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## CALCULATION OF THE GROUND-STATE IONIZATION ENERGY FOR SHALLOW DONORS IN $n$ -Ge SINGLE CRYSTALS WITHIN THE $\Delta_1$ -MODEL FOR THE CONDUCTION BAND

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*On the basis of the Ritz variational method, the ionization energies for the ground states of Sb, P, and As donors in  $n$ -Ge single crystals are calculated in the framework of the  $\Delta_1$ -model for the conduction band and taking the dispersion law anisotropy and the chemical shift into account. A comparison of theoretical results with corresponding experimental data shows that the model of impurity's Coulomb potential can be used as a rough approximation only for Sb impurities in Ge, making no allowance for the chemical shift. For the P and As impurities, when the potential field of an impurity ion is not Coulombic, the calculations have to be carried out with regard for a chemical shift.*

*Keywords:* Ritz variational method, chemical shift,  $\Delta_1$ -minimum, anisotropy factor.

### 1. Introduction

Single crystalline germanium is widely used in various fields of science and engineering as a raw material to manufacture diodes, triodes, power rectifiers, dosimetry devices, and meters measuring the strength of dc and ac magnetic fields [1]. One of its main applications is the fabrication of optical elements for an infra-red equipment; in particular, it is used in ground-, air-, and sea-based thermal imagers operating in the wavelength interval from 2.5 to 14  $\mu\text{m}$  [2]. Single crystalline germanium is also a promising material for nanoelectronics. A high mobility of electrons allows nanotransistors with highly conducting channels to be created, with the switching time of about picoseconds [3, 4]. The application of nanostructures with self-assembled Ge/Si nanoislands opens new prospects in the development of opto- and nanoelectronics [5]. Arrays of Ge (GeSi) quantum dots can be applied to manufacture photodetectors and light emitting diodes in the near infra-red spectral range [6].

The optical and electric properties of semiconductor devices considerably depend on the lattice deformation and the spatial distribution of point defects. Recently, heterostructures with and without strained boundaries have found a wide application to micro-

electronic devices [7]. In silicon-germanium heterostructures with quantum dots, elastic deformation fields arise at the heterointerface owing to the mismatch between the lattice constants in germanium and silicon. The interaction of point defects with the deformation field, which can emerge as a result of those defects, and inhomogeneities in the crystal system (e.g., a heterointerface) gives rise to the spatial redistribution of defects and, under certain conditions, to the formation of self-assembled defect-deformation structures [8]. Therefore, the study of electric, optical, and photo-electric properties of semiconductors in the presence of a deformation is a challenging issue from both the theoretical and practical viewpoints.

Variations in the specific resistance of  $n$ -Ge single crystals under the influence of directed uniaxial deformations ( $P < 1.6$  GPa) were considered in work [9]. The deformation-induced redistribution between the minima of the same type  $L_1$  was the main mechanism of the observed tensorial resistive effect. An essential reconstruction of the band spectrum of  $n$ -Ge owing to the  $(L_1 - \Delta_1)$ -type inversion of the absolute minimum in the conduction band by imposing strong uniaxial elastic deformations ( $P \approx 2.4$  GPa) was obtained experimentally for the first time in work [10]. As a result, the deformation-induced phase transition metal-insulator was observed.

In order to quantitatively interpret various material properties at such a radical reconstruction, one has to know the parameters of  $\Delta_1$ -minima. In works [11,12], the components of the effective mass tensor, parameter of effective mass anisotropy, and constants of the deformation potential for the  $\Delta_1$ -minimum in  $n$ -Ge were determined. A common issue for those works is the fact that the ultimate result was obtained on the basis of the data of various experiments, which can insert additional errors to the values of sought parameters. In our works [13,14] on the basis of experimental data concerning only the longitudinal piezoresistance of single crystals and the theory of anisotropic scattering, the corrected values were found for the components of the effective mass tensor and the constants of the deformation potential for the  $\Delta_1$ -minimum of the conduction band in  $n$ -Ge single crystals.

This work was aimed at studying the influence of the  $(L_1 - \Delta_1)$ -type inversion of the absolute minimum in  $n$ -Ge single crystals on a change of the ionization energy of shallow donors. It is known that the ionization energy of a shallow level is described by the parameters of a valley, whose wave functions describe its state, when  $k_0 a \gg 1$ , where  $a$  is the Bohr radius, and  $k_0$  the distance between the valley minima in the quasimomentum space [15]. In the case of  $n$ -Ge, this condition is satisfied for both the  $L_1$ - and  $\Delta_1$ -valleys. In addition, it is also known that the Schrödinger equation for shallow impurity levels in multivalley semiconductors has no exact analytical solution. Therefore, in practice, approximate methods to find eigenfunctions and eigenvalues of a Hamiltonian are used, as a rule [16]. In work [17] on the basis of the Ritz variational method, an analytical expression for the ionization energies of shallow levels was derived in the case of the isotropic dispersion law with regard for the screening of the impurity ion field. For  $n$ -Ge, this approach is inapplicable, because the isoenergetic surfaces for both  $L_1$ - and  $\Delta_1$ -valleys are ellipsoids of revolution. In this case, the anisotropy of effective masses has to be taken into account first of all, as was done in work [18] on the basis of perturbation theory for the ellipsoidal energy surfaces in CdS and ZnO crystals. In the cited work, the anisotropy factor, which depends on the effective mass ratio and the dielectric permittivities of a material along the principal axis of the ellipsoid and perpendicularly to it, was chosen as a small parameter. The indicated factors, as well as the fact that the

energy levels of the ground states of shallow donors in germanium single crystals undergo a substantial chemical shift associated with the correction of the central cell potential [16,19], were taken into account in this work while considering the  $\Delta_1$ -model for  $n$ -Ge.

## 2. Calculation of the Ionization Energy of Shallow Donors in $n$ -Ge on the Basis of the Ritz Variational Method

### 2.1. No chemical shift

In the case of ellipsoidal isoenergetic surface in the effective mass approximation, the Hamiltonian for an electron localized at the donor looks like [15]

$$\hat{H} = -\frac{\hbar^2}{2m_{\perp}} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) - \frac{\hbar^2}{2m_{\parallel}} \frac{\partial^2}{\partial z^2} - \frac{Zq^2}{\varepsilon \sqrt{x^2 + y^2 + z^2}}, \quad (1)$$

where  $Z$  is the absolute value of the ion charge,  $q$  the elementary charge,  $m_{\perp}$  and  $m_{\parallel}$  are longitudinal and transverse, respectively, components of the electron effective mass tensor, and  $\varepsilon$  is the dielectric permittivity of the material. Using the Wheeler–Dimmock transformation [20],

$$x = x_1, \quad y = y_1, \quad z = z_1 \left( \frac{m_{\perp}}{m_{\parallel}} \right)^{1/2}, \quad (2)$$

let us write down the Schrödinger equation in the form

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (3)$$

where

$$\hat{H} = -\frac{\hbar^2}{2m_{\perp}} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right) - \frac{Zq^2}{\varepsilon \sqrt{x_1^2 + y_1^2 + z_1^2(1-\alpha)}}, \quad (4)$$

$$\alpha = 1 - \gamma, \quad \gamma = \frac{m_{\perp}}{m_{\parallel}}, \quad (5)$$

is the anisotropy factor, and  $\gamma = \frac{m_{\perp}}{m_{\parallel}}$ . Hamiltonian (4) in the spherical coordinate system looks like

$$\hat{H}_1 = -\frac{\hbar^2}{2m_{\perp}} \nabla^2(r, \theta, \varphi) - \frac{Zq^2}{\varepsilon r} f(\alpha, \theta), \quad (6)$$

where

$$f(\alpha, \theta) = \frac{1}{\sqrt{1 - \alpha \cos^2 \theta}}. \quad (7)$$

The trial function for the electron ground state is sought in the form

$$\psi_{1s} = ce^{-\sqrt{\frac{x^2+y^2}{a^2} + \frac{z^2}{b^2}}}. \quad (8)$$

In the spherical coordinate system,

$$\psi_{1s} = ce^{-r\sqrt{\frac{\sin^2 \theta}{a^2} + \frac{\cos^2 \theta}{b^2}}}, \quad (9)$$

where  $c$ ,  $a$ , and  $b$  are unknown variational parameters. Then the expression for the average energy of the system in the state given by the trial function (9) reads

$$E(c, a, b) = \frac{\int_V \psi_{1s}^* \hat{H}_1 \psi_{1s} dV}{\int_V |\psi_{1s}|^2 dV}. \quad (10)$$

Calculating the integrals in the numerator and the denominator of Eq. (10), we obtain the following dependence of the average ground state energy on the variational parameters:

$$\begin{aligned} E(a, b) = & -\frac{\hbar^2}{m_{\perp}} \frac{1}{a^2 b} \left( \left( -\frac{3ab}{8} \right) \frac{\ln \frac{a+\sqrt{a^2+b^2}}{a-\sqrt{a^2+b^2}}}{\sqrt{a^2-b^2}} + \right. \\ & + \frac{b^2-a^2}{2b} + \frac{m_{\perp} Z q^2}{\varepsilon \hbar^2} \frac{a^2 b^2}{\sqrt{b^2(\alpha b^2 + a^2 - b^2)}} \times \\ & \left. \times \arctg \left( \frac{\sqrt{\alpha b^2 + a^2 - b^2}}{b\sqrt{1-\alpha}} \right) \right). \quad (11) \end{aligned}$$

The variational parameters are determined from the following system of equations:

$$\begin{cases} \frac{\partial E(a, b)}{\partial a} = 0, \\ \frac{\partial E(a, b)}{\partial b} = 0. \end{cases} \quad (12)$$

Substituting the solution into expression (11), we can calculate the ionization energy of the impurity in the ground state,  $E_{1s}$ .

## 2.2. Chemical shift

The chemical shift depends on the impurity origin. Therefore, in our case, we should construct such a potential that takes the specific nature of the impurity ion into account. Some aspects of this problem were considered for the first time in work [21] by an example of shallow donors in silicon. The authors of work [22] proposed the following form for the impurity ion potential with regard for its ‘‘core’’:

$$U(r) = -\frac{q^2}{\varepsilon r} \left( 1 + Ae^{-\frac{r}{r_0}} \right) e^{-\frac{r}{R}}. \quad (13)$$

Here, the parameter  $A$  characterizes the efficiency of the impurity ion ‘‘core’’,  $r_0$  equals half the distance between two nearest neighbor atoms in the crystal (for germanium,  $r_0 = 1.225 \times 10^{-10}$  m), and  $R$  is the screening radius. In the most general case, the screening radius looks like [23]

$$R_0^2 = \frac{\hbar^3 \varepsilon}{16\pi^2 q^2 (m^*)^{3/2} (2kT)^{1/2} \Phi_{-1/2}(E_F^*)}, \quad (14)$$

where  $m^*$  is the effective mass, and

$$\Phi_{-1/2} = \int_0^{\infty} \frac{x^{-1/2} dx}{e^{x-E_F^*} + 1}$$

is the Fermi integral with an index of  $-1/2$ . In order to calculate this integral, one should know the reduced Fermi energy  $E_F^* = \frac{E_F}{kT}$ . The electron concentration in the conduction band equals [24]

$$n = \frac{2N_C}{\sqrt{\pi}} \Phi_{1/2}, \quad (15)$$

where

$$\begin{aligned} N_C &= 2 \left( \frac{2\pi m^* kT}{h^2} \right)^{3/2}, \\ m^* &= N^{2/3} (m_{\parallel} m_{\perp}^2)^{1/3}, \end{aligned} \quad (16)$$

and  $N$  is the number of equivalent valleys. Knowing the effective density of states in the conduction band,  $N_C$ , it is easy to find the Fermi integral with an index of  $1/2$  from expression (15):

$$\Phi_{1/2} = \int_0^{\infty} \frac{x^{1/2} dx}{e^{x-E_F^*} + 1}, \quad (17)$$

where  $x = \frac{E}{kT}$  is the reduced electron energy. The Fermi energy value  $E_F^*$  obtained from Eq. (17) makes it possible to determine the Fermi integral with an index of  $-1/2$  and, hence, the screening radius (14).

In work [22], with regard for the values of longitudinal and transverse components of the effective mass tensor for the  $L_1$ -minimum in the conduction band of  $n$ -Ge and the experimental values of ionization energy for the ground states of Sb, P, and As impurities [ $E_{1s}(\text{Sb}) = 9.6$  meV,  $E_{1s}(\text{P}) = 12$  meV, and  $E_{1s}(\text{As}) = 12.7$  meV [25]], the parameter  $A$  for those impurities in germanium was found, respectively, to be  $A(\text{Sb}) = 11.29$ ,  $A(\text{P}) = 32.34$ , and  $A(\text{As}) = 34.67$ . Then, in the case of ellipsoidal isoenergetic surfaces in view of transformations (2), the Hamiltonian for an electron in field (13) reads

$$\hat{H}_2 = -\frac{\hbar^2}{2m_\perp} \nabla^2(r, \theta, \phi) - \frac{q^2}{\varepsilon r} f(\alpha, \theta) \left(1 + A e^{-\frac{r}{r_0 \cdot f(\alpha, \theta)}}\right) e^{-\frac{r}{R \cdot f(\alpha, \theta)}}. \quad (18)$$

In the framework of the variational method, the average energy for an electron in the state given by the trial function (9) equals

$$E(a, b) = \frac{\int_V \psi_{1s}^* \hat{H}_2 \psi_{1s} dV}{\int_V |\psi_{1s}|^2 dV} = -\frac{\hbar^2}{m_\perp a^2 b} \left( \left(-\frac{3ab}{8}\right) \frac{\ln \frac{a + \sqrt{a^2 + b^2}}{a - \sqrt{a^2 + b^2}}}{\sqrt{a^2 - b^2}} + \frac{b^2 - a^2}{2b} + \frac{2m_\perp q^2}{\varepsilon \hbar^2} \int_0^\pi d\theta f(\alpha, \theta) \phi(\alpha, \theta, a, b, R, r_0, A) \right), \quad (19)$$

where

$$\phi(\alpha, \theta, a, b, R, r_0, A) = \frac{1}{\left(2 \left(\frac{\sin^2 \theta}{a^2} + \frac{\cos^2 \theta}{b^2}\right)^{1/2} + \frac{1}{R f(\alpha, \theta)}\right)^2 + A} + \frac{1}{\left(2 \left(\frac{\sin^2 \theta}{a^2} + \frac{\cos^2 \theta}{b^2}\right)^{1/2} + \frac{\frac{1}{R} + \frac{1}{r_0}}{f(\alpha, \theta)}\right)^2}. \quad (20)$$

By solving the system of equations (12) with respect to the unknown variational parameters, we can use expression (19) to determine the ionization energy of the ground state for various shallow impurities.

### 3. Results of Numerical Calculations and Conclusions

In order to calculate the ionization energy for shallow donors within the  $\Delta_1$ -model for the conduction band in  $n$ -Ge single crystals, one should know the components of the effective mass tensor for the corresponding minimum and the dielectric permittivity of a material. For the  $\Delta_1$ -minimum, the parameters  $m_\parallel = 1.65m_0$  and  $m_\perp = 0.32m_0$ , where  $m_0$  is the free electron mass, were found, as was indicated above, in work [13]. The dielectric permittivity for germanium,  $\varepsilon = 16$ , is well known [25]. In work [26], by analyzing the dependences of the impact ionization field on the uniaxial pressure along the crystallographic direction [100] for  $n$ -Ge single crystals doped with Sb and As impurities to the concentration  $n = N_d = 1.8 \times 10^{14} \text{ cm}^{-3}$ , the ionization energies of ground states for those impurities were determined provided the  $(L_1 - \Delta_1)$ -type inversion of the absolute minimum. On the basis of the method used in work [26], the authors of work [27] found the ionization energy for the ground state of P impurity with the concentration  $n = N_d = 1.15 \times 10^{14} \text{ cm}^{-3}$  associated with  $\Delta_1$ -valleys.

In Table, the calculation results for the ionization energy of shallow-donor ground states in  $n$ -Ge single crystals taking and not taking the chemical shift for those impurities into account are quoted. In order to compare the theoretical results obtained in this work with the experimental data of works [26, 27], the calculations were executed for the concentrations of Sb, P, and As impurities that were used in those works. The results of calculations testify that, when changing from the  $L_1$ -model to the  $\Delta_1$ -one for the conduction band in  $n$ -Ge single crystals, the ionization energies of ground states of the Sb, P, and As

**Ionization energies for the ground states of shallow donors in  $n$ -Ge associated with  $\Delta_1$ -valleys**

Ionization energy of the shallow donor ground state $E_{1s}^{\Delta_1}$ , meV		
No chemical shift	With chemical shift	Experimental results [26, 27]
30.4	Sb: 32.6 As: 42.5 P: 39	Sb: $(35 \pm 2)$ As: $(45 \pm 2)$ P: $(41 \pm 2)$

impurities essentially increase. The Coulomb potential model for an impurity ion can be used in a rough approximation only for the Sb impurity in Ge. For the P and As impurities, the calculations must be carried out with regard for the chemical shift, i.e. when the specific character of the impurity ion potential field, which is not Coulombic, manifests itself.

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РОЗРАХУНОК ЕНЕРГІЇ ІОНІЗАЦІЇ  
ОСНОВНОГО СТАНУ НЕВЕЛИКИХ ДОНОРІВ  
В  $\Delta_1$ -МОДЕЛІ ЗОНИ ПРОВІДНОСТІ  
МОНОКРИСТАЛІВ  $n$ -Ge

Резюме

На основі варіаційного методу Рітца розраховано енергію іонізації основного стану донорів Sb, P, As для  $\Delta_1$ -моделі зони провідності монокристалів  $n$ -Ge з врахуванням анізотропії закону дисперсії та хімічного зсуву. Порівняння одержаних теоретичних результатів з відповідними експериментальними даними показують, що модель кулонівського потенціалу домішки може бути використана в грубому наближенні лише для домішки Sb в Ge без врахування хімічного зсуву. Для домішок P та As розрахунки необхідно вже проводити з врахуванням хімічного зсуву, тобто, коли потенціал поля іона домішки не є кулонівським.