and e$_g$ irreducible representation of the O_h (or T_d) point group. The t$_{2g}$ and e$_g$ wave functions may consist of mixed atomic functions. For covalent crystals we chose the modified d function (d*)

$$|\gamma\rangle = N_\gamma|d_\gamma\rangle + \lambda_\gamma|p_\gamma\rangle, \tag{1}$$

where $\gamma = t_{2g}$ or e_g is the irreducible representation of the cubic group, d and p are the central transition

Table 1. The crystal-field energy matrix for the $3d^{*3}$ electron system.

$^4T_1$	$t_2^2(^3T_1)e$	$t_2e^2(^3A_2)$			
$t_2^2(3T_1)e$	$A_1 - 5B_1 + 2A_2 + 2B_2 + 2Dq + 4\alpha$	$6B_3 - 4\alpha$			
$t_2e^2(3A_2)$		$A_4 - 8B_4 + 2A_2 - 4B_2 + 8Dq + 10\alpha$			
^2E	t_2^3	$t_2^2(^1A_1)e$	$t_2^2(^1E)e$	e^3	
t_2^3	$3A_1 - 6B_1 + 3C_1 - 12Dq + 18\alpha$	$-6\sqrt{2}B_3$	$3\sqrt{2}B_3 - 6\sqrt{2}\alpha$	0	
$t_2^2(^aA_1)e$		$A_1 + 10B_1 + 5C_1 + 2A_2 - 2B_2 + C_2 - 2Dq + 10\alpha$	$-10B_2 + 4\alpha$	$\sqrt{3}(2B_2 + C_2) - 4\sqrt{3}\alpha$	
$t_2^2(^1E)e$			$A_1 + B_1 + 2C_1 + 2A_2 - 2B_2 + C_2 - 2Dq + 16\alpha$	$-2\sqrt{3}B_2 - 4\sqrt{3}\alpha$	
e^3				$3A_4 - 8B_4 + 4C_4 + 18Dq + 18\alpha$	
$^2T_1$	t_2^3	$t_2^2(^3T_1)e$	$t_2^2(^1T_2)e$	$t_2e^2(^3A_2)$	$t_2e^2(^1E)$
t_2^3	$3A_1 - 6B_1 + 3C_1 - 12Dq + 18\alpha$	$3B_3 - 6\alpha$	$-3B_3 + 6\alpha$	0	$-2\sqrt{3}B_2 - 4\sqrt{3}\alpha$
$t_2^2(^3T_1)e$		$A_1 - 5B_1 + 2A_2 + 5B_2 + 3C_2 - 2Dq_+ 24\alpha$	$-3B_2 + 6\alpha$	$3B_3 + 2\alpha$	$-3\sqrt{3}B_2 + 2\sqrt{3}\alpha$
$t_2^2(^1T_2)e$			$A_1 + B_1 + 2C_1 + 2A_2 - 7B_2 + C_2 - 2Dq + 18\alpha$	$-3B_3 + 6\alpha$	$\sqrt{3}B_3 + 2\sqrt{3}\alpha$
$t_2e^2(^3A_2)$				$A_4 - 8B_4 + 2A_2 + 2B_2 + 3C_2 + 8Dq + 22\alpha$	$-2\sqrt{3}B_2 - 4\sqrt{3}\alpha$
$t_2e^2(^1E)$					$A_4 + 2C_4 + 2A_2 - 2B_2 + C_2 + 8Dq + 14\alpha$
$^2T_2$	t_2^3	$t_2^2(^3T_1)e$	$t_2^2(^1T_2)e$	$t_2e^2(^1A_1)$	$t_2e^2(^1E)$
t_2^3	$3A_1 + 5C_1 - 12Dq + 14\alpha$	$-3\sqrt{3}B_3 - 2\sqrt{3}\alpha$	$5\sqrt{3}B_3 - 2\sqrt{3}\alpha$	$4B_2 + 2C_2 - 8\alpha$	$2B_2 + 4\alpha$
$t_2^2(^3T_1)e$		$A_1 - 5B_1 + 2A_2 - B_2 + 3C_2 - 2Dq + 18\alpha$	$-3B_2 + 6\alpha$	$-3\sqrt{3}B_3 + 2\sqrt{3}\alpha$	$-3\sqrt{3}B_3 + 2\sqrt{3}\alpha$
$t_2^2(^1T_2)e$			$A_1 + B_1 + 2C_1 + 2A_2 + 3B_2 + C_2 - 2Dq + 14\alpha$	$\sqrt{3}B_3 + 2\sqrt{3}\alpha$	$-\sqrt{3}B_3 - 2\sqrt{3}\alpha$
$t_2e^2(^1A_1)$				$A_4 + 8B_4 + 4C_4 + 2A_2 - 2B_2 + C_2 + 8Dq + 14\alpha$	$10B_2 - 4\alpha$
$t_2e^2(^1E)$					$A_4 + 2C_4 + 2A_2 - 2B_2 + C_2 + 8Dq + 14\alpha$
(t_2^3)	$^4A_2 = 3A_1 - 15B_1 - 12Dq + 12\alpha$				
$t_2^2(^3T_1)e$	$^4T_2 = A_1 - 5B_1 + 2A_2 - 10B_2 - 2Dq + 12\alpha$				
$t_2^2(^1E)e$	$^2A_1 = A_1 + B_1 + 2C_1 + 2A_2 - 12B_2 + C_2 - 2Dq + 20\alpha$				
$t_2^2(^1E)e$	$^2A_2 = A_1 + B_1 + 2C_1 + 2A_2 + 8B_2 + C_2 - 2Dq + 12\alpha$				

metal d orbital and the valence electron orbital of the ligand ions, respectively. N_γ are the normalization coefficients, λ_t and λ_e are the orbital mixing coefficients. Since the electrostatic repulsion of two t_{2g} electrons is the same as that of two e_g electrons for the pure d orbital, we define the two covalent factors N_t and N_e (or orbital deformation factors) as the ratio between the electrostatic repulsion of two d^* electrons and two d electrons:

$$N_t^4 = \langle t_2t_2 \| t_2t_2 \rangle / \langle dd \| dd \rangle,$$

$$N_t^2 N_e^2 = \langle t_2e \| t_2e \rangle / \langle dd \| dd \rangle,$$

$$N_\mathrm{t}^3N_\mathrm{e} = \langle \mathrm{t_2t_2}\|\mathrm{t_2e}\rangle/\langle \mathrm{dd}\|\mathrm{dd}\rangle,$$
$$N_\mathrm{e}^4 = \langle \mathrm{ee}\|\mathrm{ee}\rangle/\langle \mathrm{dd}\|\mathrm{dd}\rangle. \qquad (2)$$

In this process, only the one-electron matrix elements of the two central metal ions are retained such as $\langle \mathrm{d}_\gamma\mathrm{d}_\gamma|\hat{H}|\mathrm{d}_\gamma\mathrm{d}_\gamma\rangle$ because the d-orbital is dominant. So these matrix elements, for instance $\langle \mathrm{d}_\gamma\mathrm{d}_\gamma|\hat{H}|\mathrm{p}_\gamma\mathrm{p}_\gamma\rangle$ and $\langle \mathrm{p}_\gamma\mathrm{p}_\gamma|\hat{H}|\mathrm{p}_\gamma\mathrm{p}_\gamma\rangle$, are neglected. Both effects of the change of the d orbital for the crystal and the contribution of the electrostatic repulsion of the ligand valence electrons are included in N_t and N_e. Using (2), the electrostatic repulsion, the crystal-field and the Tress correction term energy matrix of the d^{*3} electron system in the strong-field scheme can be obtained as in Table 1. From the table one can see that the Racah parameter A is important for calculating the electrons states when the covalence has been considered. This, however is neglected in the classical crystal-field theory. The contribution of the change of the crystal-field parameter Dq and the Tress correction term to the optical and magnetic properties is much smaller than that of the Racah parameters, so the differences from the change of Dq and the Tress term have been neglected as compared with the Racah parameters A, B and C. The relationship between the Racah parameters in the conventional crystal-field and those in the covalent crystal-field can be written as

$$\begin{aligned} &X_1 = N_\mathrm{t}^4X_0, \quad X_2 = N_\mathrm{e}^2N_\mathrm{t}^2X_0, \quad X_3 = N_\mathrm{e}N_\mathrm{t}^3X_0,\\ &X_4 = N_\mathrm{e}^4X_0, \quad X = A,B,C, \end{aligned} \qquad (3)$$

where A_0, B_0, C_0 denote the Racah parameters of the free ions.

2.2. The Energy Matrix of the d^{*7} System

In the t$_2$ and e electron shell, the t_2^6 and e^4 terms are closed-shell configurations. The $\mathrm{t}_2^m(m \geq 3)$ configuration can be considered as the t_2^{6-m} hole in the t_2^6 closed shell, the $\mathrm{e}^n(n \geq 2)$ configuration can be treated as an e^{4-n} hole configuration in the e^4 closed shell, since the same terms occur between t_2^{6-m} and t_2^m configurations and the e^{4-n} and e^n configurations. Then the $\mathrm{t}_2^{6-m}\mathrm{e}^{4-n}$ hole configuration can be considered as a complementary configuration of the $\mathrm{t}_2^m\mathrm{e}^n$ electron configuration in the $\mathrm{t}_2^6\mathrm{e}^4$ closed shell and has the same terms as the $\mathrm{t}_2^m\mathrm{e}^n$ configuration [13, 14]. We can obtain the following terms in the d^{*7} configuration from the d^{*3} configuration:

$$\begin{aligned} \mathrm{d}^{*3}:\ & \mathrm{t}_2^3(^4\mathrm{A}_2, {}^2\mathrm{E_a}, {}^2\mathrm{T_{1a}}, {}^2\mathrm{T_{2a}}),\\ & \mathrm{t}_2^2\mathrm{e}(^4\mathrm{T}_2, {}^2\mathrm{A}_1, {}^2\mathrm{A}_2, {}^4\mathrm{T_{1a}}, {}^2\mathrm{E_b}, {}^2\mathrm{E_c}, {}^3\mathrm{T_{1b}},\\ & \quad {}^3\mathrm{T_{1c}}, {}^2\mathrm{T_{2b}}, {}^2\mathrm{T_{2c}}),\\ & \mathrm{t_2e}^2(^4\mathrm{T_{1b}}, {}^2\mathrm{T_{1d}}, {}^2\mathrm{T_{1e}}, {}^2\mathrm{T_{2d}}, {}^2\mathrm{T_{2e}}),\\ & \mathrm{e}^3(^2\mathrm{E_d});\\ \mathrm{d}^{*7}:\ & \mathrm{t}_2^3\mathrm{e}^4(^4\mathrm{A}_2, {}^2\mathrm{E_a}, {}^2\mathrm{T_{1a}}, {}^2\mathrm{T_{2a}}),\\ & \mathrm{t}_2^4\mathrm{e}^3(^4\mathrm{T}_2, {}^2\mathrm{A}_1, {}^2\mathrm{A}_2, {}^4\mathrm{T_{1a}}, {}^2\mathrm{E_b}, {}^2\mathrm{E_c},\\ & \quad {}^3\mathrm{T_{1b}}, {}^3\mathrm{T_{1c}}, {}^2\mathrm{T_{2b}}, {}^2\mathrm{T_{2c}}),\\ & \mathrm{t}_2^5\mathrm{e}^2(^4\mathrm{T_{1b}}, {}^2\mathrm{T_{1d}}, {}^2\mathrm{T_{1e}}, {}^2\mathrm{T_{2d}}, {}^2\mathrm{T_{2e}}),\\ & \mathrm{t}_2^6\mathrm{e}^1(^2\mathrm{E_d}). \end{aligned}$$

According to the work by Griffith [15] and Richardson and Jassen [16] the non-diagonal electrostatic matrix elements of the complementary states d^{10-N} $(N < 5)$ remain the same as in the d^N matrix, but there are different diagonal matrix elements between the t_2^m and t_2^{6-m} configuration, and the e^n and e^{4-n} configuration. The simple relation can be written as

$$\begin{aligned} &\langle \mathrm{t}_2^{6-m}\mathrm{e}^{4-n}|\hat{H}_\mathrm{e-e}|\mathrm{t}_2^{6-m}\mathrm{e}^{4-n}\rangle - \langle \mathrm{t}_2^m\mathrm{e}^n|\hat{H}_\mathrm{e-e}|\mathrm{t}_2^m\mathrm{e}^n\rangle\\ &= (3-m)a + 4(3-m)b + (24-4m-6n)\left(\frac{c}{\sqrt{3}} + d\right)\\ &\quad + (6-3n)e + (5n-10)f + (2m+3n-12)g\\ &\quad + (2m+3l-12)\frac{h}{\sqrt{3}} - 2(3-m)j, \end{aligned} \qquad (4)$$

where the electrostatic parameters $a - j$ are defined approximately in the following form:

$$\begin{aligned} a &= (\xi^2,\xi^2) = N_\mathrm{t}^4(A_0 + 4B_0 + 3C_0),\\ b &= (\xi^2,\eta^2) = N_\mathrm{t}^4(A_0 - 2B_0 + C_0),\\ c &= (\theta\varepsilon,\xi^2) = 2\sqrt{3}N_\mathrm{t}^2N_\mathrm{e}^2B_0,\\ d &= (\varepsilon^2,\xi^2) = N_\mathrm{t}^2N_\mathrm{e}^2(A_0 - 2B_0 + C_0),\\ e &= (\varepsilon^2,\varepsilon^2) = N_\mathrm{e}^4(A_0 + 4B_0 + 3C_0),\\ f &= (\theta\varepsilon,\theta\varepsilon) = N_\mathrm{e}^4(4B_0 + C_0),\\ g &= (\theta\xi,\theta\xi) = N_\mathrm{t}^2N_\mathrm{e}^2(B_0 + C_0),\\ h &= (\varepsilon\eta,\theta\eta) = \sqrt{3}N_\mathrm{t}^2N_\mathrm{e}^2B_0,\\ i &= (\eta\zeta,\theta\xi) = \sqrt{3}N_\mathrm{t}^3N_\mathrm{e}B_0,\\ j &= (\eta\zeta,\eta\zeta) = N_\mathrm{t}^4(3B_0 + C_0). \end{aligned} \qquad (5)$$

The cubic crystal field is usually expressed with the parameter Dq. For the t$_{2\mathrm{g}}$ and e$_\mathrm{g}$ orbitals, the cubic crystal field can be described with the cubic crystal parameter Dq such that

$$\langle \mathrm{t}_2|V_\mathrm{c}|\mathrm{t}_2\rangle = -4Dq,\ \langle \mathrm{e}|V_\mathrm{c}|\mathrm{e}\rangle = 6Dq. \qquad (6)$$

The cubic crystal-fields for the $t_2^m e^n$ terms and their complementary terms $t_2^{6-m} e^{4-n}$ are

$$\begin{aligned}
&\langle t_2^m e^n | V_c | t_2^m e^n \rangle = (-4m + 6n)Dq, \\
&\langle t_2^{6-m} e^{4-n} | V_c | t_2^{6-m} e^{4-n} \rangle = -(-4m + 6n)Dq.
\end{aligned} \tag{7}$$

The cubic crystal energy for a d^{*N} system and for a d^{*10-N} system can be added to the diagonal matrix elements. From (4) we noted that the difference between the $t_2^{6-m} e^{4-n}$ configuration of the d^{*7} system and the $t_2^m e^n$ configuration of the d^{*3} system is just same and got the difference as

$$\begin{aligned}
&G1(t_2^4 e^3) = (5A_1 - 10B_1 + 5C_1) \\
&\quad + (10A_2 - 10B_2 + 5C_2) + (3A_4 - 8B_4 + 4C_4), \\
&G2(t_2^5 e^2) = (10A_1 - 20B_1 + 10C_1) \\
&\quad + (8A_2 - 8B_2 + 4C_2), \\
&G3(t_2^3 e^4) = (12A_2 - 12B_2 + 6C_2) \\
&\quad + (6A_4 - 16B_4 + 8C_4), \\
&G4(t_2^6 e) = (15A_1 - 30B_1 + 15C_1) \\
&\quad + (6A_2 - 6B_2 + 3C_2) - (3A_4 - 8B_4 + 4C_4).
\end{aligned} \tag{8}$$

Thus, adding these terms from (7) and (8) to the corresponding diagonal matrix elements of the d^{*3} electron system, we can obtain the electrostatic repulsion and the crystal-field matrix of the d^{*7} electron system in the strong-field scheme form.

It should be pointed out that in the cubic crystal-field, the energy difference between the $^4t_2$ and $^4A_2$ states is not the usual 10Dq, and this energy difference connects to covalent factors N_t and N_e, and the Racah parameters A_0, B_0 and C_0. In a d^{*3} system, the energy difference can be written as

$$\begin{aligned}
&E\left[^4T_2(t_2^2 e)\right] - E\left[^4A_2(t_2^3)\right] = 2(A_2 - A_1) \\
&\quad + 10(B_1 - B_2) + 10Dq,
\end{aligned} \tag{9a}$$

and in a d^{*7} system, the energy difference is

$$\begin{aligned}
&E\left[^4T_2(t_2^4 e^3)\right] - E\left[^4A_2(t_2^3 e^4)\right] = \\
&\quad 3(A_1 - A_4) + 8(B_4 - B_2) \\
&\quad + (5C_1 - C_2 - 4C_4) - 10Dq.
\end{aligned} \tag{9b}$$

Therefore, Dq cannot be obtained simply from the energy difference between the $^4T_2$ and $^4A_2$ states for both d^{*3} and d^{*7} systems. The difference can be obtained from experimental data of the optical spectra.

3. The Energy Levels of the d^{*7} Electron and d^{*3} Hole System

The Racah parameters A_0, B_0 and C_0 of a Co^{2+} ion have been determined experimentally [15, 17] as

$$\begin{aligned}
&A_0 = 16118\ \text{cm}^{-1}, \quad B_0 = 1115\ \text{cm}^{-1}, \\
&C_0 = 4366\ \text{cm}^{-1}.
\end{aligned} \tag{10}$$

A parameter ε is introduced to describe the difference between the covalent factors N_t and N_e, that is

$$\varepsilon = 1 - N_t^2 / N_e^2 \tag{11}$$

for the d^{*N} ion in a tetrahedral crystal-field [8]. As the covalence increases, the ratio of the two factors N_t and N_e decreases and the difference between them increases. Therefore, ε increases with increasing covalence. When the contribution from the covalence is ignored, putting the covalent parameter $N_t = N_e$, the energy level matrix can be reduced to the classical crystal-field result, and the energy levels can be calculated by a d^3 hole system instead of the d^7 electron system.

The energy levels of Co^{2+} can be calculated using the matrix of Table 1 for the d^{*3} hole system as well as using the matrix for the d^{*7} electron system as a function of ε and the covalent factor N_e. The variations of energy levels for the Co^{2+} ion versus ε for d^{*7} electron and for the d^{*3} hole systems are shown in Figs. 1 and 2, respectively. (We have chosen only thirteen energy levels for clarity in these figures.)

It is worth noting that the values of the $^4T_2$, $^4T_{1a}$ and $^4T_{1b}$ levels for the d^{*7} electron system decrease rapidly with the increase of ε in Fig. 2, whereas they do not for the d^{*3} hole system in Figure 1. For large ε, $^4T_2$ may turn into the ground state when Co^{2+} is considered with a d^{*7} electron system, whereas $^4T_2$ will remain as its ground state when Co^{2+} is explained with a d^{*3} hole system. Since ε describes the difference between the t_2 and e orbitals, a larger ε means a stronger covalence and a larger difference between N_t and N_e. When $\varepsilon = 0$ (a pure d^N system), the contribution of the Racah parameter A is zero and a d^7 electron system can be explained with a d^{*3} hole system. As ε increases, the contribution from the Racah parameter also increases. When the same covalent factors are introduced in both the d^{*7} electron and d^{*3} hole system, the contribution of the electrostatic repulsion for the d^{*7} system is larger than that for the d^{*3} system. The calculated energy levels for the d^{*7} electron system are different from those for the d^{*3} hole system using the same covalent factors.

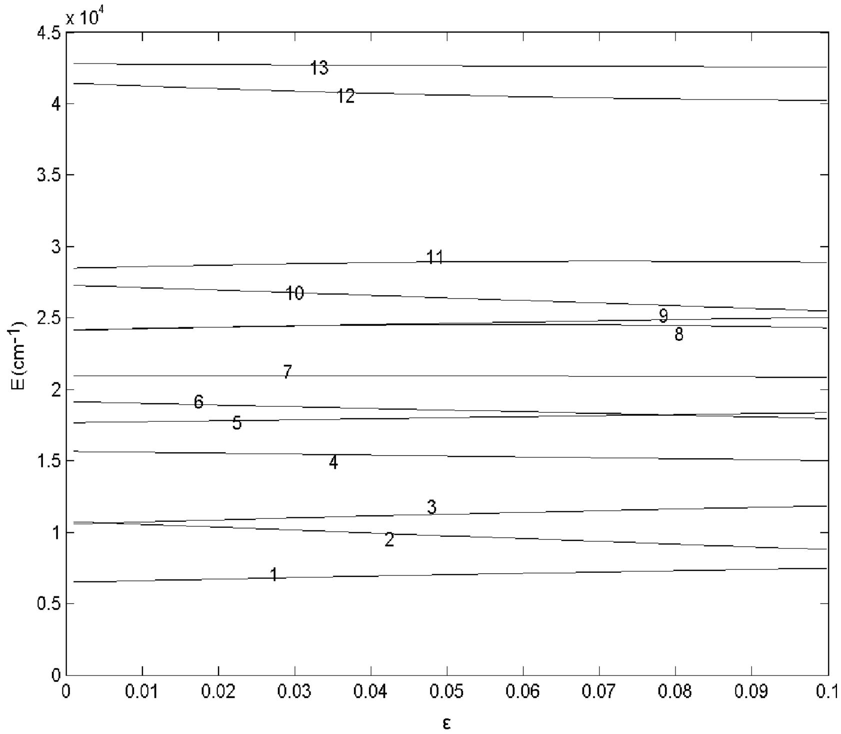

Fig. 1. Variation of the energy levels of Co^{2+} for the d^{*3} hole system with the covalent factor ε. The energy levels E are the difference between the $^{2S+1}\Gamma$ term and the ground state $^4A_2$ term: 1, $^4T_2$; 2, ^2E_a; 3, $^4T_{1a}$; 4, $^2A_1$; 5, $^4T_{1b}$; 6, ^2E_b; 7, $^2T_{1c}$; 8, $^2T_{2c}$; 9, $^2T_{1d}$; 10, $^2T_{2d}$; 11, ^2E_c; 12, ^2E_d; 13, $^2T_{2e}$. The fixed values of $Dq = 650$ cm^{-1} and $N_e = 0.8500$ are used in the calculation.

The Co^{2+} ion has a $3d^7$ electron configuration. The absorption optical spectra of Co^{2+} in ZnSe were measured and published in [3] and [4]. From the energy matrix and equations $(4) \sim (10)$ using $\alpha_0 = 80$ cm^{-1}, $N_t = 0.8623$, $N_e = 0.8780$ and $|Dq| = 612$ cm^{-1}, we have calculated the energy level transitions of Co^{2+} in ZnSe by using the d^{*7} electron system and the d^{*3} hole system energy matrix, respectively. The results of the calculation are listed in Table 2. It is obvious that the results calculated by using the d^{*7} electron system, but not by using the d^{*3} hole system, agree well with the experimental data.

Using the mean-field and multiple corrections method, Fazzio et al. [2] have studied three lines in the region 19059 $\sim$ 20785 cm^{-1} and obtained three doublets, $^2T_{1c}$, ^2E_c, $^2T_{2c}$, in this region. Our calculation shows that the three doublet lines should be $^2T_{1c}$, $^2T_{1d}$, $^2T_{2c}$ in this region, the results are in good agreement with the experimental data. For the tetrahedral field such as ZnSe N_e is lager than N_t [8] since the covalence of the t_{2g} orbital is stronger than that of the e_g

Table 2. Energy levels of Co^{2+} in ZnSe (in cm^{-1}).

	ZnSe:Co^{2+} Calculation (d^{*3} hole)	Calculation (d^{*7} electron)	Experiment
$^4A_2 \rightarrow {}^4T_2$	6551	3499	3500 [3]
$^4T_{1a}$	10766	6074	6000 – 6500 [3]
$^4T_{1b}$	18092	13522	13500 – 14200 [3]
^2E_a	11595	11406	
^2E_b	20248	17263	
^2E_c	30228	22913	
^2E_d	44089	39486	
$^2A_1$	16572	13610	
$^2A_2$	29079	26026	
$^2T_{1a}$	12211	11936	
$^2T_{1b}$	19151	16271	
$^2T_{1c}$	22588	18826	19034 [4]
$^2T_{1d}$	25412	19472	19589 [4]
$^2T_{1e}$	33303	28251	
$^2T_{2a}$	15851	14379	
$^2T_{2b}$	18811	16100	
$^2T_{2c}$	25831	20497	20492 [4]
$^2T_{2d}$	29766	26413	
$^2T_{2e}$	46224	41058	
	$Dq = 612$ cm^{-1}	$Dq = -612$ cm^{-1},	

$N_t = 0.8623$, $N_e = 0.8780$ and $\alpha = 80$ cm^{-1}.

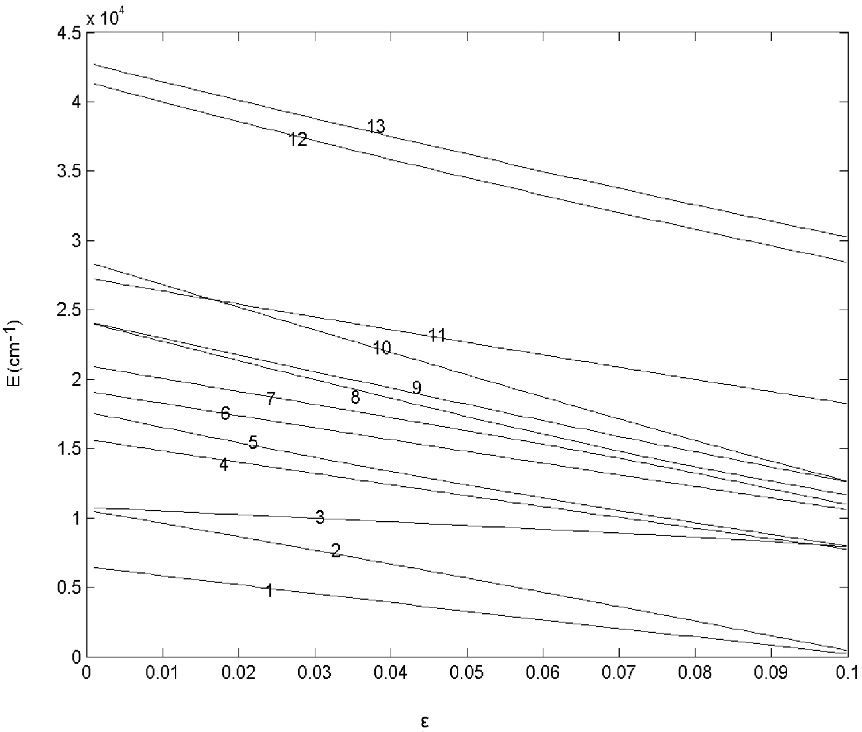

Fig. 2. Variation of the energy levels of Co^{2+} for the d^{*7} hole system with the covalent factor ε. The energy levels E are the difference between the $^{2S+1}\Gamma$ term and the ground state $^4A_2$ term: 1, $^4T_2$; 2, ^2E_a; 3, $^4T_{1a}$; 4, $^2A_1$; 5, $^4T_{1b}$; 6, ^2E_b; 7, $^2T_{1c}$; 8, $^2T_{2c}$; 9, $^2T_{1d}$; 10, ^2E_c; 11, $^2T_{2d}$; 12, ^2E_d; 13, $^2T_{2e}$. The fixed values of $Dq = -650$ cm^{-1} and $N_e = 0.8500$ are used in the calculation.

orbital. The different between the t$_{2g}$ and e$_g$ orbitals induce that energy level of the Co^{2+} ion should be calculated with the d^{*7} electron system instead of the d^{*3} hole system. That is to say the values of the covalent factors may affect the calculated result greatly when the covalence is considered in the investigation of the optical and magnetic properties, especially in the calculation of the spin-Hamiltonian parameters [10, 11]. This suggests that the d^{*7} electron system should be used to investigate the optical and magnetic properties of the semiconductor containing Co^{2+} ion, but the d^{*3} hole system should not.

4. Conclusion

For a pure d^N electron system, the Racah electrostatic parameter A does not contribute to the energy levels, since the contribution is identically equal for all the energy terms. However, the contribution of covalence must be considered for the optical and magnetic properties in a strong covalence compound. If the model of distinguishing of the radial parts of the t and e orbitals of the d electrons has been adopted, one should calculate the energy levels by using a d^{*N} electron system instead of a pure d^N electron system or the d^{10-N} hole system.

The energy matrix of the d^{*7} and d^{*3} system has been obtained and the energy levels of Co^{2+} for the d^{*7} electron system and d^{*3} hole system have been calculated. The results show that the variation of the energy levels with the covalence of the d^{*7} electron system is much larger than that for the d^{*3} hole system and could affect an investigation of the optical and magnetic properties for a semiconductor containing Co^{2+}.

Acknowledgement

The work was supported by the Science Foundation of Sichuan Education Committee (Grant No. 407/2003).

[1] B. Clerjaud, J. Phys. C **18**, 3615 (1985).
[2] A. Fazzio, M. J. Caldas, and A. Zunger, Phys. Rev. B **30**, 3430 (1984).
[3] J. M. Baranowski, J. M. Allen, and G. L. Pearson, Phys. Rev. **160**, 627 (1967).
[4] J. M. Noras, H. R. Szawelska, and J. W. Allen, J. Phys. C: Solid State Phys. **14**, 3255 (1981).
[5] H. A. Weakliem, J. Chem. Phys. **36**, 2117 (1962).
[6] U. Kaufmann and J. Schneider, Solid State Commun. **25**, 1113 (1978).
[7] A. G. O'Neill and J. W. Allen, Solid State Commun. **46**, 833 (1983).
[8] D. Curie, C. Barthou, and B. Canny, J. Chem. Phys. **61**, 3048 (1974).
[9] M.-L. Du and H.-Y. Tae, Phys. Rev. B **59**, 4881 (1999).
[10] J.-J. Chen and M.-L. Du, Phys. Status Solidi B **241**, 2994 (2004).
[11] J.-J. Chen and M.-L. Du, Z. Naturforsch. **57a**, 745 (2002).
[12] Y. Y. Zhou, Physica B **322**, 61 (2002).
[13] S. Sugano, Y. Tanabe, and H. Kamimura, Multiples of Transition Metal Ions in Crystal, Academic Press, New York 1970.
[14] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Dover Publication, Inc., New York 1986.
[15] J. S. Griffith, The Theory of Transition Metal Ions, Cambridge University Press, London 1961.
[16] J. W. Richardson and G. J. M. Janssen, Phys. Rev. B **39**, 4958 (1989).
[17] H. A. Skinner and F. H. Sumner, J. Inorg. Nucl. Chem. **4**, 245 (1957).