Zero-field splitting parameters and local structures for tetragonal Cr^{2+} centers in Cr^{2+}-doped ZnSe semiconductors*

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The inter-relation between zero-field splitting (ZFS) parameters and local lattice structures of the $(CrSe_4)^{6-}$ clusters in ZnSe semiconductors has been established by using the complete diagonalization (of the energy matrix) method. On the basis of this, the local lattice distortions, the ZFS parameters D, a, F and the optical spectrum for Cr^{2+} ions doped into ZnSe are theoretically investigated, and the contributions of the spin singlets have been taken into account. The calculated ZFS parameters are in good agreement with the experimental values. From our calculations, the tetragonal distortion parameters $\Delta R = 0.091$Å and $\Delta\theta = 4.28°$ of Cr^{2+} in ZnSe are acquired, and the results suggest that there exists a tetragonal expansion distortion for the local lattice structure of $(CrSe_4)^{6-}$ clusters in ZnSe crystals. The influence of the spin singlets on ZFS parameters is also discussed, indicating that the contributions to ZFS parameters a and F cannot be ignored.

Keywords: zero-field splitting parameters, optical spectroscopy, local lattice structure, Cr^{2+}-doped ZnSe complex system

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1. Introduction

The ZnSe semiconductor doped with Cr^{2+} is one of the most promising complexes, with many attractive spectroscopic properties, laser properties, and nonlinear optical properties, and thus has been widely used in, e.g., optoelectronic and spintronic devices.[1–11] In general, the above properties or behaviors are closely related to the local lattice structures and electronic states of the doped transition-metal impurities, which can be analyzed by means of the electron paramagnetic resonance (EPR) technique. EPR is recognized as a powerful tool to investigate the local lattice structures. Therefore, simulation of the EPR spectra of materials with transition-metal dopants would be helpful to understand their properties.[12–15] As is well known, EPR experiments have been carried out for Cr^{2+} doped in ZnSe semiconductors by Wit *et al.*[16] and Vallin *et al.*[17] They have obtained, respectively, $|a| = 0.024$ cm^{-1} and $D = -2.48$ cm^{-1}. However, F has been assumed to be zero in their analysis. Actually, F is not equal to zero and we will estimate its value using our method. Since the ZFS parameters of an impurity ion in a crystal are sensitive to its immediate local environment, some useful information on local lattice structures for the tetragonal Cr^{2+} centers can be acquired from the EPR analysis. Accordingly, the theoretical studies of the ZFS parameters for Cr^{2+} in ZnSe are of significance. Zhou and co-workers[18] have studied the ZFS parameters of the Cr^{2+}-doped ZnSe complex system based on the (160×160)-dimensional energy matrix in which the spin singlets are neglected. Nevertheless, it is still insufficient to have a comprehensive understanding of the information about the Cr^{2+} centers in ZnSe crystals, because the spin-singlet states can affect the fine structure splitting of the ground state, i.e. have an influence on the ZFS parameters of the ground state.

The present article is aimed at investigating the local lattice structures of the tetragonal Cr^{2+} centers in ZnSe by simulating the experimental ZFS parameters and optical spectrum. By diagonalizing the complete energy matrix (210×210) including all the spin states, the local lattice distortion is determined. Simultaneously, the effect of the spin singlets on ZFS parameters a, D, and F for the ground orbital singlet is also studied. The calculated ZFS parameters show good agreement with the observed values. In addition, information related to a and F is also obtained and expected to be confirmed by experiments. The results are discussed.

2. Basic theory and calculations

ZnSe crystallizes in the zincblende structure, in which the Zn^{2+} ion is surrounded by four Se^{2-} ions. Its local lattice structure parameters are $R_0 = 2.45$ Å and $\theta_0 = 54.7356°$ (R_0 and θ_0 represent the Zn–Se bond length and the angle between the Zn–Se bond and the C_4 axis of the host crystal ZnSe).[19] When Cr^{2+} ions are doped into ZnSe crystals, they usually occupy the host Zn^{2+} sites and $(CrSe_4)^{6-}$ clusters with D_{2d} point group symmetry are formed, suggesting that the local lattice

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structure exhibits a tetragonal distortion which is often characterized by two parameters ΔR and $\Delta\theta$ (see Fig. 1). Thus, the local lattice structure parameters R and θ for the Cr^{2+}-doped ZnSe complex system may be expressed as

$$R = R_0 + \Delta R, \quad \theta = \theta_0 + \Delta\theta. \tag{1}$$

The ZFS parameters of Cr^{2+} centers in ZnSe crystals are calculated using the microscopic spin Hamiltonian theory. The effective spin Hamiltonian for tetragonal $(CrSe_4)^{6-}$ clusters under zero magnetic field interaction can be expressed as[20]

$$\begin{aligned} H_S &= D(S_Z^2 - 2) + \frac{a}{120}(35S_Z^4 - 155S_Z^2 + 72) \\ &\quad + \frac{a}{48}(S_+^4 + S_-^4) + \frac{F}{180}(35S_Z^4 - 155S_Z^2 + 72), \end{aligned} \tag{2}$$

where a, D, and F are so-called ZFS parameters. a relates to a fourth-order spin operator and represents the cubic ZFS parameter; D and F are, respectively, concerned with the second- and fourth-order spin operators and stand for axial ZFS parameters.

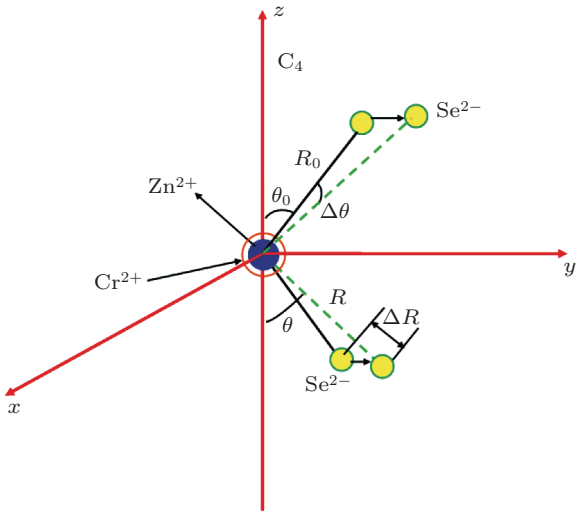


Fig. 1. (color online) Local lattice structure distortion of Cr^{2+}-doped ZnSe complex system.

Diagonalizing the matrix corresponding to the above spin Hamiltonian under the ground state, the ZFS parameters are expressed as follows:

$$\begin{aligned} &a = E_2 - E_1, \quad D = -\frac{1}{7}(E_3 - E_1 - E_2 + E_4), \\ &F = \frac{3}{7}(3E_4 - 3E_2 - 4E_3 + 4E_1), \end{aligned} \tag{3}$$

where E_i $(i = 1, \ldots, 4)$ are the fine structure energy levels of the ground orbital singlet split, which can be acquired by diagonalizing the complete energy matrix.

In the crystal field framework, the perturbation Hamiltonian of a $3d^4$ ion in a tetragonal crystal field has the following form:

$$H = V_e(B, C) + H_{s.o.}(\zeta) + V_{CF}(Dq, \delta, \mu), \tag{4}$$

where the three terms represent, respectively, the electrostatic Coulomb interaction, the spin–orbit coupling interaction, and the crystal field interaction.

Based on the strong field basis functions of Griffith,[21] the 210×210 complete energy matrix for a $3d^4$ configuration ion corresponding to the above Hamiltonian is constructed.[22] Diagonalization of the complete energy matrix yields the energy levels and eigenvectors as functions of the Racah parameters B and C, spin–orbit coupling coefficient ζ, and crystal field parameters Dq, μ, and δ. The crystal field parameters, which depend upon the local lattice structure of the impurity center, can be expressed as follows:

$$\begin{aligned} Dq &= \frac{A_4}{24R^5}\left(10\cos^4\theta - \frac{20}{3}\cos^2\theta - \frac{2}{3}\right), \\ \mu &= -\frac{8A_2}{7R^3}\left(3\cos^2\theta - 1\right) \\ &\quad - \frac{A_4}{R^5}\left(5\cos^4\theta - \frac{110}{21}\cos^2\theta + \frac{25}{21}\right), \\ \delta &= -\frac{6A_2}{7R^3}\left(3\cos^2\theta - 1\right) \\ &\quad + \frac{A_4}{R^5}\left(5\cos^4\theta - \frac{110}{21}\cos^2\theta + \frac{25}{21}\right), \end{aligned} \tag{5}$$

where $A_2 = -eq_\tau\langle r^2\rangle$, and $A_4 = -eq_\tau\langle r^4\rangle$.

Taking $\theta = \cos^{-1}(1/\sqrt{3})$ in Eq. (5) for the cubic approximant, we have

$$Dq_0 = -\frac{2A_4}{27R_0^5}, \quad \mu = 0, \quad \delta = 0. \tag{6}$$

The ratio $\langle r^2\rangle/\langle r^4\rangle = A_2/A_4 = 0.12205$ can be obtained from the radial wave function.[23] A_4 is almost a constant for the $(CrSe_4)^{6-}$ tetragonal cluster, and its value can be estimated from the cubic crystal field parameter Dq by employing the expression $Dq_0 = -2A_4/27R_0^5$. Grebe *et al.*[24] have fitted the spectra of the Cr^{2+}-doped ZnSe complex system for a cubic approximant and obtained $Dq_0 = -480$ cm^{-1}, $B = 510$ cm^{-1}, and $C = 3053$ cm^{-1}. On this basis, we obtain $A_4 = 62.8064$ a.u. and $A_2 = 7.6655$ a.u. The optical spectra can be determined by employing the above parameters. The calculated energy levels are listed in Table 1, together with the experimental values. One can see that the calculated values are in a good agreement with the experimental data. Thereby, the above parameters are reasonable for the following calculations.

Additionally, owing to the sensitivity of the spin–orbit coupling coefficient ζ in the calculations, ζ is considered as an adjustable parameter to obtain more accurate calculated results. Therefore, the calculated ZFS parameters of Cr^{2+} ions in ZnSe crystals are finally obtained by adjusting parameters ΔR, $\Delta\theta$, and ζ. The results are presented and compared with the observed values in Table 2.

Table 1. Experimental and theoretical energy levels of ZnSe:Cr^{2+} (in units of cm^{-1}).

	$^5T_{2g}(^5D)$	$^5E_g(^5D)$	$^3T_{1g}(^3H)$	$^3T_{2g}(^3H)$	$^3T_{1g}(^3H)$	$^3T_{2g}(^3F)$	$^3E_g(^3H)$	$^3T_{1g}(^3F)$
Cal.	0	4800	11233	12950	14949	15777	16429	17003
Obsd.[24]	0	5525	11500	12950	14950	–	16400	17000

3. Results and analysis

3.1. Local lattice structure distortion of Cr^{2+}-doped ZnSe system

As can be seen from Table 2, the calculated results are consistent with the observed values and the experimental ZFS parameters can be satisfactorily explained using the lattice distortion parameters: $\Delta R = 0.091$ Å, $\Delta\theta = 4.28^\circ$ with $\zeta = 210.6$ cm^{-1}. Simultaneously, we also obtain that the sign of a is positive and the value of F is equal to -0.0239. Comparing with the similar $(CrS_4)^{6-}$ clusters in Cr^{2+}-doped II–VI semiconductors, the above results can be regarded as reasonable. $\Delta R > 0$ and $\Delta\theta > 0$ indicate that the local lattice structure around the tetragonal Cr^{2+} center in the ZnSe semiconductor has an expansion distortion. This distortion may be partly ascribed to the fact that the radius of Cr^{2+} ion ($r = 0.89$ Å) is larger than that of Zn^{2+} ($r = 0.74$ Å).[25] As a result of this, four Se^{2-} ions are pushed upwards and downwards by the central Cr^{2+} ion. Consequently, this tetragonal distortion can be considered as reasonable from the above point of view. Simultaneously, the calculated results also confirm that some useful information on the local lattice structure of $3d^n$ impurity center in crystals (which is different from the corresponding structure in the host crystals) can be acquired by analyzing the optical and EPR spectra. From the above calculations, the local lattice structure parameters $R = 2.541$ Å and $\theta = 59.0156^\circ$ of the impurity ion Cr^{2+} in the ZnSe crystal are estimated.

Table 2. The ZFS parameters of the Cr^{2+}-doped ZnSe system as a function of ζ, ΔR, and $\Delta\theta$. In the calculations, $Dq_0 = -480$ cm^{-1}, $B = 510$ cm^{-1}, and $C = 3053$ cm^{-1}. a, D, F, considering all the spin states; a', D', F', neglecting the spin-singlet states.

ζ/cm^{-1}	ΔR/Å	$\Delta\theta$/(°)	a/cm^{-1}	D/cm^{-1}	F/cm^{-1}	a'/cm^{-1}	D'/cm^{-1}	F'/cm^{-1}
205	0.06	4.7	0.0187	–2.265	-0.0199	0.0147	–2.265	–0.0126
	0.08	4.5	0.0201	–2.318	–0.0204	0.0165	–2.318	–0.0141
	0.091	4.28	0.0216	–2.343	–0.0214	0.0180	–2.342	–0.0148
	0.11	4.0	0.0240	–2.387	–0.0227	0.0201	–2.386	–0.0157
	0.13	3.8	0.0265	–2.438	–0.0242	0.0222	–2.437	–0.0168
210.6	0.06	4.7	0.0208	–2.393	–0.0220	0.0166	–2.392	–0.0144
	0.08	4.5	0.0224	–2.449	–0.0229	0.0185	–2.448	–0.0157
	0.091	**4.28**	**0.0241**	**–2.475**	**–0.0239**	0.0196	–2.474	–0.0160
	0.11	4.0	0.0269	–2.522	–0.0257	0.0226	–2.521	–0.0178
	0.13	3.8	0.0296	–2.576	–0.0269	0.0255	–2.575	–0.0195
215	0.06	4.7	0.0227	–2.495	–0.0241	0.0179	–2.495	–0.0154
	0.08	4.5	0.0244	–2.554	–0.0249	0.0185	–2.553	–0.0147
	0.091	4.28	0.0262	–2.581	–0.0258	0.0210	–2.581	–0.0168
	0.11	4.0	0.0293	–2.631	–0.0279	0.0244	–2.630	–0.0193
	0.13	3.8	0.0323	–2.687	–0.0295	0.0266	–2.687	–0.0198
Expt.			|0.024|	–2.48				

3.2. Contributions of spin singlets to the ZFS of the Cr^{2+}-doped ZnSe complex system

To illustrate the contributions of the spin singlets to the ZFS parameters of the Cr^{2+}-doped ZnSe complex system, the following ratios are defined:

$$r_a = \left|\frac{a-a'}{a}\right|, \quad r_D = \left|\frac{D-D'}{D}\right|, \quad r_F = \left|\frac{F-F'}{F}\right|, \qquad (7)$$

where a, D, and F are the ZFS parameters taking into account all the spin states, and a', D', and F' are those neglecting the spin singlets. Based on complete diagonalization (of the energy matrix), the theoretical results of the contributions from the spin singlets to the ZFS parameters are given in Table 3. From Table 3, it can be seen that the effect of the spin singlets on the rank-4 ZFS parameters is larger than that on the rank-2 one. In other words, the spin singlets have almost no influence on the second-order ZFS parameter D. However, the contributions of the spin singlets to a and F cannot be neglected. The results are different from those of Rudowicz *et al.*[26], who think the contributions of the spin-singlet states of $3d^4$ or $3d^6$ at the tetragonal symmetry sites to the ZFS parameters are negligible. Moreover, the calculated results obviously suggest that the larger the ratio r, the more the spin singlets contribute to ZFS parameters. Therefore, this implies a situation worthy of attention: the effect of the spin singlets on the ZFS should be taken into account to obtain more accurate and reasonable calculated ZFS parameters.

Table 3. Spin-singlet state contributions to the ZFS parameters a, D, and F.

ζ/cm^{-1}	ΔR/Å	$\Delta\theta$/(°)	r_a	r_D	r_F
205	0.06	4.7	0.214	0.0000	0.367
	0.08	4.5	0.179	0.0000	0.309
	0.091	4.28	0.167	0.0004	0.308
	0.11	4.0	0.163	0.0004	0.304
	0.13	3.8	0.162	0.0004	0.292
210.6	0.06	4.7	0.202	0.0004	0.345
	0.08	4.5	0.174	0.0004	0.314
	0.091	**4.28**	0.167	0.0004	0.331
	0.11	4.0	0.160	0.0004	0.307
	0.13	3.8	0.139	0.0004	0.275
215	0.06	4.7	0.211	0.0000	0.361
	0.08	4.5	0.204	0.0004	0.401
	0.091	4.28	0.198	0.0000	0.349
	0.11	4.0	0.167	0.0004	0.308
	0.13	3.8	0.156	0.0000	0.329

4. Conclusions

Employing the complete diagonalization (of the energy matrix) method, the local lattice structures around Cr^{2+} centers in the ZnSe crystal are theoretically investigated so as to determine the characteristics of the local lattice distortion. Through the above analysis, we can draw the following conclusions. (i) The local lattice distortion parameters $\Delta R = 0.091$ Å and $\Delta\theta = 4.28°$ around the Cr^{2+} centers are determined. This suggests that the local lattice structures of the tetragonal Cr^{2+} centers in ZnSe crystals have a tetragonal expansion distortion, which may be partly attributed to the mismatch of the radius of the Cr^{2+} ion ($r = 0.89$ Å) and the Zn^{2+} ion ($r = 0.74$ Å). (ii) The positive sign of a for the ZnSe:Cr^{2+} complex system is obtained from the calculations. Additionally, the value of F is also estimated. The information can be considered as reasonable comparing with Cr^{2+} ions doped into the rest of the II–VI semiconductors, i.e. ZnS, CdTe, and GaAs. Of course, they should be further checked by experiments in future. (iii) The contributions from the spin singlets to the rank-4 ZFS parameters a and F are very important. Hence, the spin singlets should be taken into account to obtain more reasonable calculated results.

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