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ELECTRONIC PROPERTIES OF SEMICONDUCTORS

A Quasi-Classical Model of the Hubbard Gap in Lightly Compensated Semiconductors

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Abstract—A quasi-classical method for calculating the narrowing of the Hubbard gap between the A^0 and A^+ acceptor bands in a hole semiconductor or the D^0 and D^- donor bands in an electron semiconductor is suggested. This narrowing gives rise to the phenomenon of a semiconductor transition from the insulator to metal state with an increase in doping level. The major (doping) impurity can be in one of three charge states (−1, 0, or +1), while the compensating impurity can be in states (+1) or (−1). The impurity distribution over the crystal is assumed to be random and the width of Hubbard bands (levels), to be much smaller than the gap between them. It is shown that narrowing of the Hubbard gap is due to the formation of electrically neutral acceptor (donor) states of the quasicontinuous band of allowed energies for holes (electrons) from excited states. This quasicontinuous band merges with the top of the valence band (v band) for acceptors or with the bottom of the conduction band (c band) for donors. In other words, the top of the v band for a p-type semiconductor or the bottom of the c band for an n-type semiconductor is shifted into the band gap. The value of this shift is determined by the maximum radius of the Bohr orbit of the excited state of an electrically neutral major impurity atom, which is no larger than half the average distance between nearest impurity atoms. As a result of the increasing dopant concentration, the both Hubbard energy levels become shallower and the gap between them narrows. Analytical formulas are derived to describe the thermally activated hopping transition of holes (electrons) between Hubbard bands. The calculated gap narrowing with increasing doping level, which manifests itself in a reduction in the activation energy ε_2 is consistent with available experimental data for lightly compensated p-Si crystals doped with boron and n-Ge crystals doped with antimony.

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1. INTRODUCTION

Covalent crystal semiconductors doped with hydrogen-like impurity atoms [1–7] are widely used as model systems for theoretical and experimental investigations of the Hubbard gap by features of the low-temperature conductivity.

The direct-current conductivity σ of three-dimensional samples of such systems at low temperatures T, which is consistent with the entire set of available experimental data, has the form [8] (see Fig. 1)

$$\sigma = \frac{1}{\rho} = \sigma_1 + \sigma_2 + \sigma_3 = \sigma_{01}\exp\left(-\frac{\varepsilon_1}{k_B T}\right) + \sigma_{02}\exp\left(-\frac{\varepsilon_2}{k_B T}\right) + \sigma_{03}\exp\left(-\frac{\varepsilon_3}{k_B T}\right), \quad (1)$$

where ρ is the specific resistance; $\sigma_{01} = 1/\rho_{01}$, $\sigma_{02} = 1/\rho_{02}$, and $\sigma_{03} = 1/\rho_{03}$ are the conductivities extrapolated to the zero reciprocal temperature $1/T \to 0$, which depend on temperature only slightly as compared with the corresponding exponents; σ_1 is caused by the transitions of holes from acceptors to the valence band (v band) or electrons from donors to the conduction band (c band); σ_2 is determined by the transitions of holes (electrons) between Hubbard bands or the transitions of holes from the A^0 to A^+ band for acceptors and electrons from the D^0 to D^- band for donors (Fig. 2); σ_3 is related to the thermally activated tunneling transitions (hops) of holes between acceptors in the A^0 band or the same for electrons between donors in the D^0 band; ε_1, ε_2, and ε_3 are the energies of the thermal activation of hole or electron conductivity in the vicinity of temperatures T_1, T_2, and T_3, where the above-mentioned conductivity mechanisms are dominant; k_B is the Boltzmann constant, and $k_B T$ is the thermal energy. It is worth noting that σ_{01} and σ_{02} only slightly depend on the dopant concentration (in accordance with a power law), while σ_{03} exponentially depends on the dopant concentration, which determines the probability of tunneling between localized states. In the experiment, the temperature dependence of σ_2 is often obtained using formula (1) by subtracting the band conductivity σ_1 and the hopping conductivity σ_3, which are more reliably approximated by straight lines on the Arrhenius scale ($\ln\sigma - 1/T$), from the total

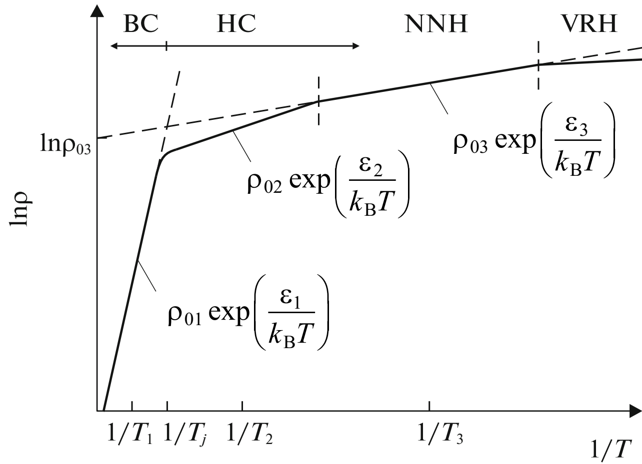

Fig. 1. Schematic representation of the dependence of the dc resistivity logarithm $\ln\rho$ of a p-type crystal semiconductor on the inverse temperature $1/T$. The regions of dominant hole transfer regimes are separated. BC is the band conductivity and ionization of acceptors with the thermal injection of holes with an activation energy of ε_1 to the allowed energy band, i.e., the v band of the crystal matrix. HC is the hopping conductivity. NNH is the hopping conductivity between nearest acceptors in charge states (0) and (−1) in the vicinity of temperature T_3. VRH is the variable-hopping-range conductivity with activation energy decreasing with temperature.

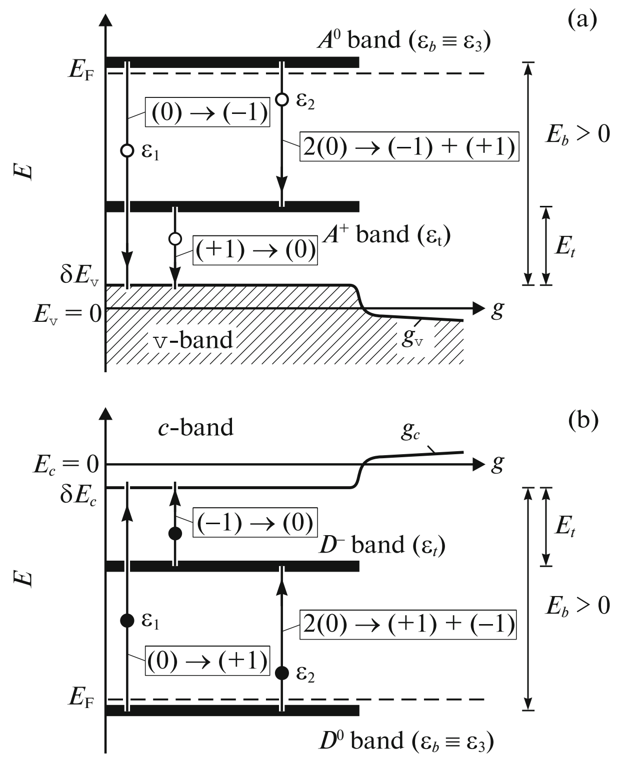

Fig. 2. (a) A^0 and A^+ are acceptor bands in the p-type semiconductor band gap and (b) D^0 and D^- are donor bands in the n-type semiconductor band gap in the band diagram (dependences of the densities of states g_v and g_c for the v and c bands on the one-electron energy E). Arrows indicate the transitions of holes (open circles) and electrons (closed circles), which lead to a change in the acceptor and donor charge states. Shifts of the top of the v band $\delta E_v > 0$ and the bottom of the c band $\delta E_c < 0$ caused by the overlap of excited states of electrically neutral impurities are shown. E_F is the Fermi level (chemical potential) and E_b–E_t is the energy gap between the lower and upper impurity bands. The activation energies of the hopping conductivity in the impurity bands $\varepsilon_b \equiv \varepsilon_3$ for the A^0 and D^0 bands and ε_t for the A^+ and D^- bands are indicated. The v-band states occupied with electrons are crosshatched.

conductivity σ. At the lowest temperatures, the regime of hopping conductivity σ_3 over nearest neighbors (nearest-neighbor hopping NNH) is altered to variable-range hopping (VRH), which is identified by a decrease in the activation energy with temperature as $\varepsilon_3 \propto T^{3/4}$ in accordance with Mott theory [5] and as $\varepsilon_3 \propto T^{1/2}$ in accordance with the Efros–Shklovskii theory [4].

The aim of this study is to investigate the concentration-related behavior of the Hubbard gap using the thermal activation energy ε_2 of the transitions of holes or electrons between Hubbard bands, which is determined by this gap. We consider lightly compensated semiconductors, in which the ratio between the concentrations of minor (compensating) and major (doping) impurities is $K \ll 1$.

The main empirical features of the conductivity σ_2 [2–6] are as follows. (i) This conductivity is observed only at low or moderate degrees of compensation slightly above $K \approx 0.5$. (ii) This conductivity is observed only in a limited dopant concentration range within about an order of magnitude, which directly precedes the critical concentration of the insulator–metal (Mott) transition [1]. (iii) This conductivity is characterized by the nearly constant pre-exponent σ_{02}, which is similar to the minimum Mott metal conductivity in the c or v band. (iv) It is commonly accepted that the thermal activation energy ε_t for migration over an upper (t) Hubbard band is much lower than the activation energy $\varepsilon_b \equiv \varepsilon_3$ for hops over a lower (b) Hubbard band.[1]

In this study, taking into account the excited states of electrically neutral major (doping) impurities in the quasi-classical approximation and using recent results of theoretical investigations of ionization equilibrium in the systems under study, we analytically and numerically calculate a decrease in the Hubbard energy gap between the A^0 and A^+ bands for acceptors and D^0 and

[1] Hereinafter, the lower Hubbard bands (A^0 for acceptors and D^0 for donors) are also referred to as b bands and the upper Hubbard bands (A^+ for acceptors and D^- for donors) are referred to as t bands.

D^- bands for donors in lightly compensated covalent crystal semiconductors with an increasing impurity concentration.

The concepts of excited states of impurity atoms were used previously to explain various manifestations of the effect of a decrease in the thermal energy of impurity ionization with an increase in the doping level. In particular, the calculations reported in [9] demonstrated for the first time that limitation of the number of excited states of electrically neutral hydrogen-like donors (or acceptors) with an increase in their concentration in a semiconductor can lead to a decrease in the thermal energy of their ionization. Later, using low-temperature photoluminescence, the authors of [10] observed a decrease in the difference between the excited- and ground-state energies of boron acceptor atoms in *p*-Si with increasing boron concentration until the transition of silicon from the insulator to metal state. Excited impurity states were used to explain the dependence of the thermal ionization energy of hydrogen-like donors S and Se on the doping level in lightly compensated *n*-GaAs crystals (upon ionization, donors pass from the electrically neutral to positively charged state) [11]. However, the possible existence of negatively charged donors was not discussed. Finally, the excited states of simple hydrogen-like impurities with one localized electron or hole were taken into account in [12] in explaining the features of the photoconductivity of lightly doped semiconductor crystals.

In [8], the low-temperature conductivity of *n*-Ge:Sb crystals was described by introducing the concept of conductivity σ_2 with the thermal activation energy ε_2, which was interpreted by Mott (see [1, 5] and references therein) as the transition of an electron between two electrically neutral donors with the formation of two oppositely charged ions (Fig. 1). In [8], the experimentally observed decrease in the ε_2 value with increasing doping level was described for the first time. After that, many competing models were proposed to explain this effect [1–5, 13, 14], which, however, required fitting parameters for the quantitative comparison of calculated and experimental data. In addition, models were proposed that explained the ε_2 decrease by the effects of screening of impurity ions [15] and the formation of an electric dipole [16] at each transition of a hole (electron) between two electrically neutral impurities. However, these models were more suitable for describing semiconductors with a moderate degree of compensation $K \approx 0.5$, when the average distance between electrically neutral and charged impurities is approximately the same and the Coulomb-field screening radius is at a minimum [17] in accordance with Debye–Hückel theory.

This study is constructed as follows. First, we consider a *p*-type semiconductor with the hopping migration of holes over the A^0 and A^+ bands and, then, an *n*-type semiconductor with the hopping migration of electrons over the D^0 and D^- bands. The results of [9, 11], where dopants with two possible charge states ((0, −1) or (0, +1) for acceptors and donors, respectively) were investigated, are generalized for the case when they can be in three charge states (−1, 0, and +1). According to [18], we assume that only electrically neutral acceptors (donors) have excited states. Then, to obtain the analytical expression, we consider narrow A^0 and A^+ (D^0 and D^-) bands with a width smaller than the thermal energy k_BT_2 and the energy gap $E_b - E_t$ between the lower (*b*) and upper (*t*) Hubbard bands.

2. IONIZATION EQUILIBRIUM BETWEEN THE A^0 AND A^+ ACCEPTOR BANDS

We consider a *p*-type crystal semiconductor moderately doped with acceptors and lightly compensated with donors. The electrical-neutrality condition in the presence of the A^0 and A^+ bands has the form

$$N_{-1} = N_{+1} + KN_a, \tag{2}$$

where $N_a = N_{-1} + N_0 + N_{+1}$ is the total concentration of acceptors in all charged states $Z = -1$, 0, and +1; KN_a is the concentration of compensating donors in the charge state +1; and $0 < K <$ is the degree of compensation.

It is worth noting that, although semiconductors with three-charge impurities or intrinsic structural defects have been used for a long time in functional electronics [19–21], the principal role played by the excited states of such impurities in the electrical and optical properties of semiconductors is still understudied [22, 23].

Let us consider the band diagram of a moderately doped *p*-type semiconductor. The acceptor energy levels are counted from the top of the *v* band of an undoped crystal; i.e., $E_v = 0$ (Fig. 2a). The transition of the acceptor from the neutral (0) to negatively charged (−1) state due to the thermal emission of a hole from the A^0 to *v* band is accompanied by absorption of the energy $E_b > 0$. The transition of an acceptor from the positively charged (+1) to neutral (0) state is accompanied by absorption of the energy $E_t > 0$ (emission of a hole from the A^+ to *v* band). The hopping transition of a hole between two electrically neutral acceptors with their transformation to a pair of negatively and positively charged ions is accompanied by absorption of the energy $E_b - E_t > 0$. According to the detailed thermodynamic-equilibrium principle, the energy $E_b - E_t$ is released upon the recombination of a pair of charged states (+1 and −1) of acceptors and their transformation to two electrically neutral acceptor states.

For the narrow A^0 and A^+ bands, the acceptor concentration in the charge state $Z = -1, 0, +1$ is [18, 24]

$$N_Z = N_a f_Z, \tag{3}$$

where the reciprocal charge-state distribution functions $1/f_Z$ of acceptors are

$$f_{-1}^{-1} = 1 + \beta_b \exp\left[\frac{E_F^{(v)} + E_b}{k_B T}\right] + \frac{\beta_b}{\beta_t}\exp\left[\frac{E_b + E_t + 2E_F^{(v)}}{k_B T}\right],$$

$$f_0^{-1} = 1 + \frac{1}{\beta_b}\exp\left[\frac{-(E_F^{(v)} + E_b)}{k_B T}\right] + \frac{1}{\beta_t}\exp\left[\frac{-(E_F^{(v)} + E_t)}{k_B T}\right],$$

$$f_{+1}^{-1} = 1 + \beta_t \exp\left[\frac{-(E_F^{(v)} + E_t)}{k_B T}\right] + \frac{\beta_t}{\beta_b}\exp\left[\frac{-(E_b + E_t + 2E_F^{(v)})}{k_B T}\right], \quad (4)$$

$E_F^{(v)} = (\delta E_v - E_F) < 0$ is the Fermi-level energy in the band gap, $\delta E_v > 0$ is the shift of the top of the v band in the band gap due to the overlap of orbitals of excited states of electrically neutral acceptors, $E_F > 0$ is the Fermi level (chemical potential) counted from the top of the v band ($E_v = 0$) of the undoped semiconductor, $E_b > 0$ and $E_t > 0$ are acceptor levels, and $\beta_b = \beta_0/\beta_{-1}$ and $\beta_t = \beta_0/\beta_{+1}$ are the level-degeneracy factors; in particular, for boron atoms in the Si:B system, according to [25], we have $\beta_b = 4$ and $\beta_t = 1/4$.

Taking into account the excited states of only electrically neutral acceptors, in formula (4) we should substitute the quantity β_0 with

$$\beta_0(l_m) = \beta_0 \sum_{l=1}^{l_m} l^2 \exp\left[\frac{(1 - l^2)E_b}{l^2 k_B T}\right], \quad (5)$$

where $l_m \geqslant 1$ is the largest number of possible excited states of an average statistical acceptor in the charge state (0) [18, 26, 27].

Then, considering the energy gap between Hubbard bands, the number l_m of excited states that can still be attributed to the discrete energy spectrum of an electrically neutral acceptor, is determined from the condition of equality of the hole-orbit radius $l_m^2 a_H$ in the excited state to half the average distance between the nearest impurity atoms $d/2$ and is used as a continuous quantity [9, 27]:

$$l_m = [(d/2)/a_H]^{1/2} \geq 1. \quad (6)$$

In formula (6), the Bohr-orbit radius a_H (see, for example, [28]), e.g., for the hole of a hydrogen-like acceptor (donor electron), is determined by the ionization potential $I_b = e^2/(8\pi\varepsilon_r\varepsilon_0 a_H)$ of a single (isolated) impurity atom in the electrically neutral state, e is the elementary charge, ε_r is the relative static permittivity of the crystal matrix, and ε_0 is the electric constant. (The complex structure of the v band and the presence of light and heavy holes in it [29], as well as the multi-valley character of the c band [4] in silicon and germanium are disregarded in our model). The average distance between nearest impurity atoms in the case of their random distribution in the crystal is

$$d = \int_0^\infty r\mathcal{P}(r)dr \approx 0.554[(1 + K)N_a]^{-1/3}, \quad (7)$$

where $\mathcal{P}(r)dr = 4\pi r^2(1 + K)N_a\exp[-4\pi r^3(1 + K)N_a/3]dr$ is the Poisson probability [30] of the fact that the impurity (acceptor or donor) atom nearest to the separated impurity atom is located at a distance from r to $r + dr$ and there are no other impurity atoms in a sphere with a volume of $4\pi r^3/3$ and its center at the separated impurity atom.

We note that, as follows from formulas (6) and (7), the maximum number of acceptor excited states is $l_m = \{0.277[(1 + K)N_a]^{-1/3}/a_H\}^{1/2} = 1$; i.e., the situation when the average statistical acceptor is ionized takes place for $K = 0.01$ at $a_H N_a^{1/3} = 0.278$, which is similar to the experimental criterion $a_H N^{1/3} \approx 0.25$ of the concentration insulator–metal phase transition (Mott transition) [1, 5, 31].

Our model has the following principal concept: the effect of excited states of electrically neutral acceptors on the position of two Hubbard energy levels (bands) E_b and E_t leads to a situation where the levels become shallower with increasing acceptor concentration due to a shift of the top of the v band $\delta E_v = I_b/l_m^2$ in the band gap (compare with [7, 32, 33]),

$$E_b = I_b - \delta E_v = \left(1 - \frac{1}{l_m^2}\right)I_b,$$

$$E_t = 0.055E_b = \left(1 - \frac{1}{l_m^2}\right)I_t, \quad (8)$$

where $I_b > 0$ and $I_t > 0$ are the energies required for the transition of a hole from an isolated (single) neutral acceptor with index b and an isolated positively charged acceptor with index t to the v band and $I_b \equiv I_H = e^2/(8\pi\varepsilon_r\varepsilon_0 a_H)$ is the Bohr energy of a single acceptor.

Then, from (8), the energy gap between the A^0 and A^+ bands is

$$(E_b - E_t)_a = \left(1 - \frac{1}{l_m^2}\right)I_2 \geq 0, \quad (9)$$

where, according to [2, 34, 35], the energy gap between Hubbard bands, or more exactly, levels for a single (isolated) acceptor is $I_2 = I_b - I_t = 0.945I_b$ and $I_t/I_b = 0.055$.

It is noteworthy that formula (8) predicts a decrease in both the energy E_b of the transition of holes from the A^0 band and the energy E_t of the transi-

tion of holes from the A^+ band to the v band with increasing N_a at $K \ll 1$, so both E_b and E_t turn to zero at $a_H N_a^{1/3} = 0.278$, when $l_m = 1$. Formulas (8) and (9) were written taking into account that $E_t/E_b = I_t/I_b = 0.055$, i.e., as for an isolated acceptor.

Taking into account formulas (6) and (7), in expression (5) we assume the l_m value to be continuous. Then, formula (5) can be written in the approximate form

$$\frac{\beta_0(l_m)}{\beta_0} \approx 1 + \int_1^{l_m} l^2 \exp\left[\frac{(1-l^2)E_b}{l^2 k_B T}\right] dl, \qquad (10)$$

where the energy E_b of ionization of the electrically neutral acceptor is determined by (8).

According to (8) and taking into account (6) and (7), the shift $\delta E_v > 0$ of the top of the v band into the band gap (Fig. 2a) due to the overlap of orbitals of excited states of electrically neutral hydrogen-like acceptors is

$$\frac{\delta E_v}{I_b} = \frac{1}{l_m^2} = \frac{2a_H}{d} \approx 3.61(1+K)^{1/3} a_H N_a^{1/3}. \qquad (11)$$

We note that the estimation of δE_v using (11) is qualitatively consistent with the calculation reported in [36], which was performed in the Hartree–Fock approximation. According to [36, 37], the shift δE_v of the top of the v band relative to the "vacuum level" into the band gap of a lightly compensated semiconductor is caused by the lowering of a potential barrier between electrically neutral hydrogen-like acceptors in the ground (unexcited) state with an increase in their concentration. The δE_v value appears much larger than the shift of the acceptor levels relative to the vacuum level [38].

3. DIFFERENTIAL ACTIVATION ENERGY OF CONDUCTIVITY UPON THE HOPPING TRANSITIONS OF HOLES FROM THE A^0 TO A^+ BAND

According to [39, 40], the density of the hopping current J_{ab} of holes in the b band (hops of single holes from acceptors in charge states (0) to acceptors in charge states (−1)) and the density of the hopping current J_{at} of holes in the t band (hops of single holes from acceptors in charge states (+1) to acceptors in charge states (0)) are

$$J_{ab} = e\frac{N_0 N_{-1}}{N_a}\left[M_{ab}\mathcal{E} - D_{ab}\frac{d}{dx}\ln\left(\frac{N_0}{N_{-1}}\right)\right],$$
$$J_{at} = e\frac{N_{+1} N_0}{N_a}\left[M_{at}\mathcal{E} - D_{at}\frac{d}{dx}\ln\left(\frac{N_{+1}}{N_0}\right)\right], \qquad (12)$$

where $e > 0$ is the hole charge, $N_0N_{-1}/N_a = N_{ab}$ is the effective concentration of holes hopping in the b (A^0) band, $N_{+1}N_0/N_a = N_{at}$ is the effective concentration of holes hopping in the t (A^+) band, M_{ab} and M_{at} are the drift hopping mobilities of holes, $\mathcal{E}$ is the strength of the external electric field along the x axis of the Cartesian system of coordinates, $\sigma_{ab} = eN_{ab}M_{ab}$ and $\sigma_{at} = eN_{at}M_{at}$ are the conductivities caused by the drift component of the hole hopping current in the b and t acceptor bands, D_{ab} and D_{at} are the hole hopping diffusivities in the b and t bands, and $N_a = N_{-1} + N_0 + N_{+1}$ is the acceptor concentration.

The differential energy of activation of the hopping electrical conductivity of holes $\sigma_{at} = eN_{at}M_{at}$ is determined as $\varepsilon_2 = -k_B d(\ln\sigma_{at})/d(1/T)$ and can be written in the form

$$(\varepsilon_2 - \varepsilon_t)_a = -k_B\left(\frac{1}{N_0}\frac{dN_0}{d(1/T)} + \frac{1}{N_{+1}}\frac{dN_{+1}}{d(1/T)}\right) \geq 0, \quad (13)$$

where $\varepsilon_t = -k_B d(\ln M_{at})/d(1/T)$ is the thermal activation energy of the hopping migration of holes with the mobility $M_{at} \propto \exp(-\varepsilon_t/k_B T)$ in the A^+ band and $\varepsilon_t \ll \varepsilon_3$ (see Fig. 2a).

To calculate the derivatives of N_0 and N_{+1} with respect to the reciprocal temperature $1/T$ in expression (13), we should take into account that in the functions f_Z described in (4) the Fermi level $E_F^{(v)}$ and level-degeneracy factors β_b and β_t are temperature-dependent in accordance with (5). Then, we take into account the relation $d(N_{-1} + N_0 + N_{+1})/d(1/T) = 0$, which follows from the temperature independence of the total acceptor concentration N_a and the relation $dN_{+1}/d(1/T) = dN_{-1}/d(1/T)$, which follows from electrical-neutrality condition (2). As a result, from formula (13) we obtain the following expression for the difference between the activation energy ε_2 of the transition of holes from the A^0 to A^+ acceptor band and the activation energy ε_t of the migration of holes in the A^+ band,

$$\left(\frac{\varepsilon_2 - \varepsilon_t}{I_2}\right)_a = \left(1 - \frac{1}{l_m^2}\right) \times\left[\frac{f_{-1}(f_0 - 2f_{+1})}{f_0 f_{-1} + f_0 f_{+1} + 4f_{-1}f_{+1}} - \frac{\Delta_a}{I_2}\right] \geq 0, \qquad (14)$$

where $I_2 = I_b - I_t = 0.995I_b = 0.995e^2/(8\pi\varepsilon_r\varepsilon_0 a_H)$, the functions f_Z for $Z = -1, 0, +1$ are determined from (4) with regard to (10), l_m is determined by (6), and Δ_a is determined by the temperature dependence of the degeneracy factor $\beta_0(T)$ for the levels of excited states of an electrically neutral acceptor and has the form

$$\Delta_a = \frac{B_1}{B_2}(2f_0 - 1)I_b,$$

$$B_1 \approx \int_1^{l_m} (l^2 - 1)\exp\left[\frac{(1-l^2)E_b}{l^2 k_B T}\right] dl \geq 0,$$

$$B_2 \approx 1 + \int_1^{l_m} l^2 \exp\left[\frac{(1-l^2)E_b}{l^2 k_B T}\right] dl \geq 1,$$

where l_m is determined by (6).

4. IONIZATION EQUILIBRIUM AND DIFFERENTIAL ACTIVATION ENERGY OF HOPPING CONDUCTIVITY UPON THE HOPPING TRANSITIONS OF ELECTRONS FROM THE D^0 to D^- BAND

In an n-type semiconductor (Fig. 2b), the electroneutrality condition in the presence of the D^0 and D^- bands has the form

$$N_{+1} = N_{-1} + KN_d, \tag{15}$$

where $N_d = N_{-1} + N_0 + N_{+1}$ is the total donor concentration in charge states $Z = -1, 0, +1$; KN_d is the concentration of acceptors compensating donors (all acceptors are in charge state (−1)); and $0 < K < 1$ is the degree of compensation of donors by acceptors.

For the narrow D^0 and D^- bands, the donor concentration in the charge state $Z = +1, 0, -1$ is [18, 24]

$$N_Z = N_d f_Z, \tag{16}$$

where, similarly to (4), the reciprocal distribution functions $1/f_Z$ for donors over the charge states $Z = +1, 0, -1$ are

$$\begin{aligned} f_{+1}^{-1} &= 1 + \beta_b \exp\left[\frac{E_F^{(c)} + E_b}{k_B T}\right] + \frac{\beta_b}{\beta_t}\exp\left[\frac{E_b + E_t + 2E_F^{(c)}}{k_B T}\right], \\ f_0^{-1} &= 1 + \frac{1}{\beta_b}\exp\left[\frac{-(E_F^{(c)} + E_b)}{k_B T}\right] + \frac{1}{\beta_t}\exp\left[\frac{E_F^{(c)} + E_t}{k_B T}\right], \\ f_{-1}^{-1} &= 1 + \beta_t \exp\left[\frac{-(E_F^{(c)} + E_t)}{k_B T}\right] + \frac{\beta_t}{\beta_b}\exp\left[\frac{-(E_b + E_t + 2E_F^{(c)})}{k_B T}\right], \end{aligned} \tag{17}$$

$E_F^{(c)} = (E_F - \delta E_c) < 0$ is the Fermi level in the band gap, $E_F < 0$ is the Fermi level (chemical potential) counted from the bottom of the c band ($E_c = 0$) of an undoped crystal, $\delta E_c < 0$ is the shift of the bottom of the c band into the band gap due to the overlap of orbitals of excited states of electrically neutral donors, $E_b > 0$ and $E_t > 0$ are the corresponding energy levels of donors, and $\beta_b = \beta_0/\beta_{+1}$ and $\beta_t = \beta_0/\beta_{-1}$ are the degeneracy factors; in particular, for Sb atoms in the Ge:Sb system [25], we have $\beta_b = 2$ and $\beta_t = 1/2$.

Taking into account the excited states of only electrically neutral donors in (17), it is necessary to replace β_0 with $\beta_0(l_m)$ (see formulas (5)–(10) for acceptors),

$$\frac{\beta_0(l_m)}{\beta_0} = \sum_{l=1}^{l_m} l^2 \exp\left[\frac{(1-l^2)E_b}{l^2 k_B T}\right] \approx 1 + \int_1^{l_m} l^2 \exp\left[\frac{(1-l^2)E_b}{l^2 k_B T}\right] dl, \tag{18}$$

where $l_m = \{0.277[(1+K)N_d]^{-1/3}/a_H\}^{1/2} \geqslant 1$ is the largest number of possible excited states of donors, which is assumed to be a continuous function, and $a_H = e^2/(8\pi\varepsilon_r\varepsilon_0 I_b)$ is the Bohr radius of a donor in the charge state (0).

The density of the steady-state current J_{db} of electrons in the b band (hops of single electrons from donors in charge states (0) to donors in charge states (+1)) and the density of the electron current J_{dt} in the t band (hops of single electrons from donors in charge states (−1) to donors in charge states (0)) is [21, 41]

$$\begin{aligned} J_{db} &= e\frac{N_0 N_{+1}}{N_d}\left[M_{db}\mathscr{E} + D_{db}\frac{d}{dx}\ln\left(\frac{N_0}{N_{+1}}\right)\right], \\ J_{dt} &= e\frac{N_{-1} N_0}{N_d}\left[M_{dt}\mathscr{E} + D_{dt}\frac{d}{dx}\ln\left(\frac{N_{-1}}{N_0}\right)\right], \end{aligned} \tag{19}$$

where $N_0 N_{+1}/N_d = N_{db}$ is the effective concentration of electrons hopping in the b (D^0) band, $N_{-1}N_0/N_d = N_{dt}$ is the effective concentration of electrons hopping in the t (D^-) band, M_{db} and M_{dt} are the drift hopping mobilities of electrons, $\mathscr{E}$ is the strength of the external electric field along the x axis, $\sigma_{db} = eN_{db}M_{db}$ and $\sigma_{dt} = eN_{dt}M_{dt}$ are the conductivities caused by the drift component of the electron hopping current in the b and t bands of donors, D_{db} and D_{dt} are the electron hopping diffusivities in the b and t bands, and concentrations N_{-1}, N_0, and N_{+1} are determined by formula (16) with regard to (17) and (18).

The difference between the donor energy levels E_b and E_t (see formulas (8) and (9)) is

$$(E_b - E_t)_d = \left(1 - \frac{1}{l_m^2}\right) I_2 \geq 0, \tag{20}$$

where $I_2 = 0.945 I_b$ is the energy gap between Hubbard levels (bands) for a single (isolated) donor [2, 34], $E_b = I_b + \delta E_c$, $E_t = I_t + \delta E_c$, and $\delta E_c = -I_b/l_m^2$ is the shift of the bottom of the c band into the band gap (Fig. 2b).

For an n-type semiconductor upon the thermal activation of electrons from the b to t band of donors, similarly to expression (14), the differential activation

energy $\varepsilon_2 = -k_B d(\ln\sigma_{dt})/d(1/T)$ of conductivity σ_{dt} can be represented as

$$\left(\frac{\varepsilon_2 - \varepsilon_t}{I_2}\right)_d = \left(1 - \frac{1}{l_m^2}\right) \times \left[\frac{f_{+1}(f_0 - 2f_{-1})}{f_0 f_{-1} + f_0 f_{+1} + 4f_{-1}f_{+1}} - \frac{\Delta_d}{I_2}\right] \ge 0, \quad (21)$$

where ε_t is the thermal activation energy of the hopping migration of electrons with the mobility $M_{dt} \propto \exp(-\varepsilon_t/k_B T)$ in the D^- band ($\varepsilon_t \ll \varepsilon_3$, Fig. 2b), the functions f_Z at $Z = -1, 0, +1$ are determined by formulas (17) with regard to (18), and $l_m \geqslant 1$ is a continuous quantity determined from (6) and (7) upon the replacement of N_a with N_d. The Δ_d value is stipulated by the temperature dependence of the degeneracy factor $\beta_0(T)$ for the levels of excited states of a neutral donor and is determined as

$$\Delta_d = \frac{B_1}{B_2}(2f_0 - 1)I_b,$$

$$B_1 \approx \int_1^{l_m} (l^2 - 1)\exp\left[\frac{(1 - l^2)E_b}{l^2 k_B T}\right] dl \ge 0,$$

$$B_2 \approx 1 + \int_1^{l_m} l^2 \exp\left[\frac{(1 - l^2)E_b}{l^2 k_B T}\right] dl \ge 1,$$

where $E_b = (1 - l_m^{-2})I_b$ is the donor ionization energy in charge state (0).

5. CALCULATION OF THE CONCENTRATION OF HOLES (ELECTRONS) INVOLVED IN HOPPING MIGRATION OVER HUBBARD BANDS

According to [21, 24], the total concentration $N_{ab} + N_{at}$ of single holes hopping over acceptors for a p-type semiconductor (concentration $N_{db} + N_{dt}$ of single electrons hopping over donors for an n-type semiconductor) enters into the screening length of the external electrostatic field, in accordance with the Debye–Hückel theory. The screening length can be measured upon the hopping migration of electrons (holes) over defects [21, 42, 43]. Using the values of the screening length, we can estimate the concentration of electrons (holes) involved in the hopping current.[2] Below, we present the results of calculations of the effective concentration of holes hopping over boron atoms in p-Si:B and electrons hopping over antimony atoms in n-Ge:Sb at the Mott parameter $a_H N_a^{1/3} = a_H N_d^{1/3} \approx 0.15$, when the dopant concentrations are several times lower than their critical concentration for the Mott transition.

[2] The Hall-effect value in the case of hopping conductivity (see, e.g., [44, 45]) over the impurity band of acceptor (donor) levels (HC in Fig. 1) is much smaller than in the case of band conductivity [46] over v or c band states (BC in Fig. 1).

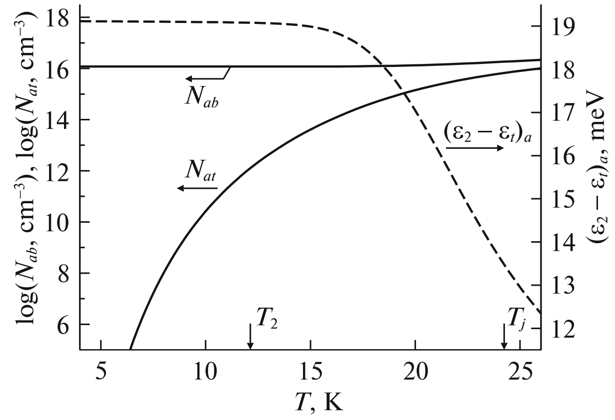

Fig. 3. Temperature dependences of the concentrations of holes hopping in the A^0 and A^+ bands of p-Si:B $N_{ab} = N_0 N_{-1}/N_a$ and $N_{at} = N_{+1}N_0/N_a$ calculated using (3) and (4) with (8) and (9) taken into account and the dependence of the differential activation energy $(\varepsilon_2 - \varepsilon_t)_a$ calculated from (14) in p-Si:B at a degree of compensation of $K = 0.01$ for $N_a = 1.2 \times 10^{18}$ cm^{-3} ($a_H N_a^{1/3} \approx 0.15$).

For a single boron atom at a silicon crystal-lattice site, we have $I_b = 44.39$ meV and $a_H = 1.41$ nm [47, 48] and, in accordance with the model of a negatively charged hydrogen ion [34, 35], we obtain $I_t = 0.055 I_b \approx 2.44$ meV and $a_{+1} = 1.45 a_H = 2.05$ nm [2]. Figure 3 shows the temperature dependences of the concentrations of holes hopping in the A^0 and A^+ bands of p-Si:B $N_{ab} = N_0 N_{-1}/N_a$ and $N_{at} = N_{+1}N_0/N_a$ calculated from (3) and (4) and the dependence of the differential activation energy $(\varepsilon_2 - \varepsilon_t)_a$ calculated from (14) at the compensation degree $K = 0.01$ for $N_a = 1.2 \times 10^{18}$ cm^{-3}. It was assumed that the hole concentration in the v band is $p \ll K(1 - K)N_a$ and the electroneutrality condition (2) is met, as well as the condition $(E_b - E_t)_a = I_2(1 - l_m^{-2})$. For a single antimony atom at a germanium crystal-lattice site [34, 35, 47, 48], $I_b = 10.45$ meV, $a_H = 4.47$ nm, $I_t = 0.055 I_b \approx 0.57$ meV, and $a_{-1} = 1.45 a_H = 6.49$ nm. Figure 4 shows the temperature dependences of the effective concentrations of electrons hopping in the D^0 and D^- bands of n-Ge:Sb $N_{db} = N_0 N_{+1}/N_d$ and $N_{dt} = N_{-1}N_0/N_d$ calculated from (16) and (17) and the dependence of the differential activation energy $(\varepsilon_2 - \varepsilon_t)_d$ calculated from (21) at a degree of compensation of $K = 0.01$ for $N_d = 3.8 \times 10^{16}$ cm^{-3}. It was assumed that the electron concentration in the c band is $n \ll K(1 - K)N_d$, the electroneutrality condition (15) in the c band is met, and $(E_b - E_t)_d = (1 - l_m^{-2})I_2$.

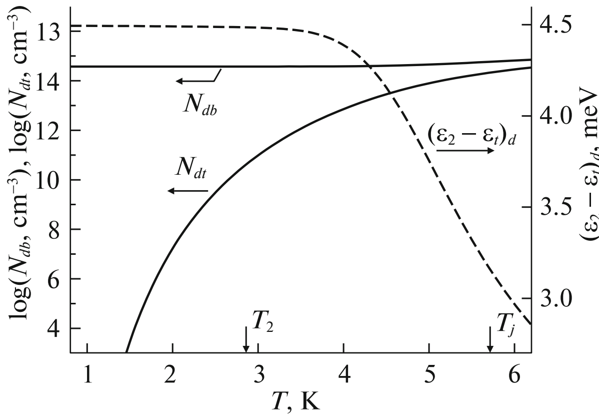

Fig. 4. Temperature dependences of the concentrations of electrons hopping in the D^0 and D^- bands of n-Ge:Sb $N_{db} = N_0N_{+1}/N_d$ and $N_{dt} = N_{-1}N_0/N_d$ calculated from (16) and (17) with (20) taken into account and the dependence of the differential activation energy $(\varepsilon_2 - \varepsilon_t)_d$ calculated from (21) in n-Ge : Sb at a degree of compensation of $K = 0.01$ for $N_d = 3.8 \times 10^{16}$ cm^{-3} ($a_HN_d^{1/3} \approx 0.15$).

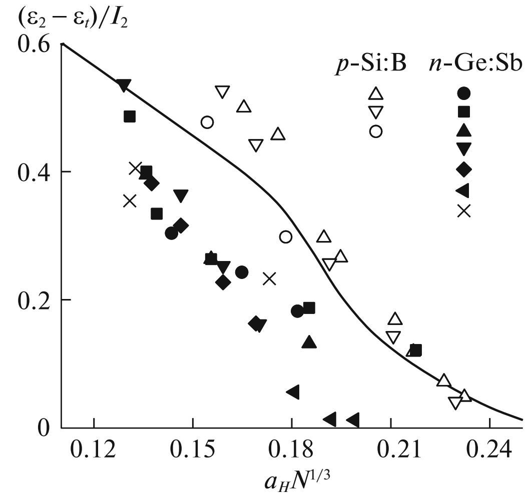

Fig. 5. Dependence of the differential thermal activation energy $\varepsilon_2 - \varepsilon_t$ on the Mott parameter $a_HN^{1/3}$ for acceptors and donors. Dots show the experimental ε_2 values for p-Si:B [50–52] and n-Ge:Sb [53–60] and the continuous curve represents the data calculated using (14) and (21) at $K = 0.01$ and the temperature $T_2 = T_j/2$.

It follows from the calculations (Figs. 3 and 4) that to make hopping conductivity σ_2 over an upper (t) Hubbard band noticeably higher than conductivity σ_3 over a lower (b) band at a temperature of $T \approx T_2$, the mobility of holes in the A^+ band of boron in silicon (electrons in the D^- band of antimony in germanium) should be higher than the mobility in the A^0 (D^0) band by five orders of magnitude. It should be noted that this corresponds to the commonly accepted pattern of the formation of a mobility threshold in the upper Hubbard band near the doping levels at which conductivity σ_2 is observed [1, 5]. In addition, it is worth noting that, in the vicinity of temperature T_2, where ε_2 is determined (measured), the concentration of ionized impurity atoms slightly increases upon heating over their concentration $2KN$ at $T \to 0$. Hence, we can disregard the broadening of the b and t impurity bands, at least for impurity concentrations not very close to the Mott transition.

6. COMPARISON OF THE CALCULATED THERMAL ACTIVATION ENERGIES OF THE TRANSITION OF HOLES (ELECTRONS) BETWEEN HUBBARD BANDS WITH EXPERIMENTAL DATA

To use lightly compensated semiconductors in practice, it is often important to know the characteristic temperature T_j at which band conductivity (BC) becomes equal to the dc hopping conductivity (HC) extrapolated to this temperature region (Fig. 1). In particular, in the development of crystal semiconductor-based photodetectors operating in the range from micro- to millimeter wavelengths, the hopping conductivity over impurity atoms should be blocked [49]. To reduce the hopping conductivity, regions of lower impurity concentration are inserted into a semiconductor device structure to form a potential barrier for electron or hole migration over impurity atoms.

It is worth noting that, at the temperature T_j, the resistivity $1/\sigma_1$ in the regime of band conductivity over v or c band states is approximately equal to the resistivity $1/\sigma_3$ in the regime of hopping conductivity over impurity atoms (see formula (1) and Fig. 1). The temperature T_j, below which the mass capture of holes to negatively charged acceptors (electrons to positively charged donors) ceases on average, is determined using the virial theorem as [17]

$$k_BT_j \approx 0.728\frac{e^2}{4\pi\varepsilon_r\varepsilon_0}(KN)^{1/3}, \quad (22)$$

where N is the major (doping) impurity concentration, KN is the minor (compensating) impurity concentration, and $0 < K < 1$. It is worth noting that, at a temperature of T_j for the p-type semiconductor, the hole concentration in the v band is much lower than the effective concentration of holes hopping over acceptors (for an n-type semiconductor, the electron concentration in the c band is much lower than the concentration of electrons hopping over donors) due to the opposite inequality for the corresponding mobilities.

Figure 5 shows the differential activation energy $\varepsilon_2 - \varepsilon_t$ calculated using formulas (14) and (21) at $K = 0.01$ and the temperature $T_2 = T_j/2$ determined from formula (22) in comparison with the experimental ε_2

values for lightly compensated semiconductors p-Si:B [50–52] and n-Ge:Sb [53–60]. The energy in Fig. 5 is normalized to the value $I_2 = I_b - I_t = 41.95$ meV for p-Si:B and $I_2 = 9.88$ meV for n-Ge:Sb. The Mott parameter $a_H N^{1/3}$ is plotted along the horizontal axis, where $a_H = e^2/(8\pi\varepsilon_r\varepsilon_0 I_b)$ is the Bohr radius. Since the permittivities for Si and Ge are $\varepsilon_r = 11.47$ [61] and $\varepsilon_r = 15.4$ [62], respectively, we have $a_H = 1.41$ nm for p-Si:B and $a_H = 4.47$ nm for n-Ge:Sb. The experimental critical concentrations for the Mott transition presented in [31] for low-level compensation $K < 0.01$ are 4×10^{18} cm^{-3} for B atoms as hydrogen-like acceptors in crystalline silicon and 1.68×10^{17} cm^{-3} for antimony atoms as hydrogen-like donors in crystalline germanium.

We note that the activation energy ε_1 is determined at the temperature $T_1 \approx 3T_j/2$ near which the thermally activated transition of holes from the A^0 to v band (of electrons from the D^0 to c band) occurs. The activation energy ε_2 is determined at a temperature of $T_2 \approx T_j/2$ near which the mass injection of holes from the A^0 to A^+ band (of electrons from the D^0 to D^- band) occurs and the hopping migration of holes in the A^+ band (electrons in the D^- band) takes place. The analysis of experimental data reported in [17] shows that, in semiconductors with moderate degrees of compensation $0.1 < K < 0.9$ at a temperature of $T_3 \approx T_j/3$, where T_j is determined from (22), hopping conductivity between the nearest impurity atoms (the NNH regime) is dominant; i.e., at T_3, the activation energy ε_3 is determined.

In addition, we note that calculation of the thermal ionization of electrically neutral hydrogen-like impurities $E_1 = E_b = (1 - l_m^{-2})I_b$, where $I_b = e^2/(8\pi\varepsilon_r\varepsilon_0 a_H)$ and $l_m = [(d/2)/a_H]^{1/2}$, performed simultaneously using formula (8) is quantitatively consistent with the experimental data for p-Si:B [52, 63] and n-Ge:Sb [54, 60, 64] in terms of the activation energy ε_1 of the band conductivity σ_1 for lightly compensated crystals. It should be taken into account that the activation energy ε_1 determined from the band conductivity (BC in Fig. 1) and the ionization energy E_1 of impurities determined using the Hall effect are related as $\varepsilon_1 \approx E_1 + [(3/2) + s]k_B T_1$ [65, 66], where s is the exponent in the temperature dependence of the hole (electron) mobility $\mu_{p(n)} \propto T^s$ in the region of determination of ε_1 at $T_1 \approx 3T_j/2$. In the case of the scattering of carriers at ionized and neutral impurities, we have $s \approx 0.5$ [67].

7. CONCLUSIONS

We suggested a quasi-classical electrostatic model of the Hubbard gap formed due to the ability of a dopant to be in one of three charge states (−1, 0, or +1) in lightly compensated semiconductors on the insulator side of the concentration insulator–metal (Mott) phase transition. We carried out analytical derivation and numerical calculation of the differential activation energy of dc hopping conductivity between Hubbard bands.

The Hubbard-band width was assumed to be much smaller than the energy gap between the bands, which corresponds to impurity concentrations far from the Mott transition. We assumed that the maximum Bohr radius of the excited state of electrically neutral dopant atoms is no greater than half the average distance between the nearest impurity (both doping and compensating) atoms. The effect of excited states of electrically neutral impurities on the position of two Hubbard energy levels (bands) with increasing doping level leads to a situation where the allowed energy-band edge shifts into the semiconductor band gap, the levels become shallower, and the gap between them narrows. We derived a formula relating the energy gap $E_b - E_t$ between the b and t Hubbard bands to the concentration of a dopant and the degree of its compensation. This allowed us to describe the dependence of the thermal activation energy ε_2 of the hopping transition of holes from a lower A^0 to upper A^+ Hubbard band for acceptors (of electrons from the D^0 to D^- band for donors) on the impurity concentration in covalent lightly compensated crystal semiconductors. The activation energies $(\varepsilon_2 - \varepsilon_t)$ calculated using the obtained formulas are quantitatively consistent with available experimental data on the activation energy ε_2 for lightly compensated p-Si and n-Ge crystals.

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