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Theoretical investigation of local structure distortion and absorption spectra for tetragonal Cr^{2+} ion in ZnSe:Cr^{2+} system

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Abstract

By analyzing the zero-field-splitting parameters a and D of Cr^{2+} ($3d^4$) ion located at tetrahedral site in ZnSe crystal, the local structure distortion and absorption spectra around Cr^{2+} in ZnSe: Cr^{2+} system have been calculated on the basis of the complete energy matrix for the d^4 configuration within the strong-filed-representation. It is shown that there exists an expansion distortion in the local lattice structure when Cr^{2+} ion is doped into ZnSe crystal. From our calculations, the distortion parameters $\Delta R = 0.20\,\mathring{A}$ and $\Delta\theta = 3.4^\circ$ are determined.

Keywords: Local structure; absorption spectra; strong-filed-representation; ZnSe: Cr^{2+}

1. Introduction

Compounds doped with transition metal and rare earth ions have attracted significant attention for potential applications in the commercial, medical and military fields, because they can emit mid-infrared (mid-IR) lasers and have good electron transport properties (Vivet, 2010; Min, 2011; Colibaba, 2009; Bluiett, 2002; Mckay, 1999). Among these compounds, ZnSe crystal doped with Cr^{2+} ion (ZnSe:Cr^{2+}) is one of the most important materials, because it is a good candidate for widely-tunable, diode-pumpable and single-frequency mid-IR lasers which are capable of operating at room temperature and lasing in the 2000-3000 nm range (Su, 1999; Kim, 2009; Demirbas, 2006). At the same time, ZnSe: Cr^{2+} has the highest optical quality and lowest losses (Page, 1997). Because the properties of the Cr^{2+} ion, such as the radius and the charge, are different from that of the Zn^{2+} ion, the local lattice structure around the Cr^{2+} ion should be different from that around the Zn^{2+} ion in the ZnSe: Cr^{2+} system. The lasing center has been assigned to Cr^{2+} ions occupying the tetrahedral cation Zn^{2+} lattice sites with tetragonal (D_{2d}) symmetry. The doped Cr^{2+} ions strongly influence the optical properties of the system (Hommerich, 2006; Sorikina, 2004; Ivanov, 2001). In order to understand the influence of Cr^{2+} ions on the properties of ZnSe: Cr^{2+} system, the local lattice structure around Cr^{2+} ion should be determined. Many works have been successfully done to determine the local properties of the crystals doped with the transition metal ions by the full energy matrix (Li, 2010; Tan, 2009) and the high-order perturbation formulas (Lin, 2013). Since the EPR zero-field-splitting (ZFS) parameters of a paramagnetic ion in crystals are very sensitive to the local structure distortion (Lakshmikantha, 2012), we can determine the local structure around the transition-metal ions in crystals by analyzing the ZFS parameters. The ZFS parameters of ZnSe: Cr^{2+} system have been studied by Zhou (1996). However, in that work, the calculations are not complete because the spin singlets are not considered. In this paper, the local lattice structure and optical absorption spectra of ZnSe: Cr^{2+} system are studied by simulating the ZFS parameters with the complete energy matrix including all the spin states of a d^4 configuration ion in tetragonal symmetry within the strong-filed-representation.

2. Theoretical Model

The ZFS Hamiltonian of Cr^{2+} in a tetrahedral D_{2d} field can be studied in terms of the following expression (Kaufmann, 1976),

$$H_{ZFS} = D(S_Z^2 - 2) + \frac{a}{120}(35S_Z^4 - 155S_Z^2 + 72) + \frac{a}{48}(S_+^4 + S_-^4) + \frac{F}{180}(35S_Z^4 - 155S_Z^2 + 72) \quad (1)$$

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where a, D, F are the ZFS parameters. Its eigenvalues E_i can be expressed as follows,

$$E_1 = 2D - \frac{2}{5}a + \frac{F}{15}$$
$$E_2 = 2D + \frac{3}{5}a + \frac{F}{15}$$
$$E_3 = -D - \frac{2}{5}a - \frac{4}{15}F$$
$$E_4 = -2D + \frac{3}{5}a + \frac{2}{5}F \qquad (2)$$

Thus we have,

$$a = E_2 - E_1$$
$$D = -\frac{1}{7}(E_3 - E_1 - E_2 + E_4)$$
$$F = \frac{3}{7}(3E_4 - 3E_2 - 4E_3 + 4E_1) \qquad (3)$$

The values of E_i can be obtained by diagonalizing the complete energy matrix of the $d^4(D_{2d}^*)$ system.

The Hamiltonian in tetrahedral D_{2d} crystal field can be written as

$$H' = V_e(B,C) + V_c^A(Dq) + H_{S.O.}(\zeta) + V^{E\theta}(\mu,\delta) \quad (4)$$

where V_e is the electrostatic energy and B, C are the Racah parameters. V_c^A is the cubic component of the crystal field and Dq is the cubic crystal field parameter. $H_{S.O.}$ is the spin-orbit coupling energy and ζ is the spin-orbit coupling parameter. $V^{E\theta}$ is the tetragonal component of the crystal field and μ, δ are the tetragonal distortion parameters.

The d^4 (D_{2d}^*) basis functions including all spin states for each irreducible representations Γ'' (i.e. A_1, A_2, E, B_1, B_2) of the double group $D_{2d}^*(d^4)$ have been constructed with $d^4(T_d^*)$ basis functions $|q_i, S\Gamma\Gamma'\gamma'\rangle$ by the formula below,

$$|q_i, S\Gamma\Gamma' \to \Gamma''\gamma''\rangle = \sum_{\gamma'} \langle \Gamma'\gamma' | \Gamma''\gamma'' \rangle |q_i, S\Gamma\Gamma'\gamma'\rangle \quad (5)$$

where, $\langle \Gamma'\gamma' | \Gamma''\gamma'' \rangle$ is the coupling coefficient. $d^4(T_d^*)$ basis functions $|q_i, S\Gamma\Gamma'\gamma'\rangle$ for each irreducible representation Γ' (i.e. A_1, A_2, E, T_1, T_2) of the double group $T_d^*(d^4)$ can be obtained with the Griffith (2009) strong-field functions $|q_i, S\Gamma M\gamma\rangle$ of the point group $T_d(d^4)$ according to the expression

$$|q_i, S\Gamma\Gamma'\gamma'\rangle = \sum_{M\gamma} \langle S\Gamma M\gamma | \Gamma'\gamma' \rangle |q_i, S\Gamma M\gamma\rangle \quad (6)$$

where γ' denotes different components of Γ'. q_i represents 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 (Eq. 4) with respect to the 210 $d^4(D_{2d}^*)$ basis functions (Eq.5) will be a diagonal-block form of six $\Gamma''\gamma''$ blocks. That is, the matrix splits into four nondegenerated matrices $A_1(33\times33)$, $A_2(23\times23)$, $B_1(27\times27)$, $B_2(27\times27)$, one two-fold degenerated matrix $E(50\times50)$. In each $\Gamma''\gamma''$ block, the component of $V_e + V_c^A + H_{S.O.}$ is a $\Gamma'\gamma'$ diagonal-block form, 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 as a linear combination of $B, C, \zeta, Dq, \mu, \delta$. The crystal field parameters can be expressed as follows,

$$Dq = \frac{1}{24}G_4(\tau)(10\cos^4\theta - \frac{20}{3}\cos^2\theta - \frac{2}{3})$$
$$\mu = -\frac{8}{7}G_2(\tau)(3\cos^2\theta - 1) - G_4(\tau)(5\cos^4\theta - \frac{110}{21}\cos^2\theta + \frac{25}{21})$$
$$\delta = -\frac{6}{7}G_2(\tau)(3\cos^2\theta - 1) + G_4(\tau)(5\cos^4\theta - \frac{110}{21}\cos^2\theta + \frac{25}{21}) \qquad (7)$$

where,

$$G_2(\tau) = -\frac{eq_\tau \langle r^2 \rangle}{R^3}$$
$$G_4(\tau) = -\frac{eq_\tau \langle r^4 \rangle}{R^5} \qquad (8)$$

R and θ denote the Cr-Se bond length and angle between Cr-Se bond and C$_4$ axes, respectively. q_τ is the charge of ligand and $-e$ is electron charge.

3. Calculations and Discussions

The local lattice structure around the Cr^{2+} displays a tetragonal distortion in ZnSe: Cr^{2+} system, shown in Fig. 1.

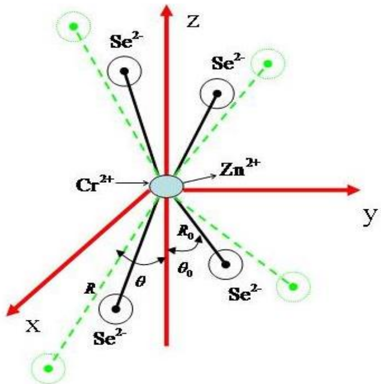

Fig. 1. The local structure distortion of ZnSe: Cr^{2+} system around Cr^{2+} ion. R and θ represent the Cr-Se bond length and angle between Cr-Se bond and Z axis. R_0 and θ_0 denote the Zn-Se bond length and angle between Zn-Se bond and Z axis of the un-doped ZnSe crystal

The tetragonal distortion can be described by two parameters ΔR and $\Delta\theta$. The local structure parameters R and θ around Cr^{2+} ion for ZnSe: Cr^{2+} system may be expressed as

$$R = R_0 + \Delta R$$
$$\theta = \theta_0 + \Delta\theta \tag{9}$$

The Zn-Se bond length and the angle between Zn-Se bond and C$_4$ axes of the host crystal ZnSe are $R_0 = 2.45\,\overset{\circ}{\mathrm{A}}$ and $\theta_0 = 54.7356^\circ$ (Wyckoff, 2011), respectively. If $\theta = \cos^{-1}(1/\sqrt{3})$ in Eq. (7) for a cubic approximation, then we have

$$Dq_0 = -\frac{2}{27} G_4(\tau)_0$$
$$\mu = 0 \text{ and } \delta = 0 \tag{10}$$

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

$$G_2(\tau) = (\frac{R_0}{R})^3 G_2(\tau)_0$$
$$G_4(\tau) = (\frac{R_0}{R})^5 G_4(\tau)_0 \tag{11}$$

The ratio $G_2(\tau)_0 / G_4(\tau)_0$ can be calculated from the radial wave function (Zhao, 2000) as well as Eq. (8), and we estimate the ratio $G_2(\tau)_0 / G_4(\tau)_0 = 2.6161$. The $G_4(\tau)_0$ can be obtained from the cubic ligand-field parameter Dq_0 by $G_4(\tau)_0 = -\frac{27}{2} Dq_0$. By the above complete energy matrix, we have fitted the experimental spectra (Grebe, 1976) of ZnSe: Cr^{2+} in a cubic approximation and got $Dq_0 = -552.5 cm^{-1}$, $B = 500 cm^{-1}$, $C = 3060 cm^{-1}$ shown in Table 1, which are in good agreement with the available experimental results.

Table 1. The absorption spectra of ZnSe: Cr^{2+} system (in cm^{-1})

Our results		Expt. (Grebe, 1976)	
$^5T_2$	0	$^5T_2$	0
^5E	5525	^5E	5525
$^3T_1$	10600	$^3T_1$	11500
$^3T_2$	12487	$^3T_2$	12950
$^3T_1$	14935	$^3T_1$	14950
$^3T_2$	15680		
^3E	16492	^3E	16400
$^3T_1$	17023	$^3T_1$	17000
$^3T_2$	18918		
^3E	20722		
$^3A_2$	20732		
$^3T_1$	20821		
$^3A_1$	22265		
$^3T_2$	22722		
$^3T_1$	24282		
^3E	25056		
$^3A_2$	34453		
$^3T_1$	35301		
$^3T_2$	36599		
$^3T_1$	38152		

Finally, we can obtain the ground-state ZFS parameters by adjusting the parameters ΔR, $\Delta\theta$ and ζ ($\zeta < \zeta_0$, where $\zeta_0 = 230cm^{-1}$ for a free Cr^{2+} ion (Griffith, 2009), as can be seen in Table 2.

It can be seen from Table 2 that the experimental results of ZFS parameters can be satisfactorily explained for the distortion parameters $\Delta R = 0.20\,\mathring{A}$, $\Delta\theta = 3.4^\circ$ at $\zeta = 206cm^{-1}$. Our calculations show that the sign of a is positive. We think it is reasonable as the experimental value of a for the similar ZnS: Cr^{2+} system is also positive (Vallin, 1974). The $\Delta R > 0$ indicates that the local lattice structure of ZnSe: Cr^{2+} system has an expansion distortion. The expansion distortion may be ascribed to the fact that the radius of Cr^{2+} ion ($r = 0.89\,\mathring{A}$) is bigger than that of Zn^{2+} ions ($r = 0.74\,\mathring{A}$) (Zhou, 2002). From our calculation, the local lattice structure parameters $R = 2.65\,\mathring{A}$, $\theta = 58.1356^\circ$ for Cr^{2+} in ZnSe have been determined.

In order to investigate the spin-singlet contributions to the ZFS parameters of ZnSe: Cr^{2+} system, the ratios

$$r_a = \left|\frac{a - a'}{a}\right|,\ r_D = \left|\frac{D - D'}{D}\right|,\ r_F = \left|\frac{F - F'}{F}\right| \tag{12}$$

versus a, D, F are calculated and plotted in Fig. 2. Where, a, D, F are the ZFS parameters considering all the spin states, and a', D', F' neglecting the spin singlets. Obviously, the larger the ratio r, the larger the spin-singlet contributions are.

Table 2. The ZFS parameters a, D and F for ZnSe:Cr^{2+} system as a function of ΔR, $\Delta\theta$ and ζ for $Dq_0 = -552.5cm^{-1}$, $B = 500cm^{-1}$, $C = 3060cm^{-1}$

$\zeta(cm^{-1})$	$\Delta R(\mathring{A})$	$\Delta\theta$(deg)	$a(cm^{-1})$	$D(cm^{-1})$	$F(cm^{-1})$
190	0.08	1.60	0.048	-1.29	-0.043
	0.10	2.0	0.036	-1.53	-0.034
	0.14	2.6	0.027	-1.79	-0.026
	0.16	3.2	0.021	-1.94	-0.021
	0.20	3.4	0.021	-2.07	-0.193
206	0.08	1.60	0.068	-1.54	-0.064
	0.10	2.0	0.05	-1.81	-0.048
	0.14	2.6	0.037	-2.12	-0.034
	0.16	3.2	0.029	-2.29	-0.027
	0.20	**3.4**	**0.029**	**-2.44**	**-0.026**
216	0.08	1.60	0.082	-1.71	-0.078
	0.10	2.0	0.061	-2.01	-0.060
	0.14	2.6	0.046	-2.34	-0.044
	0.16	3.2	0.036	-2.52	-0.035
	0.20	3.4	0.036	-2.69	-0.033
Expt. (Valin, 1974)			±0.024	-2.48	---
Expt. (Kramushchenko, 2013)			---	-2.48	---

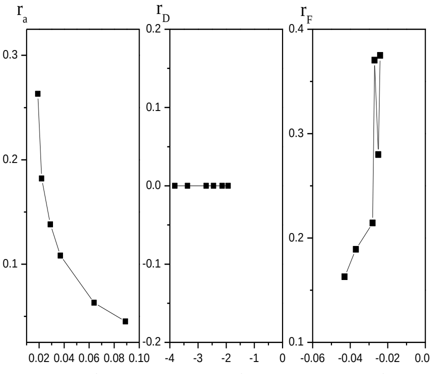

Fig. 2. Variation of ratio r with a, D and F

From this figure, we can see that r_a decreases gradually along with the increasing of a. r_F fluctuates with the increasing of F, and r_D is independent of the change of D. It can also be seen that r_D is always zero, which shows that the spin-singlet contribution to D is negligible. However, r_a and r_F are comparatively large. For instance, when $a = 0.022cm^{-1}, r_a = 0.182$ and $F = -0.025cm^{-1}$, $r_F = 0.28$, which shows that the contributions of the spin singlets to a and F are important. The contributions arise from the interaction of the spin quintuplets with both the spin triplets and the spin singlets via the spin-orbit coupling. However, the selection rule of spin-orbit coupling shows that the spin singlets do not affect the quintuplets directly but indirectly via the spin triplets.

4. Conclusions

The local lattice structure around Cr^{2+} ion in ZnSe: Cr^{2+} system has been determined by simulating the zero-field-splitting parameters a, D and F with the complete energy matrix in the strong-field scheme. From the calculations, we have the following conclusions:

(1) The local structure around Cr^{2+} ion has an expansion distortion when it is doped into ZnSe crystal. The distortion parameters $\Delta R = 0.20\,\mathring{A}$ and $\Delta\theta = 3.4^{\circ}$ have been determined.

(2) The sign of a for ZnSe: Cr^{2+} system is positive.

(3) The value of F for ZnSe: Cr^{2+} system is presented in theory for the first time. However, there is no experimental value of F in the present, so we hope it can be measured as soon as possible.

(4) The spin-singlet contribution to D is negligible, but the contributions to a and F are important for ZnSe: Cr^{2+} system.

The present results may provide a reference for further experimental studies of the crystals doped with transition-metal ions. Of course, more experimental and theoretical investigations are needed to elucidate the present results.

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