1. Introduction

Transition-metal ion impurities in strongly covalent crystals, show often unusual electronic structures and magnetic properties. To explain these, many calculations are based on the classical crystal-field model [1–6]. Some significant studies of the optical spectrum and EPR parameters of 3d2 ion impurities in CdS crystals have been done [7–9]. As there is strong covalence in II–VI semiconductors, it is difficult to explain the optical and magnetic properties of V3+ impurities in CdS by means of conventional crystal-field theory. Fazzio et al. [2] suggested that the t2g orbit should be different from the eg orbit in the covalent crystal, and they studied many-electron multiple effects in the spectra of 3dn ion impurities in semiconductors. However, since the classical crystal-field model [10, 11] neglects the difference, this model should be corrected for covalent crystals but not for ionic crystals.

In this paper we consider the difference between the t2g and eg orbit, treat the 3d2 energy matrix based on the Sugano-Tanable scheme [10], and derive the ground state g-factor in the trigonal system from a two spin-orbit coupling parameter model for the g factor is included. The model is applied to the calculation of the optical spectrum of CdS:V3+ in the Td system and the gyromagnetic factor in the trigonal system. The calculated results agree well with experimental findings.

2. The Crystal Field Model

For the covalence effects we chose the linear combination of atomic orbital (LCAO) basis, in which the one-electron function has the form

\[ |\gamma\rangle = N_\gamma (d_\gamma + \lambda_\gamma p_\gamma) \]

where \( \gamma = t_{2g} \) or \( e_g \) is the irreducible representation of the Oh or Td group, \( N_\gamma \) and \( \lambda_\gamma \) are the normalization factor and the orbital mixing coefficients of the atomic orbitals. d and p are the central transition-metal d-orbital and the valence-electron orbital of the ligand ions, respectively.

In the Sugano-Tanable scheme [10], the Hamiltonian of a d2 ion at a trigonal MX4 cluster can be written as

\[
\hat{H} = \hat{H}_a(A, B, C) + \hat{H}_b(B, C) + \hat{H}(\Delta) + \hat{H}(v, v') + \hat{H}_s(\zeta_{2g}, \zeta_{eg}) + \hat{H}_\text{Trees}(\alpha) + \hat{H}_Z. \quad (2)
\]

where \( \hat{H}_a(A, B, C) \), \( \hat{H}_b(B, C) \), \( \hat{H}(\Delta) \), \( \hat{H}(v, v') \), \( \hat{H}_s(\zeta_{2g}, \zeta_{eg}) \), \( \hat{H}_\text{Trees}(\alpha) \) and \( \hat{H}_Z \) are the diagonal and the off-diagonal terms of electrostatic Coulomb interaction, the tetrahedral crystal field, the trigonal part of the crystal field, the spin-orbit Hamiltonian of the central-metal ion and the ligand ion, the Trees correction term, and the Zeeman term, respectively. A, B, and C are the Racah parameters, and \( \zeta \) is the spin-orbit coupling parameter of the central metal ion. 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 Oh or Td point group.
Table 1. The crystal field energy for a 3d $^2$ ion in the T_d system.

<table>
<thead>
<tr>
<th>( A_1 )</th>
<th>( t_2 )</th>
<th>( e^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_2^2 )</td>
<td>( A_1 + 10B_1 + 5C_1 + 8Dq + 8\alpha_1 )</td>
<td>( \sqrt{6}(2B_2 + C_2 - 4\alpha_2) )</td>
</tr>
<tr>
<td>( e^2 )</td>
<td>( A_1 + 8B_1 + 4C_4 - 12Dq + 12\alpha_4 )</td>
<td></td>
</tr>
<tr>
<td>( 3T_1 )</td>
<td>( t_2^3 )</td>
<td>( t_2 )</td>
</tr>
<tr>
<td>( t_2 )</td>
<td>( A_1 - 5B_1 + 8Dq + 10\alpha_1 )</td>
<td>(-6B_1 + 4\alpha_4 )</td>
</tr>
<tr>
<td>( t_2 )</td>
<td>( A_1 + 4B_1 - 2Dq + 4\alpha_2 )</td>
<td></td>
</tr>
<tr>
<td>( 1E )</td>
<td>( t_2^3 )</td>
<td>( t_2 )</td>
</tr>
<tr>
<td>( e^2 )</td>
<td>( A_1 + B_1 + 2C_1 + 8Dq + 14\alpha_1 )</td>
<td>( A_1 + 2C_3 + 12Dq + 12\alpha_4 )</td>
</tr>
<tr>
<td>( 1T_2 )</td>
<td>( t_2^3 )</td>
<td>( t_2 )</td>
</tr>
<tr>
<td>( t_2 )</td>
<td>( A_1 + B_1 + 2C_1 + 8Dq + 14\alpha_1 )</td>
<td>(-\sqrt{3}(2B_1 + 4\alpha_3) )</td>
</tr>
<tr>
<td>( t_2 )</td>
<td>( A_1 + 2C_2 - 2Dq + 12\alpha_2 )</td>
<td></td>
</tr>
<tr>
<td>( 3A_2 )</td>
<td>( t_2 )</td>
<td></td>
</tr>
<tr>
<td>( e^2 )</td>
<td>( A_1 - 8B_4 - 12Dq + 12\alpha_4 )</td>
<td></td>
</tr>
</tbody>
</table>

The separation between the ground state \( ^3A_2(F) \) and the first excited state \( ^3T_2(F) \) differs from the classical crystal field result [10, 11]. In this case, the cubic crystal field parameter $A$ is not equal to $10Dq$, the first excited state separation consists of cubic crystal-field and Coulomb interaction. It distinguishes Sugano-Tanable approach. But the present energy matrix can be reduced to the Sugano-Tanable approach by putting $N_1 = N_2$ for the covalent parameters.

3. The g-factor Formula of the Ground State in the Trigonal System

For explaining the magnetic properties of the strong covalence in these II-VI semiconductors we adopt a two spin-orbit coupling parameter model [3, 4] to calculate the g-factor. According this model, the perturbation Hamiltonian appropriate for a 3d$^2$ ion in an external magnetic field is

$$
\hat{H}' = \hat{H}_0(B, C) + \hat{H}(\nu, \nu') + \hat{H}_\text{so}(\zeta_\nu, \zeta_\nu') + \hat{H}_z,
$$

where $\hat{H}_\text{so}(\zeta_\nu, \zeta_\nu')$ is the two spin-orbit Hamiltonian term [3, 4], and $\zeta_\nu$ and $\zeta_\nu'$ are the spin-orbit coupling parameters of the central ion ($\zeta_\nu$) and the ligand ion ($\zeta_\nu'$). Using the one-electron basis function (1) and the perturbation-loop method [3, 4], we obtain the first- and third-order perturbation expression of the $g$-factor for a 3d$^2$ ion in trigonal symmetry:

$$
\Delta g_{\|} = g_{\|} - g_a = \Delta g_{\|}(\zeta_\nu) + \Delta g_{\|}(\zeta_\nu') + \Delta g_{\|}(\zeta_{\nu}, \zeta_{\nu'}),
$$

$$
\Delta g_{\|}(\zeta_\nu) = -4k_\nu \frac{\zeta_\nu}{E_1} - [g_a(\zeta_\nu)^2 + k_\nu \frac{\zeta_\nu}{E_1} + k_{\nu, \|} \frac{\zeta_\nu}{E_1} + (g_a - k_{\nu, \|}) (\zeta_\nu')^2)/E_1^2
$$

$$
+ (g_a - k_{\nu, \|}) \frac{\zeta_{\nu, \|}}{E_1} + 2g_a \nu^2/E_1^2
$$

$$
+ 2\sqrt{2}k_\nu \nu'(k_\nu \zeta_{\nu, \|} + k_{\nu, \|} \zeta_\nu)/E_1 E_3
$$

$$
+ 8k_\nu \frac{\zeta_{\nu, \|}}{E_1} (\nu + \nu')/\sqrt{8}/E_1^2,
$$

$$
\Delta g_{\|}(\zeta_{\nu, \nu'}) = 4k_{\nu, \nu'} \frac{\zeta_{\nu, \nu'}}{E_1} - [g_a(\zeta_{\nu, \nu'})^2 - k_{\nu, \nu'} \frac{\zeta_{\nu, \nu'}}{E_1}]
$$

$$
+ k_{\nu, \nu'} \frac{\zeta_{\nu, \nu'}}{E_1} (E_1 + E_3) + 2g_a \nu'^2/E_3^2
$$

$$
+ 2\sqrt{2}k_\nu \nu'(k_{\nu, \nu'} \zeta_\nu + k_{\nu, \nu'} \zeta_{\nu, \nu'})/E_1 E_3
$$

$$
+ 8k_{\nu, \nu'} \frac{\zeta_\nu}{E_1} (\nu + \nu')/\sqrt{8}/E_3^2,
$$

$$
\Delta g_{\|}(\zeta_{\nu, \nu}, \zeta_{\nu'}) = [2g_a \zeta_{\nu, \nu'} \zeta_{\nu'} - k_{\nu, \nu'} \zeta_{\nu, \nu'}]
$$

$$
- (g_a - k_{\nu, \nu'}) \frac{\zeta_{\nu, \nu} \zeta_{\nu'}}{E_1 E_3}
$$

$$
+ (2g_a - k_{\nu, \nu'}) \frac{\zeta_{\nu, \nu} \zeta_{\nu'}}{E_1 E_3},
$$

where $\hat{H}_0(B, C)$ is the central free metal ion energy matrix.
\[ \Delta g_{\perp} = g_\perp - g_\parallel = \Delta g_{\perp}(\zeta_d^0) + \Delta g_{\perp}(\zeta_p^0) + \Delta g_{\perp}(\zeta_d^p, \zeta_p^p), \]
\[ \Delta g_{\perp}(\zeta_d^0) = \Delta g_0(\zeta_d^0) = -3\sqrt{2}v'(k_\perp \zeta_d^0 + k_\parallel \zeta_d^p)/E_1 E_3, \]
\[ \Delta g_{\perp}(\zeta_p^0) = \Delta g_0(\zeta_p^0) = -3\sqrt{2}v'(k_\parallel \zeta_p^0 + k_\perp \zeta_p^p)/E_1 E_3, \]
\[ \Delta g_{\perp}(\zeta_d^p, \zeta_p^p) = \Delta g_{\perp}(\zeta_d^p, \zeta_p^p). \]

where
\[ g_\perp = 2.0023 \text{ is the free-electron } g \text{-factor.} \]
\[ (\zeta_d^0), (\zeta_p^0), \text{and } (\zeta_d^p, \zeta_p^p) \text{ denote the contributions to the SH parameters from the central metal ion, the ligand ion and the mixed ones, respectively.} \]
\[ E_1, E_2, \text{ and } E_3 \text{ are the zero-order energy separations:} \]
\[ E_1 = E(3T_2) - E(3A_2) = (A_2 - 8B_2 + 12\alpha_2), \]
\[ (A_4 - 8B_4 + 12\alpha_4) + 10Dq, \]
\[ E_2 = E(3T_2 b) - E(3A_2) = (A_2 + 2C_2 - 2Dq + 12\alpha_2), \]
\[ (A_4 - 8B_4 + 12Dq + 12\alpha_4), \]
\[ E_3 = E(3T_1 a) - E(3A_2) = (A_2 - 5B_1 + 10Dq + 10\alpha_1), \]
\[ (A_4 - 8B_4 - 12Dq + 12\alpha_4). \]

From the present g-factor formula one can see that the difference between the \( t_{2g} \) and \( e_g \) orbitals can not be neglected. If we put \( N_i = N_c \) for the covalent parameters, the g-factor formula can also simplify the crystal field theory [10, 11].

**4. Application**

The ion \( V^{3+} \) has a \( 3d^2 \) ion electron configuration and possesses a \( 3A_2(F) \) ground state in \( T_d \) symmetry. The II–VI semiconductor CdS has a tetrahedrally coordinated structure with a bond length 0.2513 nm [12]. But there is a small trigonal perturbation when \( V^{3+} \) ion impurities are in the crystal [8]. The experimental values [13–15] of the Racah parameters and the spin-orbit coupling parameters for \( V^{3+} \) and the ligand ion \( S^{2–} \) are listed in Table 2. Using the covalence parameters \( N_i = 0.9121 \) and \( N_c = 0.8625 \), which are determined from the optical spectra, we can calculate the mixing coefficients by means of a group overlap integral [3, 4]. Taking the trigonal crystal field parameters \( v = 32 \text{ cm}^{-1} \) and \( v' = -60 \text{ cm}^{-1} \), we have calculated the g-factor for CdS:V\(^{3+}\). A comparison between the calculated and observed values is given in Table 3.

**5. Summary**

The optical spectrum and the gyromagnetic factor of CdS:V\(^{3+}\) have been calculated satisfactorily by means of the present covalent model. In this model we suggest that the difference between the \( t_{2g} \) and \( e_g \) orbitals should be considered for the strongly covalent crystal-field case, and the energy matrix and the g-factor formula of Sugano-Taube approach must be corrected. The calculated results

---

**Table 2. The Racah and spin-orbit coupling parameters of \( V^{2+}, V^{3+}, \) and \( S^{2–} \) free ions (in cm\(^{-1}\)).**

<table>
<thead>
<tr>
<th>Ion</th>
<th>( A_0 )</th>
<th>( B_0 )</th>
<th>( C_0 )</th>
<th>( \zeta_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V^{2+} )</td>
<td>11873</td>
<td>766</td>
<td>2855</td>
<td>167</td>
</tr>
<tr>
<td>( V^{3+} )</td>
<td>13346</td>
<td>861</td>
<td>4165</td>
<td>209</td>
</tr>
<tr>
<td>( S^{2–} )</td>
<td>365</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ ^{a} \text{[13–15].} \]

\[ ^{b} \text{Using the relationship } A_0(V^{3+}) = A_0(V^{2+}) \cdot B_0(V^{3+})/B_0(V^{2+}) \text{ to estimate the Racah Parameter } A_0 \text{ of a free } V^{3+} \text{ ion.} \]

**Table 3. The comparison between the calculated and observed values of the optical spectra (in cm\(^{-1}\)) and \( g \) values for CdS:V\(^{3+}\), (taking the Trees correction parameter \( a_0 = 80 \text{ cm}^{-1}\)).**

<table>
<thead>
<tr>
<th>g Shift Values</th>
<th>Calculated Values</th>
<th>Experimental Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta g_0(\zeta_d^0) )</td>
<td>-0.0927</td>
<td>1.9341 ± 0.001</td>
</tr>
<tr>
<td>( \Delta g_0(\zeta_p^0) )</td>
<td>0.0236</td>
<td>0.0009</td>
</tr>
<tr>
<td>( g_\parallel )</td>
<td>1.9341</td>
<td>1.931 ± 0.001</td>
</tr>
<tr>
<td>( g_\perp )</td>
<td>-0.0951</td>
<td>0.0233</td>
</tr>
<tr>
<td>( \Delta g(\zeta_d^p, \zeta_p^p) )</td>
<td>1.9306</td>
<td>1.931 ± 0.001</td>
</tr>
</tbody>
</table>

\[ ^{a} \text{[7].} \]

\[ ^{b} \text{[8].} \]
by means of the modified Sugano-Tanabe approach agree well with the experimental findings. It shows that the present model is certainly needed for covalent hosts.

Acknowledgement

The project was supported by Science Foundation of the Sichuan Education Committee (Grant No. 25/2000).