Theoretical Investigation of the Optical Spectrum and the Gyromagnetic *g* Factor of CdS:V^{3+}

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We present a covalence crystal field model based on a cluster approach for a $3d^2$ ion in a T_d system, in which not only the effect of the difference between the t_{2g} and e_g orbit but also 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 Cd S:V^{3+} in the T_d system and the gyromagnetic factor in the trigonal system. The calculated results agree well with experimental findings.

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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 $3d^2$ ion impurities in Cd S 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 V^{3+} impurities in Cd S by means of conventional crystal-field theory. Fazzio et al. [2] suggested that the t_{2g} orbit should be different from the e_g orbit in the covalent crystal, and they studied many-electron multiple effects in the spectra of $3d^n$ 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 t_{2g} and e_g orbit, treat the $3d^2$ electric 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 [3, 4]. As an example, we use the model to calculate the optical spectrum in the T_d system and ground state *g*-factor in trigonal symmetry for Cd S:V^{3+}. The calculated results agree well with the experimental data.

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

$$|\gamma\rangle = N_\gamma(|d_\gamma\rangle + \lambda_\gamma|p_\lambda\rangle)\,,$$

where $\gamma = t_{2g}$ or e_g is the irreducible representation of the O_h or T_d group. N_γ and λ_γ are the normalization factor and the orbital mixing coefficients of the atomic orbits. 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 d^2 ion at a trigonal MX_4 cluster can be written as

$$\hat{H} = \hat{H}_a(A,B,C) + \hat{H}_b(B,C) + \hat{H}(\Delta) + \hat{H}(\nu,\nu') + \hat{H}_{so}(\zeta_d,\zeta_p) + \hat{H}_{Trees}(\alpha) + \hat{H}_Z, \quad (2)$$

where $\hat{H}_a(A,B,C)$, $\hat{H}_b(B,C)$, $\hat{H}(\Delta)$, $\hat{H}(\nu,\nu')$, $\hat{H}_{so}(\zeta_d,\zeta_p)$, $\hat{H}_{Trees}(\alpha)$ 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 ζ 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 O_h or T_d point group.

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Table 1. The crystal field energy for a 3d^2 ion in the T$_d$ system.

$^1A_1$	t_2^2	e^2
t_2^2	$A_1+10B_1+5C_1+8Dq+8\alpha_1$	$\sqrt{6}\,(2B_2+C_2-4\alpha_2)$
e^2		$A_4+8B_4+4C_4-12Dq+12\alpha_4$
$^3T_1$	t_2^2	$t_2\,e$
t_2^2	$A_1-5B_1+8Dq+10\alpha_1$	$-6B_3+4\alpha_3$
$t_2\,e$		$A_2+4B_2-2Dq-4\alpha_2$
^1E	t_2^2	e^2
e^2	$A_1+B_1+2C_1+8Dq+14\alpha_1$	$\sqrt{3}\,(2B_2+4\alpha_2)$
t_2^2		$A_4+2C_4-12Dq+12\alpha_4$
$^1T_2$	t_2^2	$t_2\,e$
t_2^2	$A_1+B_1+2C_1+8Dq+14\alpha_1$	$-\sqrt{3}\,(2B_3+4\alpha_3)$
$t_2\,e$		$A_2+2C_2-2Dq+12\alpha_2$
$^1T_1\,(t_2\,e)=A_2+4B_2+2C_2-2Dq+20\alpha_2$		
$^3T_2\,(t_2\,e)=A_2-8B_2-2Dq+12\alpha_2$		
$^3A_2\,(e^2)=A_4-8B_4-12Dq+12\alpha_4$		

In the crystal-field model, the contribution of the Racah parameter A is equal for all energy terms; thus it is omitted in the energy matrix of the Sugano-Tanable approach [10]. Because of the strong covalence in II–VI semiconductors, the difference between the t$_{2g}$ and e$_g$ orbits should be considered [5, 6]. The value of the Racah parameter A is generally large. The influence of the parameter A is also great for the energy structure; when $N_t \neq N_e$, the difference cannot be neglected. According to (1) and (2), we derive the new energy matrix in T$_d$ symmetry (see Table 1), and give the Trees correction in strong-field scheme.

The relationship between the Racah parameters in the crystal field and the Racah parameters of the central free metal ion can be written as

$$X_1=N_t^4X_0,\quad X_2=N_e^2N_t^2X_0,\quad X_3=N_eN_t^3X_0,\quad X_4=N_e^4X_0$$
$$X=A,B,C,\alpha, \tag{3}$$

where A, B, C denote the Racah parameters in the crystal, A_0, B_0, C_0 are the Racah parameters of a free central metal ion, and α denotes the Trees correction parameter.

In this process, only the one-electron matrix elements of both central metal ions are retained such as $\langle d_\gamma d_\gamma|\hat{H}|d_\gamma d_\gamma\rangle$, since that d-orbit is dominant. So the other matrix elements are neglected. Because the difference between the t$_{2g}$ and e$_g$ orbits is not neglected here, the separation between the ground state ^{3}A$_2$(F) and the first excited state ^{3}T$_2$(F) differs from the classical crystal field result [10, 11]. In this case, the cubic crystal field parameter Δ 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 $N_t=N_e$ 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 extermal magnetic field is

$$\hat{H}'=\hat{H}_b(B,C)+\hat{H}(\nu,\nu')+\hat{H}_{so}(\zeta_d,\zeta_p)+\hat{H}_z, \tag{4}$$

where $\hat{H}_{so}(\zeta_d,\zeta_p)$ is the two spin-orbit Hamiltonian term [3, 4], and ζ_d and ζ_p are the spin-orbit coupling parameters of the central ion (ζ_d) and the ligand ion (ζ_p). 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:

$$\Delta g_\parallel=g_\parallel-g_s=\Delta g_\parallel(\zeta_d)+\Delta g_\parallel(\zeta_p)+\Delta g_\parallel(\zeta_d,\zeta_p),$$

$$\begin{aligned}\Delta g_\parallel(\zeta_d)=&-4k_-\zeta_d^{te}/E_1-[g_s(\zeta_d^{te})^2+k_-\zeta_d^{te}\zeta_d^{t}\\&-k_+(\zeta_d^{te})^2/2]/E_1^2-(g_s-k_+/2)(\zeta_d^{te})^2/E_2^2\\&-k_-\zeta_d^{te}\zeta_d^{t}/(E_1E_2)+2g_e\nu'^2/E_3^2\\&+2\sqrt{2}k_-\nu'(k_-\zeta_d^{t}+k_+\zeta_d^{te})/E_1E_3\\&+8k_-\zeta_d^{te}(\nu+\nu'/\sqrt{8})/5E_1^2,\end{aligned}$$

$$\begin{aligned}\Delta g_\parallel(\zeta_p)=&\,4k_-\zeta_p^{te}/E_1-[g_s(\zeta_p^{te})^2-k_-\zeta_p^{te}\zeta_p^{t}\\&-k_+(\zeta_p^{te})^2/2]/E_1^2-(g_s-k_+/2)(\zeta_p^{te})^2/E_2^2\\&+k_-\zeta_p^{te}\zeta_p^{t}/(E_1E_2)+2g_e\nu'^2/E_3^2\\&+2\sqrt{2}k_-\nu'(k_-\zeta_p^{t}-k_+\zeta_p^{te})/E_1E_3\\&-8k_-\zeta_p^{te}(\nu+\nu'/\sqrt{8})/5E_1^2,\end{aligned}$$

$$\begin{aligned}\Delta g_\parallel(\zeta_d,\zeta_p)=&\,[2g_s\zeta_d^{te}\zeta_p^{t}-k_+\zeta_d^{te}\zeta_p^{te}\\&-k_-(\zeta_d^{te}\zeta_p^{t}-\zeta_d^{t}\zeta_p^{te})]/E_1^2\\&+(2g_s-k_+)\zeta_d^{te}\zeta_p^{t}/E_2^2\\&-k_-(\zeta_d^{te}\zeta_p^{t}-\zeta_d^{t}\zeta_p^{te})]/(E_1E_2),\end{aligned}$$

$$\Delta g_\perp = g_\perp - g_s = \Delta g_\perp(\zeta_d) + \Delta g_\perp(\zeta_p) + \Delta g_\perp(\zeta_d, \zeta_p)\,,$$

$$\begin{aligned}\Delta g_\perp(\zeta_d) = \Delta g_{\|}(\zeta_d) &- 3\sqrt{2}v'(k_- \zeta_d^t + k_+ \zeta_d^{te})/E_1 E_3 \\ &- k_- \zeta_d^{te}(v + \sqrt{2}v')/E_1^2\,,\end{aligned}$$

$$\begin{aligned}\Delta g_\perp(\zeta_p) = \Delta g_{\|}(\zeta_p) &- 3\sqrt{2}v'(k_- \zeta_p^t + k_+ \zeta_p^{te})/E_1 E_3 \\ &+ k_- \zeta_p^{te}(v + \sqrt{2}v')/E_1^2\,,\end{aligned}$$

$$\Delta g_\perp(\zeta_d, \zeta_p) = \Delta g_{\|}(\zeta_d, \zeta_p)$$

with

$$\zeta_d^{te} = N_t N_e \zeta_d^0\,, \quad \zeta_d = N_t^2 \zeta_d^0\,, \quad \zeta_p^{te} = N_t N_e \lambda_t \lambda_e \zeta_p^0/2\,,$$
$$\zeta_p^t = N_t \lambda_t^2 \zeta_p^0/2\,, \quad k_- = N_t N_e(1 - \lambda_t \lambda_e/2)\,,$$
$$k_+ = N_t^2(1 + \lambda_t^2/2)\,,$$

where $g_s = 2.0023$ is the free-electron g-factor. (ζ_d), (ζ_p), and (ζ_d, ζ_p) denote the contributions to the SH parameters from the central metal ion, the ligand ion and the mixed ones, respectively. E_1, E_2, and E_3 are the zero-order energy separations:

$$\begin{aligned}E_1 &= E(^3T_2) - E(^3A_2) \\ &= (A_2 - 8B_2 + 12\alpha_2) \\ &\quad - (A_4 - 8B_4 + 12\alpha_4) + 10Dq\,,\end{aligned}$$

$$\begin{aligned}E_2 &= E(^1T_2\, b) - E(^3A_2) \\ &= (A_2 + 2C_2 - 2Dq + 12\alpha_2) \\ &\quad - (A_4 - 8B_4 + 12Dq + 12\alpha_4)\,,\end{aligned}$$

$$\begin{aligned}E_3 &= E(^3T_1\, a) - E(^3A_2) \\ &= (A_1 - 5B_1 + 8Dq + 10\alpha_1) \\ &\quad - (A_4 - 8B_4 - 12Dq + 12\alpha_4)\,.\end{aligned}$$

From the present g-factor formula one can see that the difference between the t_{2g} and e_g orbits can not be neglected. If we put $N_t = N_e$ for the covalent parameters, the g-factor formula can also simplicy 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 Cd S 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 $N_t = 0.9121$ and $N_e = 0.8625$, 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 $v = 32$ cm^{-1} and $v' = -60$ cm^{-1}, we have calculated the g-factor for Cd S:V^{3+}. A comparison between the calculated and observed values is given in Table 3.

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

Free ions[a]	A_0	B_0	C_0	ζ^0
V^{2+}	11873	766	2855	167
V^{3+}	13346[b]	861	4165	209
S^{2-}				365

[a] [13–15].
[b] Using the relationship $A_0(\mathrm{V}^{3+}) = A_0(\mathrm{V}^{2+}) \cdot B_0(\mathrm{V}^{3+})/B_0(\mathrm{V}^{2+})$ to estimate the Racah Parameter A_0 of a free V^{3+} ion.

Table 3. The comparison between the calculated and observed values of the optical spectra[a] (in cm^{-1}) and g values[b] for Cd S:V^{3+}, (taking the Trees correction parameter $a_0 = 80$ cm^{-1}).

	Calculated Values	Experimental Values
$^3A_2 \to {}^3T_2$	4921	4921
$\to {}^3T_1$(F)	7840	8000~10000
$\to {}^3T_1$(P)	14630	14500
$\to {}^1E$(D)	8159	8250
$\to {}^1T_2$(D)	13800	13700
$\to {}^1A_1$(G)	13090	12700
g Shift Values	Calculated	Experimental
$\Delta g_{//}(\zeta_d)$	–0.0927	
$\Delta g_{//}(\zeta_p)$	0.0236	
$\Delta g(\zeta_d, \zeta_p)$	0.0009	
$g_{//}$	1.9341	1.934±0.001
$\Delta g_\perp(\zeta_d)$	–0.0951	
$\Delta g_\perp(\zeta_p)$	0.0233	
$\Delta g(\zeta_d, \zeta_p)$	0.0009	
$g_\perp$	1.9306	1.931±0.001

[a] [7],
[b] [8].

5. Summary

The optical spectrum and the gyromagnetic factor of Cd S: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 orbits should be considered for the strongly covalent crystal-field case, and the energy matrix and the g-factor formula of Sugano-Tanabe approach must be corrected. The calculated results 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.

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