

Heavy Hole Interaction with Intrinsic Acceptor Defects in CdTe: Ab Initio Calculations

O.P. Malyk*, S.V. Syrotyuk

Lviv Polytechnic National University, 12, S. Bandera St., 79013 Lviv, Ukraine

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In the present paper, the way to describe the energy spectrum, wave function, and self-consistent potential in a semiconductor with a sphalerite structure at a predetermined temperature is proposed. Using this approach, within the framework of the supercell method, the temperature dependences of the ionization energy of intrinsic acceptor defects in cadmium telluride are calculated. In addition, on the basis of this method, the temperature dependences of the heavy hole effective mass, optical and acoustic deformation potentials, as well as the heavy hole scattering parameters on ionized impurities, polar optical, piezooptic and piezoacoustic phonons are established. Within the framework of short-range scattering models, the temperature dependences of the heavy hole mobility and the Hall factor in CdTe crystals with defect concentrations of 1×10^{20} - 1×10^{22} cm⁻³ are considered.

Keywords: Transport phenomena, Crystal defects, CdTe, Ab initio calculation.

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1. INTRODUCTION

The physical properties of cadmium telluride (CdTe), namely the required band gap and the required value of the absorption coefficient, provide ample opportunities for its use as a photovoltaic converter of solar energy. On the other hand, the electrical and optical properties of CdTe are largely determined by the structure of crystal lattice defects, in particular, intrinsic point defects. Therefore, the study of the defect structure of cadmium telluride is an important applied task. In the literature, a large number of works are devoted to the problem of studying the defect structure of cadmium telluride on the basis of the ab initio approach [1-7]. However, the main disadvantage of these works is the lack of a direct relationship between the structure of point defects and the kinetic properties of CdTe, which directly determine the electrical properties of the material. In the current work, this problem will be solved in two stages.

At the first stage, using the density functional theory, first-principles calculations of the energy characteristics of the crystal are performed: the energy spectrum, the electron wave function and the self-consistent potential of the crystal lattice. Usually, it is assumed that the abovementioned characteristics relate to the ground state of the crystal ($T = 0$ K). In the present article, a new method of calculating the abovementioned parameters of a sphalerite semiconductor at a given temperature is developed. With the help of this method, for a predetermined temperature, the heavy hole scattering parameters by intrinsic acceptor defects of cadmium telluride are calculated. At the second stage, the temperature dependences of the ionization energies of intrinsic acceptor defects in CdTe are calculated using the supercell method. On the basis of ionization energies of intrinsic acceptor defects and the scattering parameters of charge carriers, it is possible to determine the Fermi level and, in turn, the kinetic coefficients of cadmium telluride. Currently, there are a number of publications in the literature devoted to the

description of transport phenomena in semiconductors, in particular in CdTe [8], where the ab initio approach is used [9-13]. However, in these publications, the relationship between the defect structure and kinetic properties is not specified.

2. CALCULATION OF THE TEMPERATURE DEPENDENCES OF THE WAVE FUNCTION, CRYSTAL POTENTIAL AND HEAVY HOLE EFFECTIVE MASS

To describe the transport phenomena in *p*-type CdTe, heavy hole short-range scattering models were used [8, 14, 15]. These short-range heavy hole scattering models include several scattering constants as parameters, which, in turn, require the calculation of the valence band wave function and the self-consistent crystal potential. Using the pre-selected exchange-correlation GGA potentials of Cd and Te (pseudopotentials) and choosing a certain mixture of these usual exchange-correlation GGA potentials and the Hartree-Fock exchange potential (this mixture is determined by the "excmix" parameter of the ABINIT code), one can obtain a set of mathematical solutions of the Schrödinger equation corresponding to the value of the parameter "excmix" in the range from 0 to 1. It is known that the accuracy and convergence of calculations are largely determined by certain values of the parameters "ecut" and "pawecutdg" of the ABINIT code. The influence of the "ecut" parameter on the quality of calculations is very strong: the greater "ecut", the better convergence of calculations. The "pawecutdg" parameter defines the energy cut-off for the fine FFT grid, as a rule, "pawecutdg" must be larger or equal to "ecut". For calculations, the following values of these parameters were chosen: "ecut" = 48 Ha, "pawecutdg" = 64 Ha. An additional study found that an increase in the value of these parameters leads to a change in the position of the energy levels of the electronic spectrum by $1 \div 2 \times 10^{-5}$ eV, which is much less than the accuracy of the experiment.

* omalyk@ukr.net

Using the proposed calculation method, separation of the physical solutions of the Schrödinger equation from the set of mathematical solutions of the Schrödinger equation was performed. The following criterion for selecting physical solutions of the Schrödinger equation was proposed: at a given temperature, the theoretical width of the band gap must coincide with its experimental value determined from the experimental expression for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ solid solution [16]:

$$E_g(x, T) = -0.302 + 1.93x - 0.81x^2 + 0.832x^3 + 5.35 \times 10^{-4} T(1 - 2x). \quad (1)$$

Based on this approach, the following values of the "exchmix" parameter were obtained for the ideal unit cell of cadmium telluride: $\text{exchmix} = 0.397$ for $T = 0$ K, $\text{exchmix} = 0.288$ for $T = 300$ K. These values of the "exchmix" parameter correspond to certain wave functions of the valence band and the self-consistent potential at 0 and 300 K. Using short-range scattering models [8, 14, 15], as well as based on the obtained wave functions and crystal potentials, the following scattering constants can be calculated at 0 and 300 K, namely:

1) Scattering constants for heavy hole polar optical (PO) phonon interaction, heavy hole piezoacoustic (PAC) phonon interaction and heavy hole piezooptic (POP) phonon interaction:

$$A_{PO} = A_{PAC} = A_{POP} = \int \psi^* (R^2 - r^2/3) \psi \, d\mathbf{r}. \quad (2)$$

The integration is carried out in a volume which contains two atoms of different sorts and is equal to 1/8 of the unit cell volume.

2) d_0 is the optical deformation potential constant, which is chosen equal to the maximum value among the three optical deformation potential constants corresponding to one longitudinal and two transverse branches of optical lattice vibrations:

$$d_{0\nu} = \alpha_0 \int \psi^* \varepsilon_\nu \cdot \mathbf{V} \psi \, d\mathbf{r}, \quad \nu = 1, 2, 3, \quad (3)$$

where the region of integration is the same as in the case of PO scattering; ε_ν is the unitary contravariant polarization vector of optical oscillations; the vector \mathbf{V} is expressed in terms of the derivatives of the self-consistent electron potential energy with respect to the coordinates of the unit cell atoms [15].

3) E_{AC} is the acoustic deformation potential constant which is chosen equal to the maximum value among the three acoustic deformation potential constants corresponding to one longitudinal and two transverse branches of acoustic lattice vibrations [8]

$$\begin{aligned} E_{AC11} &= -(-I_1/4 + I_2/2 + I_3/2), \\ E_{AC1\perp} &= -(I_1/4 - I_2/4 + I_3/2), \\ E_{AC2\perp} &= -(I_1/2 + I_2/2 - I_3/4), \end{aligned} \quad (4)$$

where $I_1 = \int \psi^* V_1' \psi \, d\mathbf{r}'$; $I_2 = \int \psi^* V_2' \psi \, d\mathbf{r}'$; $I_3 = \int \psi^* V_3' \psi \, d\mathbf{r}'$; V_1', V_2', V_3' are the projections of the vector \mathbf{V} in the oblique coordinate system created by the primitive vectors of the zinc blende structure, and the region of integration is the same as in the case of PO scattering.

4) The ionized impurity scattering constant

$$A_{II} = \int_{\Omega} \Psi^* \frac{1}{r} \Psi \, d\mathbf{r}, \quad (5)$$

where integration is carried out throughout the spherical elementary cell.

As seen from (2)-(5), these scattering constants are expressed in terms of integrals over the wave function Ψ and the crystal potential U . Using three-dimensional B-spline interpolation and the finite displacement method [8], one can obtain the values of these integrals. Since the values of Ψ and U depend on temperature, then, accordingly, the scattering parameters will depend on temperature. Assuming the simplest, linear temperature dependence, one can calculate the temperature dependences of the scattering constants:

$$A_{PO} = (12.2 + 1.84 \times 10^{-3} T) \times 10^{-20} m^2, \quad (6a)$$

$$d_0 = -43.1 - 0.018 T \text{ eV}, \quad (6b)$$

$$E_{AC} = -3.07 - 2.28 \times 10^{-3} T \text{ eV}, \quad (6c)$$

$$A_{II} = (0.442 - 8.90 \times 10^{-6} T) \times 10^{10} m^{-1}. \quad (6d)$$

Based on equations (6a)-(6d), one can determine the temperature dependences of the heavy hole transition probabilities and, in turn, the kinetic coefficients of p -type cadmium telluride.

The determination of the heavy hole effective mass was performed based on the dispersion law $E(k)$ in the vicinity of the Γ point, which was established on the basis of ab initio calculations. The vicinity of the Γ point was chosen in the form of a cube, the edges of which were parallel to the Cartesian coordinate axes and for which the magnitude of the wave vector varied from -0.02 to 0.02 (reduced coordinates in πa_0 units, a_0 is the lattice constant). Each edge of the cube was divided into eight intervals. Using the obtained dependence $E(k)$ and three-dimensional B-spline interpolation, one can obtain the tensor of the inverse effective mass. This tensor was reduced to the principal axes (for cadmium telluride, one of these axes coincides with the [100] direction). As a result, we obtained the diagonal components of the inverse effective mass tensor and, accordingly, the components of the heavy hole effective mass: $m_1 = m_2 = m_{\perp hh} = 0.516 m_0$, $m_3 = m_{\parallel hh} = 0.037 m_0$. Different numerical values of this parameter are presented in the literature: from $m_{hh} = 0.4 m_0$ to $m_{hh} = 0.72 m_0$ [17]. Noteworthy is the work [17], where measurements were performed for the [100] direction. A comparison of these data shows that the calculated values of the effective mass components are close enough to the experimental values. The above method of calculation was performed for 0 and 300 K. Assuming a linear dependence, we obtained the temperature dependence of the heavy hole effective mass:

$$m_{hh} = (0.214 + 9.902 \times 10^{-5} T) m_0. \quad (7)$$

3. DETERMINATION OF THE TEMPERATURE DEPENDENCES OF THE ACCEPTOR IONIZATION ENERGY OF DIFFERENT TYPES OF INTRINSIC DEFECTS

In the proposed study, intrinsic acceptor defects are considered, namely $V_{Cd} - Te_{Cd}$, V_{Ca} . The study of the energy spectrum of the CdTe defect structure was carried out within the framework of the supercell method

on the basis of the ABINIT code: for $V_{Cd} - Te_{Cd}$ – supercell $Cd_{14}Te_{17}$ ($2 \times 1 \times 2$ sphalerite cubic structure); for V_{Ca} – supercell Cd_7Te_8 ($1 \times 1 \times 2$ sphalerite cubic structure). The same calculations were carried out for the ideal supercells Cd_8Te_8 ($1 \times 1 \times 2$ sphalerite cubic structure) and $Cd_{16}Te_{16}$ ($2 \times 1 \times 2$ sphalerite cubic structure). The result of calculations of the energy spectra of these supercells are presented in Table 1.

Table 1 – Energy spectrum of ideal and defect supercells

1×1×2 sphalerite cubic structure					
$T = 0, E_g = 1.65$ eV, $exchmix = 0.09$			$T = 300$ K, $E_g = 1.48$ eV, $exchmix = 0.0182$		
Energy levels of ideal Cd_8Te_8 , eV	Energy levels of defect, eV	Acceptor ionization energy, eV	Energy levels of ideal Cd_8Te_8 , eV	Energy levels of defect, eV	Acceptor ionization energy, eV
$E_c - 1 \times (4.194)$ (0) $E_v - 2 \times (2.541)$ (2)*	V_{Cd} $1 \times (3.733)$ (0) $1 \times (2.003)$ (0) $1 \times (2.003)$ (2)	At $T = 0$ p -type At $T \geq 0$ $\Delta E_A = 1.192$	$E_c - 1 \times (4.108)$ (0) $E_v - 2 \times (2.620)$ (2)	V_{Cd} $1 \times (3.660)$ (0) $1 \times (2.065)$ (0) $1 \times (2.065)$ (2)	$\Delta E_A = 1.040$
2×1×2 sphalerite cubic structure					
$T = 0, E_g = 1.65$ eV, $exchmix = 0.076$			$T = 300$ K, $E_g = 1.48$ eV, $exchmix = 0.00571$		
Energy levels of ideal $Cd_{16}Te_{16}$, eV	Energy levels of defect, eV	Acceptor ionization energy, eV	Energy levels of ideal $Cd_{16}Te_{16}$, eV	Energy levels of defect, eV	Acceptor ionization energy, eV
$E_c - 1 \times (4.130)$ (0) $E_v - 2 \times (2.478)$ (2)	$V_{Cd} - Te_{Cd}$ $1 \times (2.899)$ (0) $1 \times (2.823)$ (0) $1 \times (2.421)$ (2)	$\Delta E_A = 0.345$	$E_c - 1 \times (4.046)$ (0) $E_v - 2 \times (2.558)$ (2)	$V_{Cd} - Te_{Cd}$ $1 \times (2.923)$ (0) $1 \times (2.848)$ (0) $1 \times (2.454)$ (2)	$\Delta E_A = 0.290$

* Notation $2 \times (2.541)$ (2) means that there is a 2-fold degenerate energy level with an occupation number equal 2

Let us first consider the calculation of the ionization energy of the V_{Ca} defect. It is seen that at $T = 0$ K, valence band electrons from the level $2 \times (2.541)$ (2) will go to the unoccupied lower level $1 \times (2.003)$ (0) of the defect (thus forming a hole in the valence band), i.e. there is complete ionization of the acceptor impurity. Therefore, at $T = 0$, cadmium telluride will have p -type conductivity. At $T = 0$ and with a slight increase in temperature, the electron transition from the valence band to the unoccupied level $1 \times (3.733)$ (0) of the defect occurs, thus forming a hole in the valence band. The ionization energy of this process is equal to $\Delta E_A = 1.192$ eV. Other electron transitions (for example, transition from the defect level $1 \times (2.003)$ (2) to the conduction band level $1 \times (4.194)$ (0)) are improbable due to the high ionization energy. A similar situation is observed at $T = 300$ K. The valence band electron ($2 \times (2.620)$ (2) energy level) will go to the defect level $1 \times (3.660)$ (0), forming a hole in the valence band. The ionization energy of this process is equal to $\Delta E_A = 1.040$ eV. After that, assuming a linear relationship, we obtain the temperature dependence of the defect ionization energy:

$$\Delta E_A = 1.192 - 5.067 \times 10^{-4} T. \quad (8a)$$

A slightly different situation takes place for the $V_{Cd} - Te_{Cd}$ defect. At $T = 0$ K, only the electron transition from the valence band to the defect level $1 \times (2.823)$ (0) occurs, which corresponds to an ionization energy of 0.345 eV. Similarly, at $T = 300$ K, the defect ionization energy will be 0.290 eV. As a result, one can obtain:

$$\Delta E_A = 0.345 - 1.833 \times 10^{-4} T. \quad (8b)$$

4. DISCUSSION

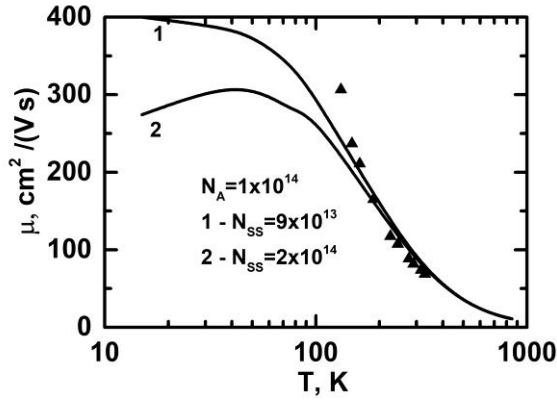
Comparison of the theoretical temperature dependences of the heavy hole mobility was made with the experimental data presented in [18]. Only defects with the lowest ionization energy were taken into account in the calculations, as they make the dominant contribution to the transport phenomena. Accordingly, it follows from equations (8a)-(8b) that the defect that gives the largest contribution is $V_{Ca} - Te_{Ca}$. The Fermi level is determined by the electroneutrality equation, which has the form:

$$p - n = N_A / \left\{ 1 + 2 \exp \left[(E_A - F) / (k_B T) \right] \right\}, \quad (9)$$

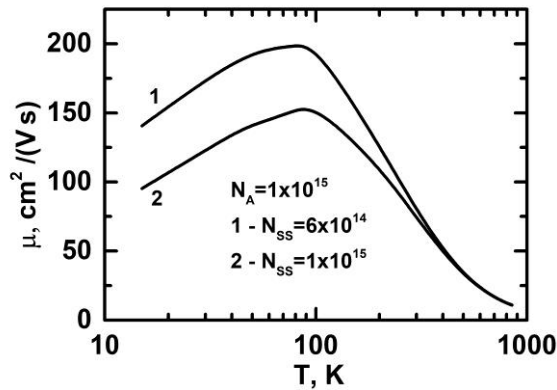
where N_A is the concentration of intrinsic defects and the defect level E_A at a given temperature is chosen according to (8b).

The calculation of the temperature dependences of the heavy hole mobility was performed on the basis of short-range scattering models [8, 14, 15] within the framework of the exact solution of the Boltzmann kinetic equation [19]. The cadmium telluride parameters used for the calculation are presented in [8]. The calculation of the temperature dependence of the heavy hole mobility in cadmium telluride crystals was performed for a defect concentration of $1 \times 10^{14} - 1 \times 10^{16} \text{ cm}^{-3}$. The results of the calculation are presented in Fig. 1. In order to cover all possible values of the heavy hole mobility at low temperature for each concentration of acceptor defects, the corresponding values of the concentration of static strain centers were selected. Comparison of the theoretical temperature dependence $\mu(T)$ with the experimental data was carried out only for the

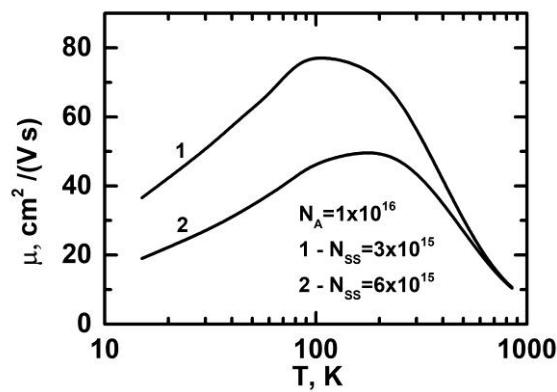
concentration of acceptor defects $1 \times 10^{14} \text{ cm}^{-3}$ (Fig. 1a). It can be seen that the experimental data agree quite well with the theory. Unfortunately, there are no experimental data in the literature for higher acceptor concentrations.



a



b

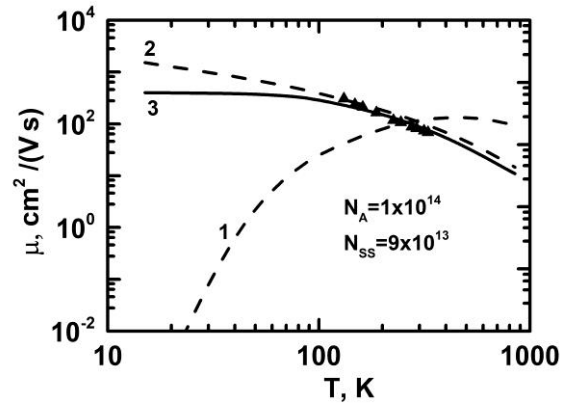


c

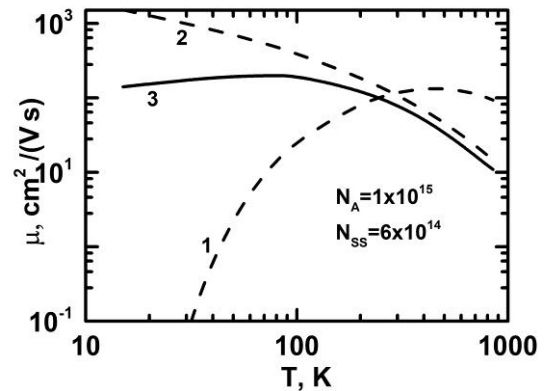
Fig. 1 – Heavy hole mobility versus temperature in cadmium telluride crystals with different defect concentrations: a – $N_A = 1 \times 10^{14} \text{ cm}^{-3}$; b – $N_A = 1 \times 10^{15} \text{ cm}^{-3}$; c – $N_A = 1 \times 10^{16} \text{ cm}^{-3}$

Fig. 2 presents a comparison of two competing approaches: short-range scattering models and long-range scattering models (relaxation time approximation). Dashed lines 1 and 2 represent the results of the calcu-

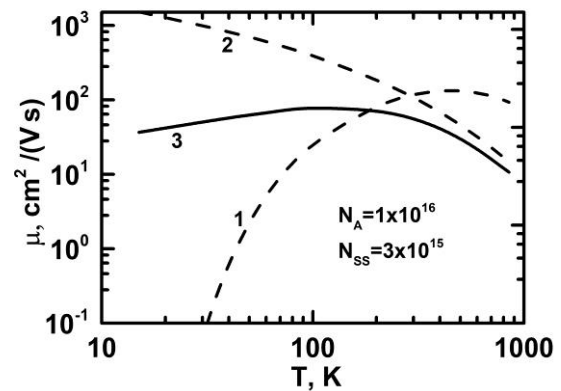
lation of the dependence $\mu(T)$ obtained in the relaxation time approximation: curve 2 describes the high-temperature region ($\hbar\omega \ll k_B T$), curve 1 describes the low-temperature region ($\hbar\omega \gg k_B T$). For cadmium telluride, the Debye temperature is $\theta_D = 239 \text{ K}$. This means that the low-temperature region will be determined by the condition $T < 24 \text{ K}$, and the high-temperature region will be determined by the condition $T > 2400 \text{ K}$.



a



b



c

Fig. 2 – Comparison of theoretical curves obtained in the framework of long-range (curves 1 and 2) and short-range (curve 3) scattering models

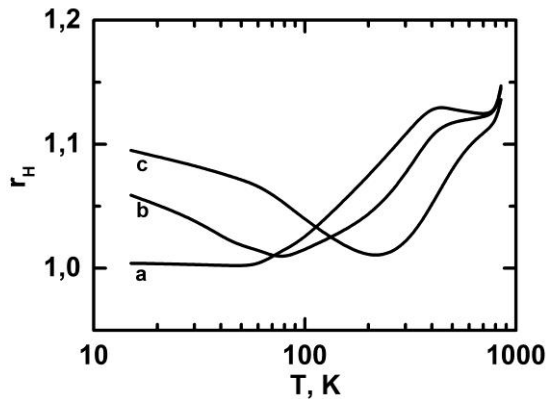


Fig. 3 – Temperature dependence of the heavy hole Hall factor. Notations of the curves are the same as in Fig. 1

The experimental points are located in the interval $T \sim \theta_D$, i.e., where the application of the relaxation time approximation (elastic scattering) is incorrect, whereas short-range scattering models allow to describe inelas-

tic scattering. Given the coincidence of curve 3 with the experiment, it can be argued that short-range scattering models provide a more adequate description of physical reality than long-range models. The dependences of the Hall factor on temperature calculated on the basis of the proposed method are shown in Fig. 3. It is seen that these dependences have minima arranged as follows: the higher the concentration of acceptor defects, the higher the temperature of the minimum.

5. CONCLUSIONS

The authors propose a new scheme for calculating the energy spectrum, wave function and potential energy of an electron in a crystal at a given temperature. Based on this, the temperature dependences of the ionization energies of defects of different types, as well as the temperature dependences of the kinetic coefficients are determined. It should be noted that the proposed calculation method can be applied to all semiconductors with a sphalerite structure.

REFERENCES

1. I. Sankin, D. Krasikov, *Phys. Status Solidi A* **215**, 1800887 (2019).
2. Su-Huai Wei, S. B. Zhang, *Phys. Rev. B: Condens. Matter Mater. Phys.* **66**, 155211 (2002).
3. Jie Ma, Su-Huai Wei, T. A. Gessert, Ken K. Chin, *Phys. Rev. B: Condens. Matter Mater. Phys.* **83**, 245207 (2011).
4. Ji-Hui Yang, Wan-Jian Yin, Ji.-Sang. Park, Jie Ma, Su-Huai Wei, *Semicond. Sci. Technol.* **31**, 083002 (2016).
5. D. Krasikov, A. Knizhnik, B. Potapkin, S. Selezneva, T. Sommerer, *Thin Solid Films* **535**, 322 (2013).
6. W. Orellana, E. Menendez-Proupin, M. A. Flores, *Phys. Status Solidi B* **256**, 1800219 (2019).
7. I. Sankin, D. Krasikov, *J. Mater. Chem. A* **5**, 3503 (2017).
8. O. Malyk, S. Syrotyuk, *Comput. Mater. Sci.* **139**, 387 (2017).
9. K. Kaasbjerg, K.S. Thygesen, K.W. Jacobsen, *Phys. Rev. B* **85**, 115317 (2012).
10. O. Restrepo, K. Varga, S. Pantelides, *Appl. Phys. Lett.* **94**, 212103 (2009).
11. O.D. Restrepo, K.E. Krymowski, J. Goldberger, W. A Windl, *New J. Phys.* **16**, 105009 (2014).
12. X. Li, J.T. Mullen, Z. Jin, K.M. Borysenko, M. Buongiorno Nardelli, K.W. Kim, *Phys. Rev. B* **87**, 115418 (2013).
13. Wu. Li, *Phys. Rev. B* **92**, 075405 (2015).
14. O.P. Malyk, S.V. Syrotyuk, *J. Elec. Materi.* **47**, 4212 (2018).
15. O.P. Malyk, *J. Elec. Materi.* **49**, 3080 (2020).
16. G.L. Hansen, J.L. Schmit, T.N. Casselman, *J. Appl. Phys.* **53**, 7099 (1982).
17. L. S. Dang, G. Neu, R. Romestain, *Solid State Commun.* **44**, 1187 (1982).
18. S. Yamada, *J. Phys. Soc. Jpn.* **15**, 1940 (1960).
19. O.P. Malyk, *J. Alloys Compd.* **371/1-2**, 146 (2004).

Взаємодія важких дірок з власними акцепторними дефектами в CdTe: ab initio розрахунків

О.П. Малик, С.В. Сиротюк

Національний університет "Львівська політехніка", вул. С. Бандери, 12, 29013 Львів, Україна

У роботі запропоновано спосіб опису енергетичного спектру, хвильової функції та самоузгодженого потенціалу в напівпровіднику зі структурою сфалериту при заданій температурі. За допомогою цього підходу в рамках методу суперкомірки розраховано температурні залежності енергії іонізації власних акцепторних дефектів у CdTe. Крім того, на основі запропонованого методу встановлено температурні залежності ефективної маси важких дірок, потенціалів оптичної та акустичної деформації, а також параметрів розсіювання важких дірок на іонізованих домішках, полярних оптичних, п'єзооптичних та п'єзоакустичних фонах. У рамках близькодійуючих моделей розсіяння розглянуто температурні залежності рухливості важких дірок і фактора Холла в кристалах CdTe з концентрацією дефектів $1 \times 10^{20} - 1 \times 10^{22} \text{ см}^{-3}$.

Ключові слова: Явища переносу, Дефекти кристалу, CdTe, Ab initio розрахунків.