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Heavy Hole Scattering on Intrinsic Acceptor Defects in Cadmium Telluride: Calculation from the First Principles

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In the present paper the way to describe the energy spectrum, the 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 holes effective mass, optical and acoustic deformation potentials, as well as of the heavy holes scattering parameters on ionized impurities, polar optical, piezooptic and piezoacoustic phonons were established. Within the framework of short-range scattering models the temperature dependences of the heavy hole mobility and Hall factor in CdTe crystals with defects concentrations $5 \times 10^{22} \div 5 \times 10^{24}$ cm^{-3} are considered.

Keywords: transport phenomena, crystal defects, CdTe, ab initio calculation.

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Introduction

The physical properties of cadmium telluride, 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 the crystal lattice defects, in particular, the intrinsic point defects. That is why the study of the defects structure of cadmium telluride is an important applied task. In the literature, a large number of works have been devoted to the problem of studying the defects structure in 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, the calculation from the first principles of the energy characteristics of the crystal is 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 presented article a new method of calculation of 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 holes scattering parameters on the 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 charge carriers scattering parameters it is possible to determine the Fermi level and, in turn, the kinetic coefficients of cadmium telluride. At present time, in the literature presents a number of publications 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 connection between defect structure and kinetic properties is not specified.

I. Calculation of temperature dependences of wave function, crystal potential and heavy hole effective mass

To describe the transport phenomena in p-type cadmium telluride the heavy hole short-range scattering models were used [8, 14, 15, 16]. These short-range heavy holes 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 "exchmix" parameter of the ABINIT code) one can obtained the totality of mathematical solutions of the Schrödinger equation corresponding to the value of the parameter "exchmix" in the limits from 0 to1. 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 parameter "pawecutdg" define the energy cut-off for the fine FFT grid, as a rule "pawecutdg" must be larger or equal to "ecut". For calculations the next values of these parameters were chosen: "ecut" = 48 Ha, "pawecutdg" = 64 Ha. An additional study found that increasing the value of these parameters leads to a change in the position of the energy levels of the electronic spectrum by $1\div2\times10^{-5}$ eV, which is much less than the accuracy of the experiment.

Using the proposed calculation method, the 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, which was determined from the experimental expression for solid solution $Hg_{1-x}Cd_xTe$ [17]:

$$E_g(x,T) = -0.302 + 1.93x - 0.81x^2 + 0.832x^3 + 5.35\times10^{-4}T(1-2x). \quad (1)$$

Based on this approach, the following values of the parameter "exchmix" were obtained for the ideal unit cell of cadmium telluride: exchmix = 0.397 for T = 0 K, exchmix = 0.288 for T = 300 K. These values of the parameter "exchmix" correspond to certain wave functions of the valence band and the self-consistent potential at 0 K and 300 K. Using the short-range scattering models [8, 14, 15, 16] , as well as based on the obtained wave functions and crystal potentials, the following scattering constants can be calculated at 0 K and 300 K, namely:

1) Scattering constants for heavy hole-polar optical (PO) phonon interaction, heavy hole-piezoacoustic (PAC) phonon 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 sort and which is equal to 1/8 of the unit cell volume.

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

$$d_{0\,\nu} = a_0 \int \psi^* \varepsilon_\nu \cdot \boldsymbol{V} \psi \, \mathrm{d}\mathbf{r}, \ \nu = 1,2,3, \quad (3)$$

where the region of integration is the same as in the case of PO scattering; $\boldsymbol{\varepsilon}_\nu$ – unitary contravariant polarization vector of the optical oscillations; vector $\boldsymbol{V}$ is expressed in terms of the derivatives of the self-consistent electron potential energy over the coordinates of the atoms of the unit cell [15].

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

$$E_{\mathrm{AC}||} = -(-I_1/4 + I_2/2 + I_3/2); E_{\mathrm{AC}1\perp} = -(I_1/4 - I_2/4 + I_3/2); E_{\mathrm{AC}2\perp} = -(I_1/2 + I_2/2 - I_3/4); \quad (4)$$

where:

$$I_1 = \int \psi^* V_1' \psi \, \mathrm{d}\mathbf{r}'; I_2 = \int \psi^* V_2' \psi \, \mathrm{d}\mathbf{r}'; I_3 = \int \psi^* V_3' \psi \, \mathrm{d}\mathbf{r}';$$

$V_1'; V_2'; V_3'$ are the projections of the vector V in an 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:

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

where integration is carried out throughout the sphalerite elementary cell.

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

Assuming the simplest, linear, temperature dependence, one can calculate the temperature dependences of the scattering constants:

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

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

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

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

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

The determination of the effective heavy holes mass was performed on the basis of the dispersion law $E(\boldsymbol{k})$ 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 ribs 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 π/a0 units, a0–lattice constant). Each rib 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 obtain the diagonal components of the inverse effective mass tensor and, accordingly, the components of the heavy holes effective mass (at T = 0 K): $m_1 = m_2 = 0.516\ m_0$; $m_3 = 0.037\ m_0$. Note that in the literature there are various numerical values of this parameter: $m_{hh} = 0.4\,m_0$ [18]; $m_{hh} = 0.41\,m_0$ [19]; $m_{hh} = 0.63\,m_0$ [20]; $m_{hh} = 0.72\,m_0$ [21]. It should be noted the work [21], where measurements were performed for the [100] direction. A comparison of these data shows that the calculated values of the components of the effective mass are close enough to the experimental values. The above method of calculation was performed for 0 K and 300 K. Assuming a linear dependence, we obtain the temperature dependence of the heavy holes effective mass:

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

It is possible to note the qualitative similarity of expression (7) to analogous expression for $Cd_xHg_{1-x}Te$ (x~0.2), obtained by fitting to experimental data [22].

II. Determination of temperature dependences of ionization energy of different types of intrinsic acceptor defects

In the proposed study the intrinsic acceptor defects are considered, namely: V_{Cd} – Te_{Cd}, V_{Cd}. The study of the energy spectrum of the defects structure of cadmium telluride was carried out within the framework the supercell method on the basis of the ABINIT code: for V_{Cd} – Te_{Cd} – supercell $Cd_{14}Te_{17}$ (2×1×2 sphalerite cubic structure); V_{Cd} – supercell Cd_7Te_8 (1×1×2 sphalerite cubic structure). The same calculations were carried out for the ideal supercell Cd_8Te_8 (1×1×2 sphalerite cubic structure) and $Cd_{16}Te_{16}$ (2×1×2 sphalerite cubic structure). The result of calculations of energy spectrums of these supercells are presented in Table 1.

Table 1

Energy spectrum of ideal and defect supercell

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×(4.194) (0) E_v– 2×(2.541) (2)*	V_{Cd} 1×(3.733) (0) 1×(2.003) (0) 1×(2.003) (2)	At T = 0 p- type. At T ≥ 0 ΔE_A =1.192	E_c – 1×(4.108) (0) E_v – 2×(2.620) (2)	V_{Cd} 1×(3.660) (0) 1×(2.065) (0) 1×(2.065) (2)	ΔE_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×(4.130) (0) E_v–2×(2.478) (2)	V_{Cd} – Te_{Cd} 1×(2.899) (0) 1×(2.823) (0) 1×(2.421) (2)	ΔE_A =0.345	E_c–1×(4.046) (0) E_v–2×(2.558) (2)	V_{Cd} – Te_{Cd} 1×(2.923) (0) 1×(2.848) (0) 1×(2.454) (2)	ΔE_A = 0.290

* *Recording 2×(2.541) (2) means that there is exist 2-fold degenerate energy level with an occupation number equal 2.*

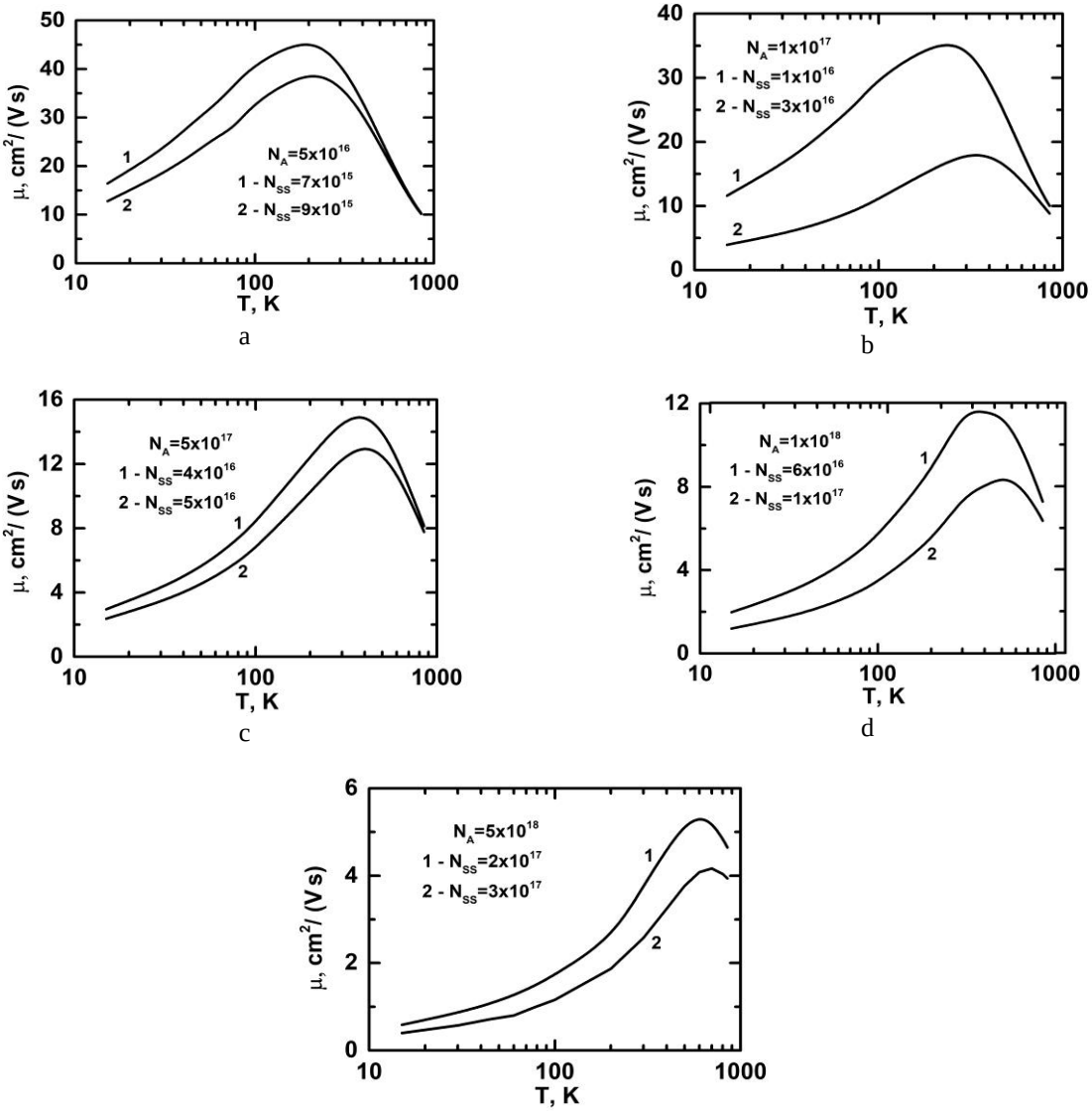

Fig. 1. Heavy hole mobility versus temperature in cadmium telluride crystals with different intrinsic defects concentration. a – $N_A = 5 \times 10^{16}$ cm^{-3}; b – $N_A = 1 \times 10^{17}$cm^{-3}; c – $N_A = 5 \times 10^{17}$cm^{-3}; d – $N_A = 1 \times 10^{18}$cm^{-3}; e – $N_A = 5 \times 10^{18}$cm^{-3}.

First let's consider the calculation of the ionization energy of the V_{Cd} defect. It is seen that at T = 0 K, the electrons of the valence band from the level 2×(2.541) (2) will pass to an unoccupied lower level 1× (2.003) (0) of defect (thus forming a hole in the valence band), i.e. there is a complete ionization of the acceptor impurity. Therefore, at T = 0, cadmium telluride will have a p-type conductivity. At T = 0 and with a slight increase in temperature the transition of the electron from the valence band to the unfilled level 1×(3.733) (0) of the defect occur, thus forming a hole in the valence band. The ionization energy of this process is equal ΔE_A =1.192 eV. Other electron transitions (for example transition from defect level 1×(2.003) (2) to conduction band level 1×(4.194) (0) are improbable due to high ionization energy. An analogical situation is observed at T = 300 K. The valence band electron (2×(2.620) (2) energy level) will pass to the defect level 1×(3.660) (0), forming a hole in the valence band. The ionization energy of this process is equal ΔE_A =1.040 eV. After that, assuming a linear relationship, we obtain the temperature dependence of the defect ionization energy:

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

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

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

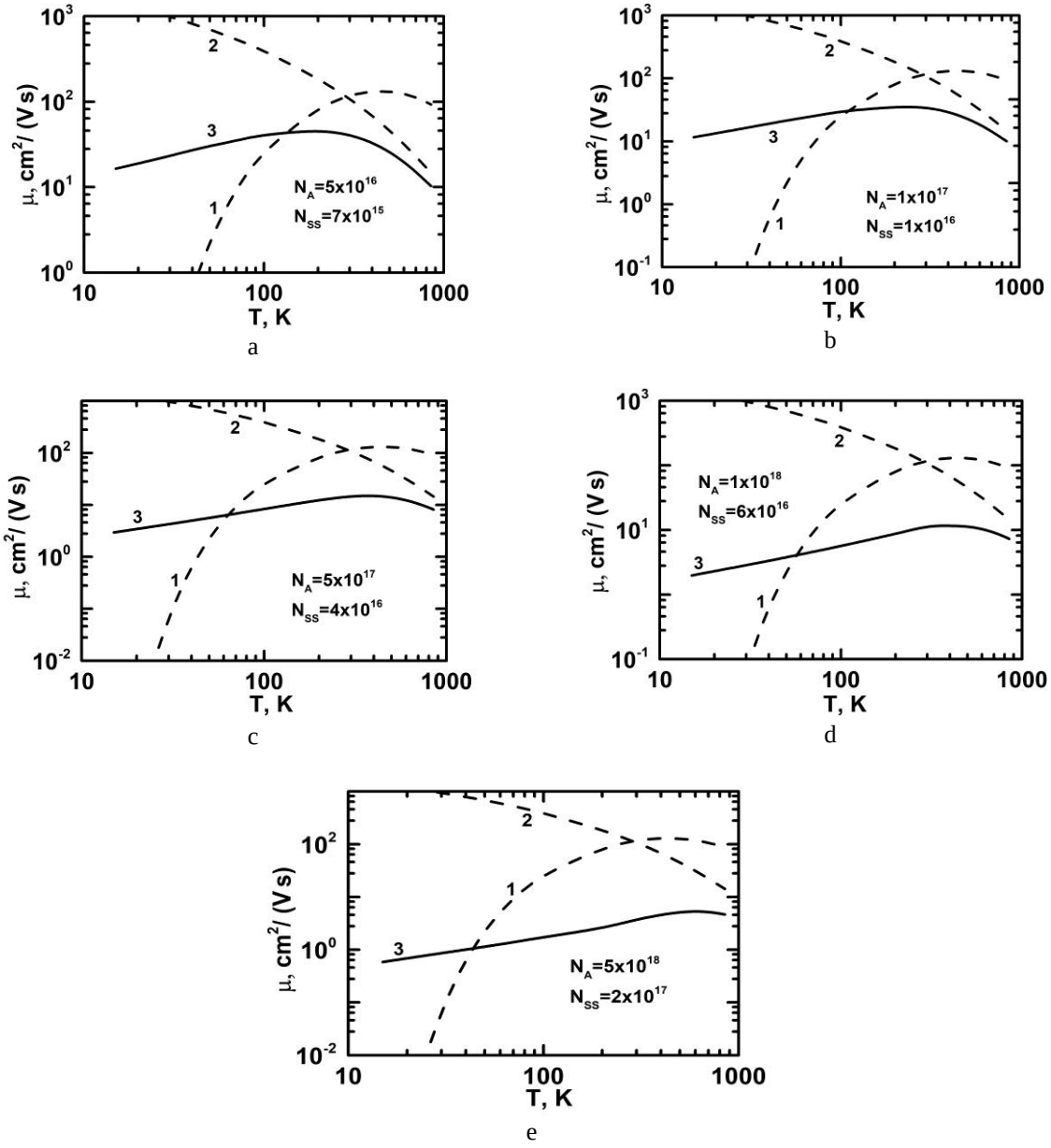

Fig. 2. Comparing of theoretical curves obtained in framework of long-range (curves 1 and 2) and short-range (curve 3) scattering models.

III. Discussion

During the calculation only defects with the lowest ionization energy were taken into account, 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 $V_{Cd} - Te_{Cd}$. The Fermi level is determined by the electroneutrality equation, which has the form:

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

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

The calculation of the temperature dependences of the carrier mobility was performed on the basis of short-range scattering models [8, 14, 15] within the framework of the exact solution of the Boltzmann's kinetic equation [23]. Cadmium telluride parameters used for calculation are presented elsewhere [8]. The calculation of the temperature dependence of the heavy holes mobility in cadmium telluride crystals was performed for the defect concentration of $5 \times 10^{16} \div 5 \times 10^{18}$ cm^{-3}. The results of the calculation are presented on Fig.1. In order to cover all possible values of the heavy holes mobility at low temperature for each concentration of acceptor defects the corresponding values of concentration of the static strain centers (N_{ss}) was selected. Unfortunately, in the literature the experimental data for the abovementioned interval of the intrinsic acceptor concentrations are absent.

Figure 2 presents a comparison of two competing approaches: short-range scattering models and long-range scat-tering models (relaxation time approximation). The dashed lines 1 and 2 represent the results of calculation of the dependence μ(T) obtained in the relaxation time

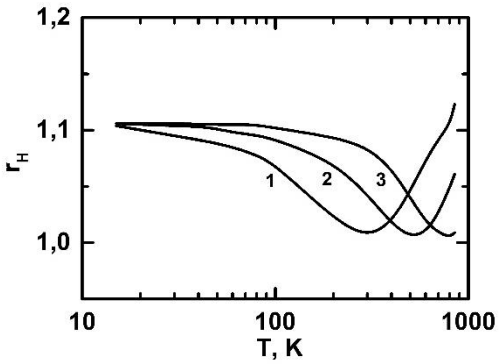

Fig. 3. The temperature dependence of heavy hole's Hall factor. 1 – $N_A = 5 \times 10^{16}$ cm^{-3}; 2 – $N_A = 5 \times 10^{17}$ cm^{-3}; 3 – $N_A = 5 \times 10^{18}$ cm^{-3}.

approximation: curve 2 describes the high-temperature region ($\hbar\omega << k_BT$), curve 1 describes the low-temperature region ($\hbar\omega >> k_BT$). For cadmium telluride the Debye temperature is $\theta_D = 239$ K. It means that the low-temperature region will be determined by the condition T <24 K, and the high-temperature region will be determined by the condition T > 2400 K. From this point of view, the application of the relaxation time approximation (elastic scattering) in the range of 24 K < T < 2400 K is incorrect. At the same time, short-range scattering models allow to describe inelastic scattering. Thus, it can be argued that short-range models give a more adequate description of physical reality than long-range models.

Calculated on the basis of the proposed method the dependences of Hall factor on temperature are presented in Fig. 3. It is seen that these dependencies have minimums, which are situated as follows - the higher the concentration of acceptor defects, the higher the temperature of minimum.

Conclusion

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 intrinsic acceptor 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.

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Розсіювання важких дірок на власних акцепторних дефектах в телуриді кадмію: розрахунок з перших принципів

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У цій роботі запропоновано спосіб опису енергетичного спектру, хвильової функції та самоузгодженого потенціалу в напівпровіднику зі структурою сфалериту при заданій температурі. З використанням цього підходу в рамках методу суперкомірки розраховано температурні залежності енергії іонізації власних акцепторних дефектів у телуриді кадмію. Крім того, на основі цього методу встановлені температурні залежності ефективної маси важких дірок, оптичних і акустичних потенціалів деформації, а також параметрів розсіювання важких дірок на іонізованих домішках, полярних оптичних, п'єзооптичних і п'єзоакустичних фононах. У рамках близькодіючих моделей розсіяння розглянуто температурні залежності рухливості важких дірок і фактора Холла в кристалах CdTe з концентрацією дефектів $5 \times 10^{22} \div 5 \times 10^{24}$ см$^{-3}$.

Ключові слова: явища переносу, дефекти кристалу, CdTe, Ab initio розрахунок.