The Local Structure Distortion of Chromium-Phosphorus Clusters as Cr^{2+} Impurity in InP Semiconductors

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By diagonalizing the complete energy matrix of a d^4 configuration ion in tetragonal symmetry, the zero-field-splitting parameters a, D and F of InP:Cr^{2+} have been studied. The local structure distortion parameters $\Delta R = 0.08$ Å and $\Delta\theta = 1.01°$ were estimated. They show an expansion distortion around Cr^{2+} in the InP semiconductor. The Jahn-Teller energy E_{JT} is found to be about 413 cm^{-1}, which agrees well with the experiment. – PACS numbers: 75.10.Dg; 76.30.-v

Key words: Zero-Field-Splitting Parameters; Local Structure; Complete Energy Matrix.

1. Introduction

The III-V semiconductors have extensively been applied in electronic and optoelectronic devices, and their optical, magnetic and electrical properties are receiving more and more attention [1 – 13]. For example, thermally detected electron paramagnetic resonance (EPR) experiments [10] on InP:Cr^{2+} have been carried out by Handley et al., from which accurate values for the zero-field-splitting (ZFS) parameters a, D and F were obtained. The parameter a relates to a fourth-order spin operator and represents a cubic ZFS parameter. The parameters D and F are, respectively, associated with the second- and fourth-order spin operators and represent axial ZFS parameters. EPR experiments show that the Cr^{2+} centers in InP semiconductors couple strongly to tetragonal phonon modes. From the absorption spectrum of the $^5T_2 \rightarrow {}^5E$ transition for the InP:Cr^{2+} system [12], a strong and broad phonon sideband has been measured besides the zero-phonon lines (ZPL), which also shows a Jahn-Teller distortion. The local symmetry of InP:Cr^{2+} becomes tetragonal (D_{2d}) by this distortion, which splits the ground state $^5T_2$ into a low lying level $^5B_2$ and a higher lying level ^5E, as shown in Figure 1. In order to understand the characterization of Cr^{2+} doped into an InP crystal, one must know the local structure around the Cr^{2+} ion, since the optical and magnetic properties of the doped crystal depend significantly on the compounds formed by the impurity ion and its nearest neighbors. As is known, the ZFS parameters are very sensitive to the local environment of a $3d^n$ impurity ion in crystals, so it is natural to study the local structure distortion around the impurity ion by calculating the ZFS parameters. Zhou and Li [9] have constructed the energy matrix of a d^4 ion in a tetragonal symmetry field and studied the ZFS parameters a, D and F of Cr^{2+} in a GaAs semiconductor. However, their matrix is not complete because the contributions of the spin singlets are not considered. The reason is probably that it is very difficult to construct

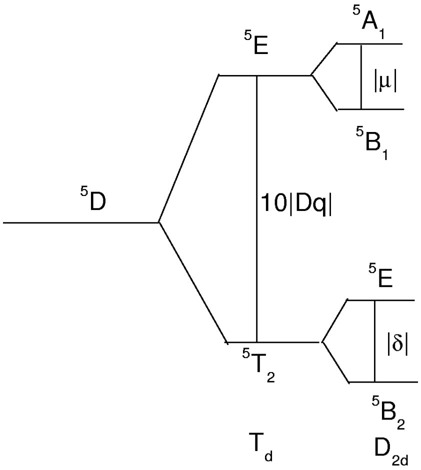

Fig. 1. Energy levels of the ground state of Cr^{2+} in a tetragonal field.

the complete energy matrix that includes the spin singlets, because the Hamiltonian matrix of d^4 ions has a dimension of 210×210 if including all the spin states, but only 160×160 if not including the spin singlets. In this paper, the complete energy matrix (210×210) of d^4 ions in tetragonal symmetry is constructed, and the ZFS parameters a, D and F of the InP:Cr^{2+} system are calculated by diagonalizing the complete energy matrix. From the calculations, the tetragonal distortion parameters ΔR and $\Delta\theta$ are estimated. The results are discussed.

2. Theoretical Model

The appropriate ZFS Hamiltonian to analyze the ZFS parameters of Cr^{2+} ($S = 2$), occupying a tetrahedral site distorted along a tetragonal axis (local symmetry D_{2d}) is [14]

$$H_{\mathrm{ZFS}} = D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + A + J,$$

where

$$A = \frac{a}{6}\left[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2+3S-1)\right]$$

and

$$J = \frac{F}{180}\left\{35S_z^4 - [30S(S+1) - 25]S_z^2 + 3S^2(S+1)^2 - 6S(S+1)\right\}. \tag{1}$$

The z axis of the coordinate system coincides with the cubic [001] axis, and the x and y axes are parallel to [100] and [010], respectively. From (1), the splitting energy levels in the ground state $^5\mathrm{B}_2(D_{2d})$ from $^5\mathrm{T}_2(T_d)$ are given as

$$E_1 = 2D - \frac{2}{5}a + \frac{F}{15}, \quad E_2 = 2D + \frac{3}{5}a + \frac{F}{15},$$
$$E_3 = -D - \frac{2}{5}a - \frac{4}{15}F, \quad E_4 = -2D + \frac{3}{5}a + \frac{2}{5}F. \tag{2}$$

Thus we have

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

The values of E_i can be obtained by a comparison with the eigenvalues of the d$^4(D_{2d}^*)$ matrix that are corresponding to the orbitally non-degenerated ground state.

The real Hamiltonian in the tetragonal field can be expressed as

$$H' = V_{\mathrm{e}}(B,C) + V_{\mathrm{c}}^{A_1}(Dq) + H_{\mathrm{S.O.}}(\zeta) + V^{E\theta}(\mu,\delta), \tag{4}$$

where V_{e} is the electrostatic energy, B and C are the Racah parameters, $V_{\mathrm{c}}^{A_1}$ is the cubic component of the crystal field, Dq the cubic crystal field parameter, $H_{\mathrm{S.O.}}$ the spin-orbit coupling energy, ζ the spin-orbit coupling parameter, $V^{E\theta}$ the tetragonal component of the crystal field, and μ, δ the tetragonal crystal field parameters. According to the irreducible representations Γ'' (i. e. A$_1$, A$_2$, E, B$_1$, B$_2$) of the double group D_{2d}^*(d^4), the basis functions for a d^4 configuration ion corresponding to (4) can be constructed by the formula

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

where, $\langle\Gamma'\gamma'|\Gamma''\gamma''\rangle$ are the coupling coefficients. $|q_i, S\Gamma\Gamma'\gamma'\rangle$ are the basis functions of O_h^*(d^4), which can be derived by the Griffith [15] strong-field functions $|q_i, S\Gamma M\gamma\rangle$ according to the expression

$$|q_i, S\Gamma\Gamma'\gamma'\rangle = \sum_{M\gamma}\langle S\Gamma M\gamma|\Gamma'\gamma'\rangle|q_i, S\Gamma M\gamma\rangle. \tag{6}$$

Thus, the complete matrix of Hamiltonian (4) with respect of the $210 D_{2d}^*$(d^4) basis functions (5) can be constructed. Each matrix element of the complete energy matrix is a linear combination of B, C, ζ, Dq, μ, and δ. The crystal field parameters for a tetragonal symmetry field can be expressed as

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

where

$$A_2 = -eq_\tau\langle r^2\rangle, \quad A_4 = -eq_\tau\langle r^2\rangle. \tag{7}$$

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})
225	0	1.82	0.041	−1.72	−0.044	0.035	−1.72	−0.033
	0.02	1.64	0.049	−1.65	−0.050	0.042	−1.65	−0.037
	0.04	1.43	0.061	−1.52	−0.059	0.055	−1.52	−0.048
	0.06	1.21	0.083	−1.33	−0.078	0.076	−1.33	−0.065
	0.08	1.01	0.116	−1.07	−0.101	0.110	−1.07	−0.090
	0.09	0.90	0.145	−0.87	−0.121	0.139	−0.87	−0.110
217	0	1.82	0.036	−1.60	−0.040	0.030	−1.60	−0.028
	0.02	1.64	0.042	−1.53	−0.044	0.036	−1.53	−0.032
	0.04	1.43	0.053	−1.41	−0.051	0.047	−1.41	−0.040
	0.06	1.21	0.071	−1.23	−0.066	0.065	−1.22	−0.054
	0.08	**1.01**	**0.100**	**−0.98**	**−0.086**	0.094	−0.98	−0.075
	0.09	0.90	0.125	−0.79	−0.103	0.119	−0.79	−0.093
200	0	1.82	0.025	−1.35	−0.027	0.021	−1.35	−0.020
	0.02	1.64	0.030	−1.29	−0.030	0.026	−1.29	−0.024
	0.04	1.43	0.038	−1.18	−0.037	0.034	−1.18	−0.030
	0.06	1.21	0.051	−1.02	−0.046	0.047	−1.02	−0.039
	0.08	1.01	0.071	−0.80	−0.059	0.067	−0.80	−0.052
	0.09	0.90	0.089	−0.64	−0.073	0.085	−0.64	−0.065
Expt. [10]			0.114	−0.97	−0.076			

Table 1. The ZFS parameters of the InP:Cr^{2+} system as a function of ΔR, $\Delta\theta$ and ζ for $Dq_0 = -669.44$ cm^{-1}, $B = 797$ cm^{-1}, $C = 3292$ cm^{-1}. a, D, F: considering all the spin states; a', D', F': neglecting the spin singlets.

R and θ denote the Cr-P bond length and angle between the Cr-P bond and the z axis, respectively, q_τ is the effective charge of the ligand, and $-e$ is electron charge. If $\theta = \cos^{-1}(1/\sqrt{3})$ in (7) for a cubic approximation, then we have

$$Dq_0 = -\frac{2A_4}{27R_0^5}, \ \mu = 0 \ \text{and} \ \delta = 0. \tag{8}$$

3. Calculations and Discussion

Chromium-doped InP is a possible high-resistivity material. To study the local structure distortion of the CrP_4^{10-} cluster in the InP:Cr^{2+} system, it is necessary to know the values of the crystal field parameters and the Racah parameters. Unfortunately, for InP:Cr^{2+} only the cubic field parameters $Dq_0 = -669.44$ cm^{-1} can be obtained from the absorption spectrum [12], because only the transition $^5T_2 \rightarrow {}^5E$ is observed. From the average covalency approximation model [16], the Racah parameters B and C can be obtained by

$$B = N^4 B_0, \quad C = N^4 C_0, \tag{9}$$

where $B_0 = 830$ cm^{-1} and $C_0 = 3430$ cm^{-1} are the free Cr^{2+} parameters [15]. The average covalency factor $N^4 \approx 0.96$ can be reasonably estimated from those of the isoelectronic $3d^4$ ion Fe^{4+} in the $CdSiP_2$ semiconductor with similar phosphorus tetrahedra [17]. Thus, $B \approx 797$ cm^{-1} and $C \approx 3292$ cm^{-1} can be obtained for InP:Cr^{2+} from (9). Because ZFS parameters are very sensitive to the spin-orbit coupling constant ζ, in the calculations ζ is treated as an adjustable parameter to obtain better ZFS values.

When Cr^{2+} substitutes the indium ion in InP, the system will undergo a static Jahn-Teller distortion. The local symmetry is reduced to tetragonal by this distortion, which can be described as

$$R = R_0 + \Delta R, \quad \theta = \theta_0 + \Delta\theta \tag{10}$$

with $R_0 = 2.541$ Å and $\theta_0 = 54.7356°$ [18]. The ratio $A_2/A_4 = 0.12205$ can be obtained from the radial wave function [19] for Cr^{2+} as well as (7). Thus, the ZFS parameters a, D and F as functions of ΔR, $\Delta\theta$ and ζ can be investigated by diagonalizing the complete energy matrix. The results are compared with the experimental findings in Table 1.

From Table 1, it can be seen that the distortion parameters $\Delta R = 0.08$ Å, and $\Delta\theta = 1.01°$ can provide a satisfactory explanation for the experimental ZFS parameters a, D and F. $\Delta R > 0$ and $\Delta\theta > 0$ show that the local structure around the tetragonal Cr^{2+} center in the InP semiconductor has an expansion distortion. It is known that the radius of Cr^{2+} ($r = 0.89$ Å) is bigger than that of the indium ion ($r = 0.81$ Å) [20]. Then, the Cr^{2+} ion will push the ligands upwards and downwards, respectively, when it is doped into the InP crystal. From our calculations, the local lattice parameters $R = 2.621$ Å and $\theta = 55.7456°$ around the impurity ion Cr^{2+} in InP are estimated. The experiment [12] shows that the Jahn-Teller energy (E_{JT}) of the $^5T_2$ ground state is of the order of about 500 cm^{-1}. From the above calculations we get the Jahn-Teller energy

Table 2. Spin singlet contributions to the ZFS parameters a, D and F.

ζ (cm^{-1})	ΔR (Å)	$\Delta\theta$ (°)	r_a	r_D	r_F
225	0	1.82	0.146	0.0	0.250
	0.02	1.64	0.143	0.0	0.260
	0.04	1.43	0.098	0.0	0.186
	0.06	1.21	0.084	0.0	0.167
	0.08	1.01	0.052	0.0	0.109
	0.09	0.90	0.041	0.0	0.091
217	0	1.82	0.167	0.0	0.300
	0.02	1.64	0.143	0.0	0.273
	0.04	1.43	0.113	0.0	0.216
	0.06	1.21	0.085	0.008	0.182
	0.08	1.01	0.060	0.0	0.128
	0.09	0.90	0.048	0.0	0.097
200	0	1.82	0.160	0.0	0.259
	0.02	1.64	0.133	0.0	0.200
	0.04	1.43	0.105	0.0	0.189
	0.06	1.21	0.078	0.0	0.152
	0.08	1.01	0.056	0.0	0.119
	0.09	0.90	0.045	0.0	0.110

$E_{\mathrm{JT}} \approx 413\ \mathrm{cm}^{-1}$, which agrees well with the experimental result. Of course, more experiments, especially ENDOR experiments, are needed to elucidate our calculations.

In Table 2, the ratios

$$r_a = \left|\frac{a-a'}{a}\right|,\ r_D = \left|\frac{D-D'}{D}\right|,\ r_F = \left|\frac{F-F'}{F}\right|, \quad (11)$$

are calculated to show the spin-singlet contribution to the ZFS parameters. It is obvious that the larger the ratio r, the larger are the spin singlet contributions. From Table 2, it can be seen that r_a and r_F are comparatively big, which shows that the contributions of the spin singlets to a and F are important. So, the spin singlets should be considered to obtain more accurate ZFS parameters.

4. Conclusion

We have reported a detailed investigation on the local structure of InP:Cr^{2+} by diagonalizing the complete energy matrix for a d^4 configuration ion in a tetragonal symmetry field. Our calculations show that the chromium-phosphorus distance ($R = 2.621$ Å), determined by fitting the ZFS parameters a, D and F, is larger than the indium-phosphorus host distance ($R = 2.541$ Å). Such an elongation of R involves a ligand outward expansion around the Cr^{2+} ion, which is a result of its larger ionic radius (0.89 Å) than that of the indium cation (0.81 Å). Our results may provide some useful information on the local structure of Cr^{2+} doped into the InP semiconductor. We also obtained the Jahn-Teller energy $E_{\mathrm{JT}} \approx 413\ \mathrm{cm}^{-1}$, which coincides well with the experimental result.

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