

ENERGY LEVELS OF SHALLOW DONORS IN CdS AND ZnO*

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The ionization energies of shallow donors in piezoelectric semiconductors calculated in the approximation of perturbation theory are presented as series with respect to the degrees of anisotropy factor. The obtained relationships are compared to the results of Déverin, Gerlach and Pollmann. In the framework of the hydrogen-like model the calculations of ionization energy are carried out for shallow donors in CdS and ZnO.

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1. Introduction

Ionization energies of shallow donors and excitons in anisotropic crystals can be investigated in the framework of the hydrogen-like model [1 to 3]. The solutions of the Schrödinger equation obtained by Déverin [4] allowed to determine the energy levels for the ground and excited states of both excitons and shallow donors in uniaxial crystals. The introduction of an effective charge factor and a good selection of the unperturbed Hamiltonian had allowed to Gerlach and Pollmann [5 - 7] to receive a more accurate solution of this problem.

In this paper we investigate the ionization energy of shallow donors presented in the form of series of the anisotropy factor degrees (up to α^6) for the ground and excited states of shallow donors. The quantitative comparison of the results obtained by means of the series is carried out to those calculated according to the relationships of Déverin [4] and Gerlach-Pollmann [5 - 7].

The numerical calculations of energy levels of shallow donors in CdS and ZnO are carried out using the experimental data from [3, 8-10].

2. The first order of perturbation theory in anisotropic crystal

The effective-mass approximation Hamiltonian for donor electron in an uniaxial crystal is [1,2]:

$$H = -\frac{\hbar^2}{2m_{\perp}^*} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) - \frac{\hbar^2}{2m_{\parallel}^*} \frac{\partial^2}{\partial z^2} - \frac{Ze^2}{[\varepsilon_{\parallel}\varepsilon_{\perp}(x^2 + y^2) + \varepsilon_{\perp}^2 z^2]^{1/2}}, \quad (1)$$

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where Ze and e are the charges of ion and electron, respectively, m_{\perp}^* , m_{\parallel}^* , ε_{\perp} , and ε_{\parallel} are the effective masses and static dielectric constants in the directions perpendicular and parallel to C-axis (which is taken to be in z-direction). Using the transformation of Wheeler and Dimmock [2].

$$x = x', \quad y = y', \quad z = z' \left(\frac{m_{\perp}^*}{m_{\parallel}^*} \right)^{\frac{1}{2}}, \quad (2)$$

the transformed Schrödinger equation in the spherical coordinate system is given as

$$(H_0 + H_{\alpha})\Psi(\vec{r}) = E\Psi(\vec{r}), \quad (3)$$

In the spherical coordinates H_0 and H_{α} are given as

$$H_0 = -\frac{\hbar^2}{2m_{\perp}^*} \bar{\nabla}^2(r, \theta, \varphi) - \frac{Ze^2}{\sqrt{\varepsilon_{\parallel}\varepsilon_{\perp}} r}, \quad (4)$$

$$H_{\alpha} = -\frac{Ze^2}{\sqrt{\varepsilon_{\parallel}\varepsilon_{\perp}} r} (f(\alpha, \theta) - 1), \quad (5)$$

$$\text{where, } f(\alpha, \theta) = \frac{1}{\sqrt{1 - \alpha \cos^2 \theta}}, \quad \alpha = 1 - \gamma, \quad \gamma = \frac{m_{\perp}^* \varepsilon_{\perp}}{m_{\parallel}^* \varepsilon_{\parallel}}. \quad (6)$$

The quantities γ and α are called as anisotropy parameter and anisotropy factor, respectively. The Schrödinger radial equation in the zeroth approximation can be written as

$$\left(-\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2} - \frac{2}{\rho} \right) \chi(\rho) = 2\varepsilon \chi(\rho), \quad (7)$$

where

$$\rho = \frac{r}{a_H^*}, \quad \varepsilon = \frac{E}{E_a}, \quad a_H^* = \frac{\hbar^2 \sqrt{\varepsilon_{\parallel}\varepsilon_{\perp}}}{m_{\perp}^* Ze^2}, \quad E_a = \frac{Ze^2}{\sqrt{\varepsilon_{\parallel}\varepsilon_{\perp}} a_H^*} = \frac{Z^2 e^4 m_{\perp}^*}{\hbar^2 \varepsilon_{\parallel}\varepsilon_{\perp}}. \quad (8)$$

The wave functions and energy levels of the unperturbed Schrödinger equation with the Hamiltonian (4) are

$$\Psi_{nlm}(\vec{r}) = R_{nl}(r) Y_{lm}(\theta, \varphi) = \frac{1}{r} \chi_{ln_r} \left(\frac{r}{a_H^*} \right) Y_{lm}(\theta, \varphi), \quad (9)$$

$$\varepsilon_{nlm}^0 = -\frac{1}{2n^2}, \quad E_{nlm}^0 = -\frac{E_a}{2n^2} = -\frac{E_0}{n^2}, \quad E_0 = Z^2 E_H \frac{m_{\perp}^*}{\varepsilon_{\perp} \varepsilon_{\parallel} m_e}, \quad E_H = \frac{m_e e^4}{2\hbar^2}. \quad (10)$$

In the case of small values of α the solutions of the total Schrödinger equation (3) can be found by means of the perturbation theory. In the first order of the perturbation theory the ionization energies are determined by the relationship

$$E_{nlm} = E_{nlm}^0 + \langle \Psi_{nlm} | H_{\alpha} | \Psi_{nlm} \rangle. \quad (11)$$

If the values of α are small, the perturbation operator H_{α} can be expressed as the series

$$H_{\alpha} = -\frac{Ze^2}{\sqrt{\varepsilon_{\parallel}\varepsilon_{\perp}} r} \left(\frac{1}{2} \alpha \cos^2 \theta + \frac{3}{8} \alpha^2 \cos^4 \theta + \frac{5}{16} \alpha^3 \cos^6 \theta + \frac{35}{128} \alpha^4 \cos^8 \theta + \right. \\ \left. + \frac{63}{256} \alpha^5 \cos^{10} \theta + \frac{231}{1024} \alpha^6 \cos^{12} \theta + \dots \right). \quad (12)$$

By substituting (12) in (11) and taking into account the radial and spherical parts of the hydrogen-like functions [11], one obtains the ionization energies of a shallow donor with the accuracy to α^6 :

$$E_{1S}^{(6)} = -E_0 \left(1 + \frac{1}{3} \alpha + \frac{3}{20} \alpha^2 + \frac{5}{56} \alpha^3 + \frac{35}{576} \alpha^4 + \frac{63}{1408} \alpha^5 + \frac{231}{6656} \alpha^6 \right), \quad (13)$$

$$E_{2S}^{(6)} = -\frac{E_0}{4} \left(1 + \frac{1}{3}\alpha + \frac{3}{20}\alpha^2 + \frac{5}{56}\alpha^3 + \frac{35}{576}\alpha^4 + \frac{63}{1408}\alpha^5 + \frac{231}{6656}\alpha^6 \right), \quad (14)$$

$$E_{2P_x}^{(6)} = E_{2P_y}^{(6)} = -\frac{E_0}{4} \left(1 + \frac{1}{5}\alpha + \frac{9}{140}\alpha^2 + \frac{5}{168}\alpha^3 + \frac{35}{2112}\alpha^4 + \frac{189}{18304}\alpha^5 + \frac{231}{33280}\alpha^6 \right), \quad (15)$$

$$E_{2P_z}^{(6)} = -\frac{E_0}{4} \left(1 + \frac{3}{5}\alpha + \frac{9}{28}\alpha^2 + \frac{5}{24}\alpha^3 + \frac{105}{704}\alpha^4 + \frac{189}{1664}\alpha^5 + \frac{231}{2560}\alpha^6 \right). \quad (16)$$

Expressions (13) - (16) are convenient for numerical calculations of ionization energy. Keeping the quadratic terms on α in (13)-(16) one obtains the results from papers [2, 8] in the zero magnetic field, and with allowance for the terms cubic in α . They are the same as in paper [12].

The relationships for the ionization energy can be also obtained without expansion (12) by substituting (5), (9), and (10) immediately in (11). Then one gets

$$E_{1S}^{Dev} = -E_0(2I1(\alpha) - 1) = -E_0(2Z_{00}(\alpha) - 1), \quad (17)$$

$$E_{2S}^{Dev} = -\frac{E_0}{4}(2I1(\alpha) - 1) = -\frac{E_0}{4}(2Z_{00}(\alpha) - 1), \quad (18)$$

$$E_{2P_x}^{Dev} = E_{2P_y}^{Dev} = -\frac{E_0}{4} \left\{ 3 \left[\left(1 - \frac{1}{2\alpha} \right) I1(\alpha) + \frac{1}{2} I2(\alpha) \right] - 1 \right\} = -\frac{E_0}{4} (2Z_{1\pm 1}(\alpha) - 1). \quad (19)$$

$$E_{2P_z}^{Dev} = -\frac{E_0}{4} \left\{ 3 \left[\frac{1}{\alpha} I1(\alpha) - I2(\alpha) \right] - 1 \right\} = -\frac{E_0}{4} (2Z_{10}(\alpha) - 1), \quad (20)$$

$$\text{where} \quad I1(\alpha) = \begin{cases} \frac{1}{\sqrt{\alpha}} \arcsin \sqrt{\alpha}, & \alpha > 0 \\ 1, & \alpha = 0 \\ \frac{1}{\sqrt{|\alpha|}} \ln \left[\sqrt{|\alpha|} + \sqrt{1 + |\alpha|} \right], & \alpha < 0 \end{cases} \quad (21)$$

$$I2(\alpha) = \frac{\sqrt{1 - \alpha}}{\alpha}. \quad (22)$$

Note, that the relations analogous with (17)-(22) were obtained for the first time by Déverin [4] under investigations of the binding energy of Wannier's excitons in anisotropic crystals.

Relations (17)-(20) can be generalized by introducing the effective charge factor $Z_{lm}(\alpha)$ [6]:

$$Z_{lm}(\alpha) = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin \theta d\theta \frac{Y_{lm}^*(\theta, \varphi) Y_{lm}(\theta, \varphi)}{\sqrt{1 - \alpha \cos^2 \theta}}. \quad (23)$$

As a result, the expression for the ionization energy can be written as

$$E_{nlm}^{Dev}(\alpha) = -\frac{E_0}{n^2} (2Z_{l|ml}(\alpha) - 1) \quad (24)$$

The introduction of the effective charge factor $Z_{lm}(\alpha)$ gives the possibility to include anisotropy characteristics of materials in the effective charges of defects.

Besides the above presented method for the determination of the ionization energy of shallow donors, the method of Gerlach-Pollmann [5 - 7] is known which allows to receive acceptable results in a wider range of anisotropy factor values.

After averaging over the angular variables it was obtained [6],

$$H = H_0^{lm} + H_p^{lm}, \quad (25)$$

where

$$H_0^{lm} = -\frac{\hbar^2}{2m_{\perp}^*} \nabla^2(r, \theta, \varphi) - \frac{Ze^2}{\sqrt{\varepsilon_{\parallel} \varepsilon_{\perp}} r} Z_{lm}(\alpha), \tag{26}$$

$$H_p^{lm} = \frac{Ze^2}{\sqrt{\varepsilon_{\parallel} \varepsilon_{\perp}} r} [Z_{lm}(\alpha) - f(\alpha, \theta)], \quad f(\alpha, \theta) = \frac{1}{\sqrt{1 - \alpha \cos^2 \theta}}, \tag{27}$$

According to [6], the eigenfunctions of the Hamiltonian H_0^{lm} with allowance for the dependence on the anisotropy factor have the form

$$\Psi_{(nl)m}(\vec{r}, \alpha) = R_{nl}(Z_{lm}(\alpha), r) Y_{lm}(\theta, \varphi). \tag{28}$$

The eigenvalues of H_0^{lm} have a parametric dependence on the anisotropy factor:

$$E_{(nl)m}^{GP} = -\frac{E_0}{n^2} Z_{l|m|}^2(\alpha). \tag{29}$$

In the first order of the perturbation theory on H_p^{lm} the energy shift is zero [6]. The contribution of the second-order perturbation is small [6,7]. So, the zeroth-order approximation (29) gives an acceptable accuracy.

3. Numerical calculations for semiconducting materials

The ionization energies of shallow donors in piezoelectric crystals were calculated using expressions (13)-(16), (17)-(20), and (29). Fig. 1 shows the calculated dependences of the ionization energy on γ for E_{1S} level in the range $\alpha > 0$ which take into account the series on the anisotropy factor degrees α^2 and α^6 (curves 1 and 2, respectively). One can see that these curves monotonously approach to the data of Déverin (curve 3). The dependences calculated by the method of Gerlach-Pollmann (curve 4) and the variational method of Faulkner (curve 5) are situated below the data of Déverin. As follows from Fig. 1, in the range $0.7 < \gamma < 1$ the ionization energies of E_{1S} level calculated by both methods are practically the same. For $\gamma < 0.7$ the variational method is more suitable.

In CdS and ZnO crystals the anisotropy factor ($\alpha > 0$) has a small value, and the ionization energies of shallow donors, estimated from relations (13) - (16), (17) - (20), and (29), are practically the same. The determinations of the ionization energies of shallow donors in piezoelectric crystals is complicated due to peculiarities of their permittivities ε_{\perp} and ε_{\parallel} . According to [8], they can be expressed as

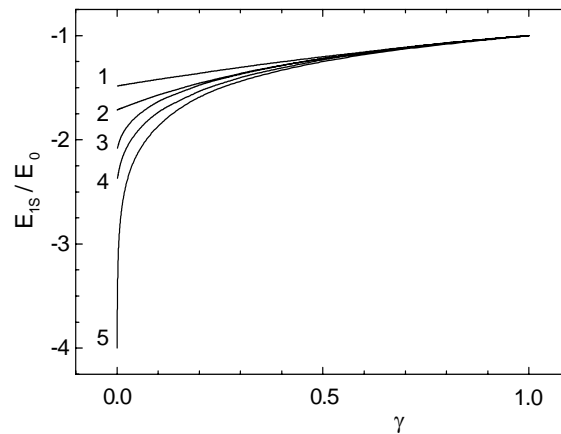


Fig. 1. Ionization energies of 1S level vs γ in the range $\alpha > 0$: at including the series on the anisotropy factor degrees α^2 and α^6 (1 and 2, respectively), 3 - the method of Déverin (17), 4 - the method of Gerlach-Pollmann (29), 5 - the variational method of Faulkner [13].

$$\varepsilon_{\perp} = \varepsilon_{0\perp} \left(1 + \sum_j \langle K_j^2 \rangle \right), \quad \varepsilon_{\parallel} = \varepsilon_{0\parallel} \left(1 + \sum_j \langle K_j^2 \rangle \right) \quad (30)$$

where $\varepsilon_{0\perp}$ and $\varepsilon_{0\parallel}$ are the static permittivities of piezoelectrics measured without taking into account the piezoelectric resonance [8]. $\sum_j \langle K_j^2 \rangle$ is the spherically averaged electromechanical coupling constant summarized over the longitudinal and transverse modes.

Table 1 presents the results of the calculations of the ionization energies of the ground and excited states for shallow donors in CdS. As follows from the calculations, their ionization energies are in a good agreement to the data of Ref. [8] which were obtained from the investigations of two-electron transitions at decomposition of exciton-donor complexes. Note, that in [8] the estimations were performed for a 1S state ionization energy only.

Table 1. Ionization energies (meV) of shallow donors in CdS.

		$\varepsilon_{0\perp} = 8.37, \varepsilon_{0\parallel} = 9.00$ [8], $m_{\perp}^* = 0.19m_e, m_{\parallel}^* = 0.187m_e$ [8], $\gamma = 0.9449, \sum_j \langle K_j^2 \rangle = 0.035$ [14], $a_H^* = 25.0 \text{ \AA}$						
		Energy states						
		E_{1S}	E_{2S}	E_{2P_x}	E_{2P_z}	$E_{2S} - E_{1S}$	$E_{2P_x} - E_{1S}$	$E_{2P_z} - E_{1S}$
1	Theory	-32.64	-8.16	-8.10	-8.28	24.48	24.54	24.36
2	Exper. data	<i>Cl</i> : -32.7 [8] -32.0 [8]				23.88 [8]	24.36 [8]	24.19 [8]
		$\varepsilon_{0\perp} = 9.02, \varepsilon_{0\parallel} = 9.53$ [3], $m_{\perp}^* = m_{\parallel}^* = 0.205m_e$ [3], $\gamma = 0.9465, \sum_j \langle K_j^2 \rangle = 0, a_H^* = 23.9 \text{ \AA}$						
		Energy states						
		E_{1S}	E_{2S}	E_{2P_x}	E_{2P_z}	$E_{2S} - E_{1S}$	$E_{2P_x} - E_{1S}$	$E_{2P_z} - E_{1S}$
1	Theory	-33.04	-8.26	-8.20	-8.38	24.78	24.84	24.66

Table 2. Ionization energies (meV) of shallow donors in ZnO.

		$\varepsilon_{0\perp} = 8.33, \varepsilon_{0\parallel} = 8.84$ [10], $m_{\perp}^* = m_{\parallel}^* = 0.32m_e$ [14], $\gamma = 0.9423, \sum_j \langle K_j^2 \rangle = 0.074$ [14], $a_H^* = 15.2 \text{ \AA}$			
		Energy states			
		E_{1S}	E_{2S}	E_{2P_x}	E_{2P_z}
1	Theory	-52.27	-13.07	-12.97	-13.28
2	Experimental data	-52.0 [10]			
		$\varepsilon_{0\perp} = 8.33, \varepsilon_{0\parallel} = 8.84$ [10], $m_{\perp}^* = m_{\parallel}^* = 0.19m_e$ [10], $\gamma = 0.9423, \sum_j \langle K_j^2 \rangle = 0, a_H^* = 23.9 \text{ \AA}$			
		Energy states			
		E_{1S}	E_{2S}	E_{2P_x}	E_{2P_z}
1	Theory	-35.80	-8.95	-8.88	-9.09

As follows from Table 2, a good agreement between the calculated ionization energies and the experimental data for ZnO crystals [10] takes place under using the effective mass $m_{\perp}^* = m_{\parallel}^* = 0.32m_e$. [14]. In the case of $m_{\perp}^* = m_{\parallel}^* = 0.19m_e$ the essential difference of the calculated ionization energies of shallow donors ($E_{1S} = 35.8$ meV) from the experimental data ($E_{1S} = 52$ meV) caused the authors of Ref. [10] to suppose that the 1S state is not a state allowed to be described by the effective mass approximation. We believe that the use of the effective mass values from [14] and the parameter $\sum_j \langle K_j^2 \rangle = 0.074$ allow to receive a coincidence with the experimental data [10] in the framework of the hydrogen-like model.

4. Conclusions

In this paper we have obtained the relationships for the ionization energies of shallow donors in the form of a series of the power of the anisotropy factor α (up to α^6) for ground and excited states.

The allowance for the permittivity anisotropy removes the degeneration of excited states typical for the isotropic hydrogen-like model.

The comparison of the calculation results obtained by the different methods based on the hydrogen-like model shows that this model allows to describe adequately the ionization energies of shallow donors in piezoelectric crystals of CdS and ZnO.

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