Local Structure Determination of Tetragonal Cr^{2+} Center in CdS Semiconductor

Xiao-Ming Tan[a], Xiao-Yu Kuang[b], and Kang-Wei Zhou[c]

[a] School of Physics and Electronic Engineering, Ludong University, Yantai 264025, China
[b] Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China
[c] Department of Physics, Sichuan University, Chengdu 610065, China

Reprint requests to T. X.-M.; E-mail: scu_txm@163.com

Z. Naturforsch. **64a,** 507 – 510 (2009); received August 28, 2008 / revised November 10, 2008

Recently, many studies for the local structure of $3d^5$ ions in octahedrally coordinated compounds are made by simulating the EPR parameters on the basis of the complete energy matrix. However, for the $3d^4$ ions in tetrahedrally coordinated compounds, the studies are relatively fewer. In this work, by diagonalizing the complete energy matrix for a d^4configuration in a tetragonal ligand-field within a strong-field representation, the local structure around Cr^{2+} in CdS crystal is studied. Our results show that there exists a compression distortion in the local lattice structure. From our calculations, the distortion parameters $\Delta R = -0.022$ Å and $\Delta\theta = -1.410°$ are obtained.

Key words: Local Structure; Energy Matrix, EPR Parameters.
PACS numbers: 75.10.Dg; 76.30.-v

1. Introduction

It is well known that electron paramagnetic resonance (EPR) is a suitable technique for the study of transition-metal impurities at low concentration levels in compounds. This technique and ligand-field theory have been used to determine the location and charge state of $3d^n$ complexes [1 – 9]. In II-VI and III-V semiconductors, the transition-metal ions, which are often encountered as trace impurities, can strongly affect the optical and electrical properties. So, many works have been made for these impurities in II-VI and III-V semiconductors. For example, the EPR spectra of CdS:Cr^{2+} were reported and the EPR zero-field-splitting parameters a and D were determined by Vallin et al. [5]. The parameter a relates to a fourth-order spin operator and represents a cubic component of the crystalline electric field. The parameter D is associated with the second-order spin operators and represents an axial component of the crystalline electric field. Their results show that CdS:Cr^{2+} system undergoes a Jahn-Teller (JT) distortion, effecting a change in the Cr^{2+} site symmetry from tetrahedral (T_d) to tetragonal (D_{2d}). In their paper, the crystal-field theory and Jahn-Teller coupling are adopted, but confined to the ^5D approximation. Recently, we have studied the spin-singlet contributions to EPR zero-field-splitting parameters [10]. Our results show that the contributions of spin singlets to the zero-field-splitting parameters a and F are very important. So, to get more accurate zero-field-splitting parameters, all spin states ($S = 2$, 1 and 0) should be considered. As is known to us, the EPR spectra are very sensitive to the local lattice structure distortion, so it is reasonable to study the local structure of CdS:Cr^{2+} system by calculating the EPR parameters. In this paper, we shall construct the complete energy matrix (210×210) of d^4 ions in tetragonal symmetry adapted to the double group chain within a strong-field representation, and study the local lattice structure of CdS:Cr^{2+} system by simulating the EPR parameters a and D with the energy matrix. The results are discussed.

2. Theory

The Hamiltonian in tetragonal field can be written as

$$H' = V_e(B,C) + V_c^{A_1}(Dq) + H_{S.O.}(\zeta) + V^{E\theta}(\mu,\delta), \quad (1)$$

where V_e is the electrostatic energy, B and C the Racah parameters; $V_c^{A_1}$ is the cubic component of the crystal-field, Dq the cubic crystal-field parameter; $H_{S.O.}$ is the spin-orbit coupling energy, ζ the spin-orbit coupling

Table 1. The energy matrix of $d^4(D^*_{2\mathrm{d}})$.

$\Gamma''\gamma''$	$\Gamma'\gamma'$
A_2 (23×23)	T_1z (23×23)

$\Gamma''\gamma''$	$\Gamma'\gamma'$
B_2 (27×27)	$T_2\zeta$ (27×27)

$\Gamma''\gamma''$	$\Gamma'\gamma'$	
B_1 (27×27)	A_2 (8×8)	
		$E\varepsilon$ (19×19)

$\Gamma''\gamma''$	$\Gamma'\gamma'$	
A_1 (33×33)	A_1 (14×14)	
		$E\theta$ (19×19)

$\Gamma''\gamma''$	$\Gamma'\gamma'$	
Ex (50×50)	T_1x (23×23)	
		$T_2\xi$ (27×27)

$\Gamma''\gamma''$	$\Gamma'\gamma'$	
Ey (50×50)	T_1y (23×23)	
		$T_2\eta$ (27×27)

parameter, and $V^{E\theta}$ is the tetragonal component of the crystal field, μ and δ the tetragonal distortion parameters.

The d^4 basis functions in a tetragonal symmery ($D^*_{2\mathrm{d}}$) for each irreducible representations Γ'' (i. e. A_1, A_2, E, B_1, B_2) of the double group $D^*_{2\mathrm{d}}(d^4)$ can be constructed with $d^4(O^*_{\mathrm{h}})$ basis functions $|q_i,S\Gamma\Gamma'\gamma'\rangle$ by the formula below:

$$|q_i,S\Gamma\Gamma'\to\Gamma''\gamma''\rangle=\sum_{\gamma'}\langle\Gamma'\gamma'|\Gamma''\gamma''\rangle|q_i,S\Gamma\Gamma'\gamma'\rangle\,, \quad (2)$$

where, $\langle\Gamma'\gamma'|\Gamma''\gamma''\rangle$ are the coupling coefficients. $|q_i,S\Gamma\Gamma'\gamma'\rangle$ for each irreducible representation Γ' (i. e. A_1,A_2,E,T_1,T_2) of the double group $O^*_{\mathrm{h}}(d^4)$ can be got with the Griffith [11] strong-field functions $|q_i,S\Gamma M\gamma'\rangle$ of the point group $O_{\mathrm{h}}(d^4)$ according to the expression

$$|q_i,S\Gamma\Gamma'\gamma'\rangle=\sum_{M\gamma}\langle S\Gamma M\gamma|\Gamma'\gamma'\rangle|q_i,S\Gamma M\gamma\rangle\,, \quad (3)$$

where γ' denotes different components of Γ', q_i stands for the ith strong-field configuration $t_2^n(S_1\Gamma_1)e^m(S_2\Gamma_2)$ in the electrostatic matrix table of Griffith for d^4 configuration. The matrix of Hamiltonian (1) with respect of the 210 $d^4(D^*_{2\mathrm{d}})$ basis functions (2) will be a block diagonal form of six $\Gamma''\gamma''$ blocks. That is, the matrix splits into four one-fold degenerated matrices $A_1(33\times 33)$, $A_2(23\times 23)$, $B_1(27\times 27)$, $B_2(27\times 27)$ and one two-fold degenerated matrix $E(50\times 50)$. In each $\Gamma''\gamma''$ block, the component of $V_{\mathrm{e}}+V_{\mathrm{c}}^{A_1}+H_{\mathrm{S.O.}}$ is a block diagonal form of $\Gamma'\gamma'$ blocks (Table 1), but the matrix elements of $V^{E\theta}$ can be at any position. Finally, each matrix element of the complete energy matrix can be expressed to be a linear combination of B, C, ζ, Dq, μ, δ. The crystal-field parameters can be expressed as

$$\begin{aligned} Dq&=\frac{1}{24}G_4(\tau)\left(10\cos^4\theta-\frac{20}{3}\cos^2\theta-\frac{2}{3}\right),\\ \mu&=\frac{8}{7}G_2(\tau)(3\cos^2\theta-1)\\ &\quad-G_4(\tau)\left(5\cos^4\theta-\frac{110}{21}\cos^2\theta+\frac{25}{21}\right),\\ \delta&=\frac{6}{7}G_2(\tau)(3\cos^2\theta-1)\\ &\quad+G_4(\tau)\left(5\cos^4\theta-\frac{110}{21}\cos^2\theta+\frac{25}{21}\right), \end{aligned} \quad (4)$$

where

$$G_2(\tau)=-\frac{eq_r\langle r^2\rangle}{R^3},\quad G_4(\tau)=-\frac{eq_r\langle r^4\rangle}{R^5}. \quad (5)$$

R and θ denote the Cr-S bond length and angle between Cr-S bond and C_4 axes, respectively, q_r is the charge of ligand, $-e$ is electron charge. With use of (4) and (5), the local structure parameters R and θ can be studied by employing the complete energy matrix.

The EPR spectrum of Cr^{2+} in a tetragonal symmetry field can be analyzed according to the following spin Hamiltonian [12]

$$\begin{aligned} H_{\mathrm{s}}&=D(S_{\mathrm{Z}}^2-2)+\frac{a}{120}(35S_{\mathrm{Z}}^4-155S_{\mathrm{Z}}^2+72)\\ &\quad+\frac{a}{48}(S_+^4+S_-^4)+\frac{F}{180}(35S_{\mathrm{Z}}^4-155S_{\mathrm{Z}}^2+72), \end{aligned} \quad (6)$$

where a, D, and F are just the EPR parameters. By combining the spin functions $|SM\rangle$ for $S=2$, we can construct a set of spin basis functions of the double group $D^*_{2\mathrm{d}}$ for spin Hamiltonian H_{s} as follows:

$$|A_1\rangle=\frac{\mathrm{i}}{\sqrt{2}}(|2-2\rangle-|22\rangle),$$

$$|A_2\rangle=\frac{1}{\sqrt{2}}(|2-2\rangle+|22\rangle),$$

Table 2. The spin-Hamiltonian matrix.

	A_1	A_2	E_x	E_y	B_2
A_1	$2D-\frac{2a}{5}+\frac{F}{15}$	0	0	0	0
A_2	0	$2D+\frac{3a}{5}+\frac{F}{15}$	0	0	0
E_x	0	0	$-D-\frac{2}{5}a-\frac{4}{15}F$	0	0
E_y	0	0	0	$-D-\frac{2}{5}a-\frac{4}{15}F$	0
B_2	0	0	0	0	$-2D+\frac{3}{5}a+\frac{2}{5}F$

$$
\begin{aligned}
|E_x\rangle &= \frac{\mathrm{i}}{\sqrt{2}}\left(|21\rangle + |2-1\rangle\right), \\
|E_y\rangle &= \frac{1}{\sqrt{2}}\left(|21\rangle - |2-1\rangle\right), \\
|B_2\rangle &= |20\rangle .
\end{aligned} \tag{7}
$$

The H_s matrix is presented in Table 2. From this Table, we can get its eigenvalues

$$
\begin{aligned}
E(A_1) &= 2D - \frac{2}{5}a + \frac{F}{15}, \\
E(A_2) &= 2D + \frac{3}{5}a + \frac{F}{15}, \\
E(B_2) &= -2D - \frac{3}{5}a + \frac{2}{5}F, \\
E(E_\gamma) &= -D - \frac{2}{5}a - \frac{4}{15}F \quad (\gamma = x, y).
\end{aligned} \tag{8}
$$

Thus, we have

$$
\begin{aligned}
a &= E(A_2) - E(A_1), \\
D &= -\frac{1}{7}\left(E(E_\gamma) - E(A_1) - E(A_2) + E(B_2)\right), \\
F &= \frac{3}{7}\left(3E(B_2) - 3E(A_2) - 4E(E_\gamma) + 4E(A_1)\right).
\end{aligned} \tag{9}
$$

The eigenvalues can be obtained by diagonalizing the complete energy matrix (210×210) of $d^4(D^*_{2d})$.

3. Calculations and Discussion

If $\theta = \cos^{-1}(1/\sqrt{3})$ in (4) for a cubic approximation, then we have

$$
\begin{aligned}
Dq_0 &= -\frac{2}{27}G_4(\tau)_0, \\
\mu &= 0 \quad \text{and} \quad \delta = 0.
\end{aligned} \tag{10}
$$

In this case, the $G_2(\tau)$ and $G_4(\tau)$ for CdS:Cr^{2+} system can be written as:

$$
\begin{aligned}
G_2(\tau) &= \left(\frac{R_0}{R}\right)^3 G_2(\tau)_0, \\
G_4(\tau) &= \left(\frac{R_0}{R}\right)^5 G_4(\tau)_0.
\end{aligned} \tag{11}
$$

Table 3. The energy levels of the ground state of CdS:Cr^{2+} (in cm^{-1}).

Free Cr^{2+} ion		tetrahedral field (T_d)		tetragonal field (D_{2d})		spin-orbit interactions	
^5D	0	^5E	4070	$^5A_1$	5514.962	A_1	5544.214
						E	5543.017
						B_1	5539.413
						B_2	5539.409
				$^5B_1$	4550.758	A_2	4580.349
						A_1	4580.333
						E	4577.451
						B_1	4576.479
		$^5T_2$	0	^5E	1189.642	E	1326.398
						B_2	1275.953
						B_1	1255.124
						E	1207.291
						A_2	1160.155
						A_1	1140.309
						E	1092.631
				$^5B_2$	0	B_2	7.330
						E	5.463
						A_2	0.159
						A_1	0

The ratio $G_2(\tau)_0/G_4(\tau)_0$ can be estimated from the radial wave function [13] as well as (5), and we estimate the ratio $G_2(\tau)_0/G_4(\tau)_0 = 2.768$. The $G_4(\tau)_0$ can be obtained from the cubic ligand-field parameter Dq_0 by $G_4(\tau)_0 = -\frac{27}{2}Dq_0$. Thus, if Racah parameters B, C, and spin-orbit parameter ζ are known, the local structure parameters R and θ can be studied with the energy matrix. Unfortunately, for CdS:Cr^{2+} system, only the cubic field parameter $Dq_0 = -407.0\ cm^{-1}$ can be obtained from the optical spectrum because only the transition $^5T_2 \rightarrow ^5E$ is obtained [5]. For Racah parameters B, C, and spin-orbit parameter ζ, we use approximately the values $B = 500\ cm^{-1}$, $C = 2850\ cm^{-1}$, and $\zeta = 223.6\ cm^{-1}$ of ZnS:Cr^{2+} here [14, 15], because the tetrahedral sites of Cr^{2+} in the two crystals have the same $(CrS_4)^{6-}$ group and similar cation-ligand distance. The calculated energy levels of the ground state of CdS:Cr^{2+} are listed in Table 3. The local lattice structure around the Cr^{2+} displays a tetragonal distortion. This distortion can be described by employing the two parameters ΔR and $\Delta\theta$. If one uses R_0 and θ_0 to

Table 4. The EPR parameters for CdS:Cr^{2+} system as a function of ΔR and $\Delta\theta$.

ΔR (Å)	$\Delta\theta$ (deg)	$a\,(\mathrm{cm}^{-1})$	$D\,(\mathrm{cm}^{-1})$	$F\,(\mathrm{cm}^{-1})$
	1.0	0.3	−1.192	−0.258
−0.01	1.410	0.164	−1.836	−0.148
	1.820	0.108	−2.206	−0.102
	1.0	0.289	−1.166	−0.247
−0.022	**1.410**	**0.159**	**−1.805**	**−0.145**
	1.820	0.105	−2.172	−0.100
	1.0	0.273	−1.130	−0.234
−0.04	1.410	0.151	−1.762	−0.140
	1.820	0.101	−2.123	−0.098
	1.0	0.243	−1.066	−0.213
−0.08	1.410	0.137	−1.680	−0.13
	1.820	0.092	−2.028	−0.092
	1.0	0.218	−1.021	−0.194
−0.12	1.410	0.125	−1.616	−0.122
	1.820	0.085	−1.951	−0.087
Exp. [5]		**0.150**	**−1.805**	

represent the Cd-S bond length and the angle between Cd-S bond and C_4 axes of the host crystal CdS, respectively, then the local structure parameters R and θ for CdS:Cr^{2+} system may be expressed as

$$R = R_0 + \Delta R, \qquad \theta = \theta_0 + \Delta\theta. \tag{12}$$

Thus, the relationship between the distortion of local lattice structure of CdS:Cr^{2+} system and the EPR parameters can be studied by diagonalizing the complete energy matrix. We finally obtained the EPR ground-state zero-field splitting by adjusting the parameters ΔR and $\Delta\theta$. The results are listed in Table 4.

From Table 4 we can see that the experimental findings of EPR parameters can be satisfactorily explained for the distortion parameters $\Delta R = -0.022$ Å and $\Delta\theta = 1.410°$. $\Delta R < 0$ indicates that the local lattice structure of CdS:Cr^{2+} system has a compression distortion. The compression distortion may be ascribed to the fact that the radius of the Cr^{2+} ion ($r = 0.89$ Å) is smaller than that of Cd^{2+} ions ($r = 0.97$ Å) [16].

4. Conclusion

The local lattice structure for the CdS:Cr^{2+} system has been studied by simulating the EPR parameters with the complete energy matrix for d^4 configuration ion in a tetragonal ligand-field. From the above studies, we can find that the EPR parameters a and D for Cr^{2+} in CdS crystal can be satisfactorily explained by considering the suitable local lattice distortions. The results show that the local lattice structure of CdS:Cr^{2+} system has a compression distortion when the Cr^{2+} ion is doped into CdS crystal. It is known that the radius of Cr^{2+} ion is smaller than that of Cd^{2+} ions. Then, the Cr^{2+} ion would pull the sulfur ligands downwards and upwards, respectively. From our calculation, the local lattice structure parameters $R = 2.498$ Å and $\theta = 56.146°$ for Cr^{2+} in CdS have been determined.

Acknowledgements

This work was supported by the Research Foundation of Ludong University (LY20072801) of China.

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