Calculation of the Activation Energy of Electrical ε_2-Conductivity of Weakly Compensated Semiconductors

Nikolai A. Poklonski, Ilya I. Anikeev, Sergey A. Vyrko, and Andrei G. Zabrodskii*

A model of tunneling (jumping) migration of charge carriers near their mobility edge in the upper band of neutral states of majority hydrogen-like impurities is proposed to calculate the energy of thermal activation of electrical ε_2-conductivity of weakly compensated semiconductors. The difference from the known Hubbard model consists in the scheme of interimpurity transitions of charge carriers and in the method of calculating the position of their tunnel mobility edge. The drift mobility edge of free charge carriers corresponds to the thermal ionization energy of majority impurities $\varepsilon_1 > \varepsilon_2$, which is located near the *c*-band bottom or the *v*-band top in *n*- and *p*-type semiconductors, respectively, and is due to the overlap of excited states of electrically neutral majority impurities. The position of the tunnel mobility edge for ε_2-conductivity is determined by taking into account the Coulomb interaction of the majority impurities in the charge states (-1) and $(+1)$. It is assumed that doping and compensating impurities form a single simple nonstoichiometric cubic lattice in a crystal matrix. The calculations of the activation energy ε_2 on the insulator side of the insulator–metal concentration phase transition for weakly compensated *p*-Si:B, *n*-Si:P, and *n*-Ge:Sb crystals quantitatively agree with known experimental data.

1. Introduction

1.1. General Concepts of the Electrical ε_2-Conductivity

The direct current (dc) electrical conductivity σ_{dc} of a doped semiconductor on the insulator side of the insulator–metal concentration phase transition (Mott transition; see, e.g., ref. [1]) at low temperatures is usually represented in the form of three exponential terms of the Arrhenius type (see, e.g., refs. [2,3])

$$\begin{aligned}\sigma_{\text{dc}} &= \sigma_1 + \sigma_2 + \sigma_3 \\ &= \sigma_{01}\exp\left(-\frac{\varepsilon_1}{k_{\text{B}}T}\right) + \sigma_{02}\exp\left(-\frac{\varepsilon_2}{k_{\text{B}}T}\right) + \sigma_{03}\exp\left(-\frac{\varepsilon_3}{k_{\text{B}}T}\right)\end{aligned} \quad (1)$$

where σ_{01}, σ_{02}, and σ_{03} are the prefactors that weakly depend on the absolute temperature T compared to the corresponding exponents; $\varepsilon_1 > \varepsilon_2 > \varepsilon_3$ are the thermal activation energies of the electrical conductivities σ_1, σ_2, and σ_3; and $k_{\text{B}}T$ is the thermal energy (see **Figure 1** that shows the plot of the logarithm of the electrical resistivity $\ln \rho_{\text{dc}} \equiv \ln(1/\sigma_{\text{dc}})$ vs the reciprocal temperature $1/T$).

Figure 1 shows the temperature $T \approx T_{\text{j}}$ at which the values of the maximum band electrical resistivity with the thermal activation energy ε_1 and the minimum hopping electrical resistivity with the thermal activation energy ε_3 are equal. The value of T_2 characterizes the temperature region in which the ε_2-conductivity is observed. The abbreviation NNH (nearest neighbor hopping) denotes the region of phonon-assisted tunnel hops of electrons between the nearest donors in the charge states (0) and (+1) [or hops of holes between the nearest acceptors in the charge states (0) and (-1)] with activation energy ε_3 (in the temperature range centered at T_3). The abbreviation VRH (variable range hopping) corresponds to the lowest temperatures where the regime of hops of electrons (or holes) optimized by both the activation energy and the length is realized. (The charges are given in units of the elementary charge *e*.)

Note that Formula (1) is used to interpret experimental data in a wide range of doping levels by majority impurities from "moderate" to "heavy," up to the Mott transition (see, e.g., refs. [4–6]). The electrical conductivity σ_1 (the so-called ε_1-conductivity) is due to "free" electrons in the *c*-band (or "free" holes in the *v*-band) originated from thermal ionization of the ground states of neutral donors (or acceptors), while σ_2 and σ_3 (ε_2- and ε_3-conductivities) are associated with different mechanisms of electron (or hole) transfer via the different charge states of the donor (or acceptor) band, forming its upper and lower band, respectively (see **Figure 2**, where schemes of charge carrier transitions in *n*- and *p*-type materials are shown).

In general, the ε_2-conductivity is associated with the thermal transitions of electrons (or holes) from the lower donor $D^{0/+}$-band with the charge states (0) and (+1) [or acceptor $A^{0/-}$-band with the charge states (0) and (-1)] to the mobility edge in the upper band with states $D^{-/0}$ (or $A^{+/0}$) and their subsequent activation-free migration through the crystal. The possibility of attaching an electron to a neutral donor [with a transition to

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N. A. Poklonski, I. I. Anikeev, S. A. Vyrko
Belarusian State University
220030 Minsk, Belarus
E-mail: poklonski@bsu.by

A. G. Zabrodskii
Ioffe Institute
194021 St. Petersburg, Russia
E-mail: andrei.zabrodskii@mail.ioffe.ru

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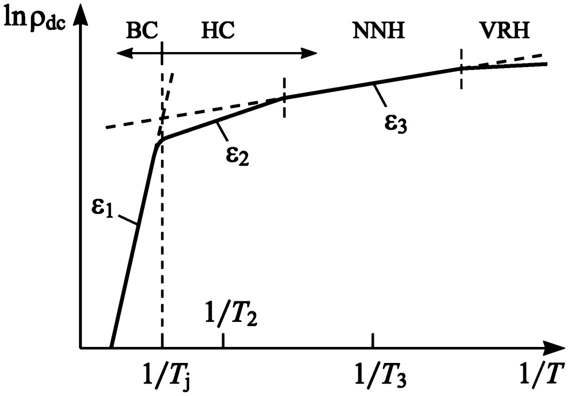

Figure 1. Scheme of the dependence of the logarithm of the direct current electrical resistivity $\rho_{\mathrm{dc}} = 1/\sigma_{\mathrm{dc}}$ of a doped weakly compensated semiconductor on the reciprocal temperature $1/T$.

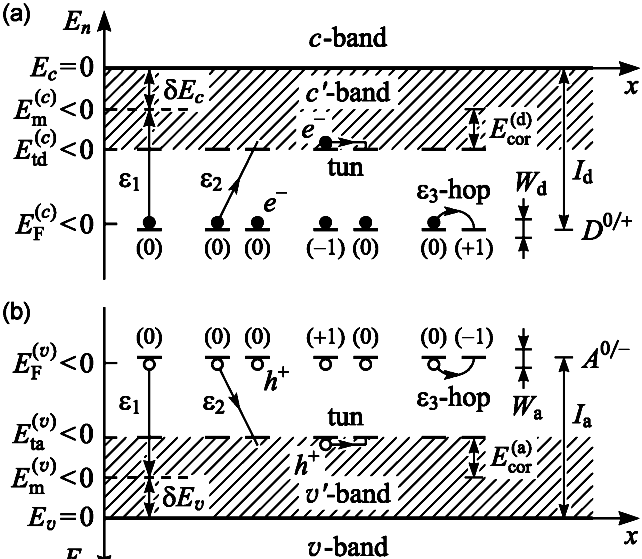

Figure 2. Scheme of the energy levels of donors near the bottom of the c-band ($E_c = 0$) of an n-type semiconductor (a) and acceptors near the top of the ν-band ($E_\nu = 0$) of a p-type semiconductor (b) for the charge states (-1), (0), and $(+1)$ of impurities; $E_{\mathrm{td}}^{(c)} < 0$ is the bottom of the c'-band, $E_{\mathrm{ta}}^{(\nu)} < 0$ is the top of the ν'-band.

the charge state (-1)] or a hole to a neutral acceptor [with a transition to the charge state $(+1)$] was first predicted in refs. [7,8].

The mechanism of the ε_3-conductivity is associated with thermally activated tunnel electrons (or holes), which hop in the lower $D^{0/+}$-band (or $A^{0/-}$-band) between the nearest donors in the charge states (0) and $(+1)$ [or acceptors in the charge states (0) and (-1)] with the participation of phonons (the NNH regime). When the temperature decreases sufficiently, the length of the hops increases, and their activation energy decreases (the VRH regime).

In Figure 2, arrows show the transitions of electrons (e^-, dark circles) and holes (h^+, open circles) for the cases of the electrical ε_1-, ε_2-, and ε_3-conductivities. The following notations are used: "ε_3-hop" is the thermally activated electron hop between the donor charge states $(0) \rightarrow (+1)$ [hole hop between the acceptor charge states $(0) \rightarrow (-1)$]; "tun" is the tunneling activation-free transition (described below) of an electron between the donor charge states $(-1) \rightarrow (0)$ at the tunnel mobility edge $E_{\mathrm{td}}^{(c)}$ in the upper donor band [a hole between the acceptor charge states $(+1) \rightarrow (0)$ at the tunnel mobility edge $E_{\mathrm{ta}}^{(\nu)}$ in the upper acceptor band]. The bottom of the c-band of the undoped crystal ($E_c = 0$) is chosen as the reference point of the electron energy E_n, and the top of the ν-band of the undoped crystal ($E_\nu = 0$) is chosen as the reference point of the hole energy E_p; x is the axis of the Cartesian coordinate system; I_{d} and I_{a} are the ionization energies of a single donor and acceptor; $E_{\mathrm{m}}^{(c)} = -\delta E_c < 0$ and $E_{\mathrm{m}}^{(\nu)} = -\delta E_\nu < 0$ are the drift mobility edges for c-band electrons and ν-band holes (shifts of the bottom of the c-band δE_c and the top of the ν-band δE_ν due to the overlap of excited states of electrically neutral donors and acceptors); $E_{\mathrm{cor}}^{(\mathrm{d})} > 0$ and $E_{\mathrm{cor}}^{(\mathrm{a})} > 0$ are the electrostatic correlation energies of the systems: "fixed donor in the charge state $(+1)$ + mobile charge state (-1) of the donor" and "fixed acceptor in the charge state (-1) + mobile charge state $(+1)$ of the acceptor"; $E_{\mathrm{F}}^{(c)} < 0$ and $E_{\mathrm{F}}^{(\nu)} < 0$ are the Fermi levels in n- and p-type materials at low temperatures; ε_1 is the thermal activation energy of "free" electrons with energy $E_n > E_{\mathrm{m}}^{(c)}$ in the conduction band ("free" holes in the valence band with energy $E_p > E_{\mathrm{m}}^{(\nu)}$); ε_2 is the thermal activation energy of an electron transition from the electrically neutral donor of the $D^{0/+}$-band to the electrically neutral donor of the c'-band (transition of a hole from the electrically neutral acceptor of the $A^{0/-}$-band to the electrically neutral acceptor of the ν'-band); ε_3 is the thermal activation energy of electron hops via states of the $D^{0/+}$-band (hole hops via states of the $A^{0/-}$-band); and W_{d} and W_{a} are the widths of the donor $D^{0/+}$-band and the acceptor $A^{0/-}$-band.

In Figure 2, it is assumed that the bottom of the c'-band corresponds to the tunnel (jumping) mobility edge $E_{\mathrm{td}}^{(c)}$ of electrons via donors in the charge states (-1) and (0). The width of the c'-band is equal to the drift mobility edge $E_{\mathrm{m}}^{(c)}$ plus the Coulomb correlation energy of two donors in the charge states (-1) and $(+1)$. The top of the ν'-band corresponds to the tunnel (jumping) mobility edge $E_{\mathrm{ta}}^{(\nu)}$ of holes via acceptors in the charge states $(+1)$ and (0). The width of the ν'-band is equal to the drift mobility edge $E_{\mathrm{m}}^{(\nu)}$ plus the Coulomb correlation energy of two acceptors in the charge states $(+1)$ and (-1).

In this paper, we are interested in calculating the value of the thermal activation energy ε_2 for a weakly compensated semiconductor in the range of doping levels from moderate to heavy, corresponding to the Mott transition. In the case of weak compensations, the region of the ε_2-conductivity is usually observed.[9] Moreover, with an increase in the compensation ratio toward moderate values, the ε_3-conductivity increases (see, e.g., ref. [10]), which reduces the region of existence of the ε_2-conductivity on the low-temperature side. A further increase in compensation significantly reduces the concentration of the majority impurities in the charge state (0), required for the ε_2-conductivity regime, as follows from all its models (see below).

1.2. Basic Models for Calculating the Activation Energy of the ε_2-Conductivity

There are two main approaches to calculate the activation energy of the ε_2-conductivity in weakly compensated semiconductors. They are common in two aspects: (i) taking into account the experimentally established fact that the insulator–metal transition occurs inside the impurity band of electronic (hole) states at doping levels noticeably lower than those at which the impurity band merges with the conduction band (or valence band)[11,12] and (ii) the ε_2-conductivity is associated with the effect of splitting of the impurity band by the Coulomb interaction, and the value of ε_2 is associated with the gap between the Fermi level, which is located in the lower impurity subband, and the drift mobility edge located in the upper impurity subband.[12]

The most common (single-center, intrasite) approach considers the effect of thermally activated capture of an electron (hole) by a neutral donor (acceptor) with the formation of a negatively (positively) charged ion. Here, the level of the highest energy charge carrier is separated by the Hubbard gap[13] from the level of the lower one, the value of which coincides with the observed value of ε_2. It is assumed that at the mobility edge, there is a transition from the hopping mechanism of electrical transfer to the classical (band) mechanism, and the energy position of the mobility edge relative to the Fermi level corresponds to the observed value of ε_2. The main disadvantage of this approach is the impossibility of quantitatively describing the value of the Hubbard gap and, consequently, the behavior of the value of ε_2 with a change in the doping level of real semiconductors, especially near the insulator–metal transition, when this value becomes small compared to the thermal ionization energy of the majority impurity.

The model proposed in this paper belongs to an alternative multisite (intersite) or "molecular" approach, a brief retrospective of the references for which is given below.

In ref. [14], to calculate the value of ε_2, the stationary Schrödinger equation was solved taking into account the splitting of the symmetric and antisymmetric terms of a negatively charged "molecule" consisting of an electrically neutral donor and a singly negatively charged donor. It is shown that the decrease in the energy gap between the $D^{0/+}$- and $D^{-/0}$-bands is directly proportional to the concentration of neutral donors and is associated with a shift of the $D^{-/0}$-band to the $D^{0/+}$-band. However, neither the model in ref. [14] nor its modifications[15–17] took into account the shift of the $D^{0/+}$-band to the c-band for an n-type semiconductor (or the $A^{0/-}$-band to the v-band for a p-type semiconductor) with an increasing concentration of doping and compensating impurities (see, e.g., ref. [18]). The possibility that the migration of electrons above their mobility edge $E_{\mathrm{td}}^{(c)}$ in the upper donor band (or holes above their mobility edge $E_{\mathrm{ta}}^{(v)}$ in the upper acceptor band) could hypothetically occur by tunneling via weakly localized states (in the terminology of refs. [19–21]—"jumping regime") was also not considered. Therefore, the models in refs. [14–17] do not adequately describe the mechanism of the ε_2-conductivity and the behavior of its activation energy.[22]

In ref. [18], an electrostatic model was proposed to describe the narrowing of the energy gap between the upper and lower impurity bands, split by the Coulomb intersite interaction, and a decrease in the value of ε_2 with an increase in the concentration of acceptors. The effect is due to a decrease in the energy of the negatively and positively charged states of donors (acceptors) due to their screening by electrons hopping via donors (holes via acceptors). The decrease in the value of ε_2 was explained by the electrostatic interaction of the two nearest donors (or acceptors) in the charge states (+1) and (−1), i.e., by the emergence of a dipole from two initially electrically neutral donors (or acceptors) as a result of the transition of a charge carrier between them—an electron (or a hole).[23]

It is shown in ref. [24] that a decrease in ε_2 is associated with the overlap of excited states of electrically neutral donors (acceptors) with an increase in their concentration that leads to a shift of the bottom of the conduction band (the top of the valence band) deeper to the band gap. As a consequence, the energy levels of donors (acceptors) become more "shallow," and the gap between the upper and lower donor (acceptor) bands narrows.

Taking into account the result of ref. [24], in ref. [25], a general conclusion is made that the decrease in the value of ε_2 is due to two factors: (i) formation of a quasi-continuous band of allowed energy values for c-band electrons (v-band holes) from the excited quantum states of donors (acceptors) in the charge state (0) and (ii) splitting of the ground (unexcited) energy levels of "molecular" pairs of donors (acceptors) in the charge states (0) into triplet and singlet states of two electrons (holes); see Formula (A1) from the Appendix.

The purpose of this work is to propose a model to describe the mechanism of the ε_2-conductivity and to quantitatively explain the behavior of the thermal activation energy ε_2 in real weakly compensated semiconductors in the range of doping levels from moderate to heavy, corresponding to the insulator–metal transition (Mott transition), as well as to compare the analytical calculations with the experimental data[26–42] for crystalline semiconductors doped with hydrogen-like impurities.

2. New Theoretical Model for Calculating ε_2

2.1. Scheme of Interimpurity Transitions of Charge Carriers

Let us consider a 3D crystalline p-type semiconductor moderately doped with acceptors with the concentration $N_{\mathrm{a}} = N_{\mathrm{a},-1} + N_{\mathrm{a},0} + N_{\mathrm{a},+1}$ and weakly compensated by donors with the concentration $N_{\mathrm{d}} = N_{\mathrm{d},+1} = KN_{\mathrm{a}}$. Here, $N_{\mathrm{a},-1}$, $N_{\mathrm{a},0}$, and $N_{\mathrm{a},+1}$ are the concentrations of acceptors in the charge states (−1), (0), and (+1), respectively, $0 < K(= N_{\mathrm{d}}/N_{\mathrm{a}}) \ll 1$ is the compensation ratio of acceptors by donors, and $N_{\mathrm{a}} + N_{\mathrm{d}} = (1 + K)N_{\mathrm{a}}$ is the total concentration of hydrogen-like impurities. All compensating donors are in the charge state (+1).

The electrical neutrality at the concentration of v-band holes $p \ll K(1 - K)N_{\mathrm{a}}$, taking into account that $N_{\mathrm{a},+1} \ll N_{\mathrm{a},-1}$, has the form

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

In the model we propose, at changing the concentration of N_a acceptors, the behavior of the thermal activation energy of the ε_2-conductivity is explained on the basis of the following assumptions: (i) the formation of a quasi-continuous spectrum of allowed hole energies due to the overlap of excited states of electrically neutral acceptors with increasing their concentration,[24,25] (ii) the thermally activated transition of two acceptors from the charge states (0) to the charge states (+1) and (−1), i.e., the formation of an electric dipole at a thermally activated transition of a hole from the localized state in the lower acceptor $A^{0/-}$-band to the tunnel mobility edge $E_{ta}^{(\nu)}$ in the upper acceptor band (see Figure 2), and (iii) the activation-free tunneling migration of holes via the localized states of acceptors above the tunnel mobility edge in the upper acceptor band.

At the hopping electrical conductivity σ_2, the first step is a thermally activated (phonon-assisted) hole transition from the acceptor in the charge state (0) with an energy level in the $A^{0/-}$-band to the nearest acceptor in the charge state (0) with an energy level at the top of the ν'-band with the formation of an electric dipole: the charge state (−1) in the $A^{0/-}$-band and the charge state (+1) at the top of the ν'-band (Figure 2). Then there is either a reverse transition of the hole with the neutralization of acceptors, or the hole, overcoming the attraction to the negatively charged acceptor, starts to migrate through the crystal. In this case, the charge state (−1) in the lower acceptor band contributes to the phonon-assisted hopping electrical conductivity σ_3 at moderate and, especially, weak compensations, and the charge state (+1) contributes to the electrical conductivity σ_2 in the upper acceptor band. Similarly, the thermal ionization process of the ground states responsible for the electrical conductivity σ_1 also stimulates the hopping electrical conductivity σ_3. Note that the upper acceptor band is characterized by an activation-free high drift mobility M_{h2} and a low concentration $N_{h2} = N_{a,+1}N_{a,0}/N_a$ of holes[43] tunneling between acceptors in the charge states (+1) and (0). In contrast, the $A^{0/-}$-band is characterized by a thermally activated low drift hopping mobility M_{h3} and a high concentration $N_{h3} = N_{a,0}N_{a,-1}/N_a$ of holes[43] hopping between acceptors in the charge states (0) and (−1). This is due to the fact that for the electrical conductivities $\sigma_2 = eN_{h2}M_{h2}$ and $\sigma_3 = eN_{h3}M_{h3}$, the inequality $\sigma_2 > \sigma_3$ is satisfied (see Figure 1). Since $N_{a,+1} \ll N_{a,-1}$ at $T \approx T_2$, then $N_{h2} \ll N_{h3}$, and the inequality $\sigma_2 > \sigma_3$ is satisfied for $M_{h2} \gg M_{h3}$.

2.2. Model of a Nonstoichiometric Simple Cubic "Lattice" of Impurity Atoms

Following refs. [44,45], we assume that the doping impurity (acceptors) with the concentration N_a and the compensating impurity (donors) with the concentration $N_d = KN_a$ form a nonstoichiometric simple cubic "lattice" with a notional translation period in the semiconductor crystal matrix (**Figure 3**)

$$d_{im} = 2R_{im} = 2[4\pi(1+K)N_a/3]^{-1/3} \approx 1.24[(1+K)N_a]^{-1/3} \tag{3}$$

where d_{im} value is equal to the diameter of a spherical region in the crystal per one atom or impurity ion (both acceptor and donor).

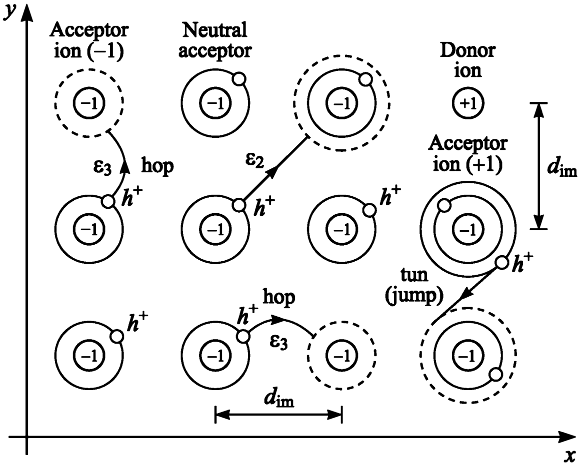

Figure 3. Two-dimensional scheme (in the xy plane) of the impurity simple cubic lattice in a crystal matrix. There are shown the transitions of holes (h^+) between acceptors in the charge states (−1), (0), and (+1) in a weakly compensated p-type semiconductor; "hop" is a hole hop between the acceptor charge states (0) → (−1) with the thermal activation energy ε_3; "tun" (or "jump") is the tunneling activation-free transition of hole between the acceptor charge states (+1) → (0); ε_2 is the thermal activation energy of a (phonon-assisted) transition of a hole between the acceptor charge states (0) → (0).

In the impurity lattice, each impurity (located at the center of the first coordination sphere) has six nearest neighbors (on the surface of the first coordination sphere) and 12 next-nearest neighbors (on the surface of the second coordination sphere with diameter $\sqrt{2}d_{im}$). Note that d_{im} value according to Formula (3) is ≈3% less than the average distance between the nearest impurities in the crystal matrix $d_{VD} = 1.28[(1+K)N_a]^{-1/3}$, determined[46] by the method of Voronoi–Dirichlet polyhedra.

Compensating impurities block a small fraction of the impurity lattice sites (Figure 3), reducing the electrical conductivity.

For impurity atoms forming a nonstoichiometric simple cubic "lattice" with the translation period d_{im} in the crystal, it is possible (by analogy with calculations from refs. [20,21]) to determine the temperature T_j at which the conductivities in the valence band σ_1 and the acceptor band ($\sigma_2 + \sigma_3$) are equal using the virial theorem at the ν-band holes concentration $p \ll K(1-K)N_a$ in the following form

$$T_j = \frac{1}{3k_B}\frac{e^2}{4\pi\varepsilon_r\varepsilon_0 R_{ch}} \approx \frac{0.677}{k_B}\frac{e^2}{4\pi\varepsilon_r\varepsilon_0}(KN_a)^{1/3} \tag{4}$$

where k_B is the Boltzmann constant, e is the elementary charge, ε_r is the low-frequency relative static permittivity (determined by ν-band electrons on the background of the ionic cores of the crystal matrix), ε_0 is the electric constant, and $R_{ch} = [4\pi(N_{a,-1} + N_{a,+1} + N_{d,+1})/3]^{-1/3} \approx 0.62(2KN_a)^{-1/3}$ is the radius of a spherical region in the crystal per impurity ion [taking into account the electrical neutrality condition (2) at $N_{a,+1} \ll N_{a,-1}$].

Note that the temperature value T_j according to Formula (4) is only 7% less than the value T_j according to models in refs. [20,21], where it is assumed that impurity atoms are randomly (Poissonian) distributed over the crystal volume.

2.3. Shift of the Top of the ν-Band into the Depth of the Band Gap

Let us calculate the shift of the top of the ν-band $\delta E_\nu > 0$ into the depth of the band gap (energy gap) of the semiconductor caused by the formation of a quasi-continuous energy spectrum due to the overlap of the excited states of acceptors with their concentration increasing. The drift mobility edge for ν-band holes $E_{\mathrm{m}}^{(\nu)} = -\delta E_\nu = E_{\mathrm{res}}$, where $E_{\mathrm{res}} < 0$ is the decrease in the thermal ionization energy of the acceptor due to the confinement of the maximum radius of the hole orbit on the acceptor because of the presence of donors in the crystal in addition to acceptors (see Figure 2). Note that in moderately and heavily doped *p*-type semiconductors on the insulator side of the Mott transition, the contribution of the exchange energy of ν-band holes to the value of $E_{\mathrm{m}}^{(\nu)}$ can be neglected (see, e.g., ref. [47]).

The decrease in the thermal ionization energy of a hydrogen-like acceptor due to the confinement of the maximum Bohr radius of the hole orbit on the acceptor is given by the formula[48–50]

$$E_{\mathrm{res}} = -I_{\mathrm{a}} a_{\mathrm{pi}}/R_{\mathrm{im}} < 0 \tag{5}$$

where $a_{\mathrm{pi}} = e^2/8\pi\varepsilon_{\mathrm{r}}\varepsilon_0 I_{\mathrm{a}}$ is the radius of the Bohr orbit of a hole on a single acceptor in the charge state (0) with the thermal ionization energy $I_{\mathrm{a}} = I_{0,-1}$ from the ground (unexcited) state to the ν-band (to the energy level $E_\nu = 0$) due to thermal fluctuations; $R_{\mathrm{im}} = [4\pi(1+K)N_{\mathrm{a}}/3]^{-1/3} \approx 0.62[(1+K)N_{\mathrm{a}}]^{-1/3}$ is the radius of the spherical region per one impurity atom (including acceptors and donors) in the crystal matrix.

From (5) for the drift mobility edge of ν-band holes, we obtain

$$E_{\mathrm{m}}^{(\nu)} \approx E_{\mathrm{res}} = -I_{\mathrm{a}} \frac{a_{\mathrm{pi}}}{R_{\mathrm{im}}} < 0 \tag{6}$$

where in the spherical region with the diameter of $2R_{\mathrm{im}} \approx 1.24[(1+K)N_{\mathrm{a}}]^{-1/3}$ inside the crystal sample all points are closer to the same impurity than to any other.

2.4. Probabilities of Finding Acceptors in the Charge States (0) and (−1)

Let us further assume that the lower acceptor band (i.e., the $A^{0/-}$-band) has a normal (Gaussian) distribution density of acceptor energy levels E_{a} in the band gap[51,52]

$$G_{\mathrm{a}} = \frac{1}{W_{\mathrm{a}}\sqrt{2\pi}} \exp\left[-\frac{(E_{\mathrm{a}} - I_{\mathrm{a}})^2}{2W_{\mathrm{a}}^2}\right] \tag{7}$$

where W_{a}^2 is the variance of acceptor thermal ionization energy levels E_{a} relative to I_{a} in the semiconductor band gap (energy gap); $\int_{-\infty}^{+\infty} G_{\mathrm{a}} \mathrm{d}(E_{\mathrm{a}} - I_{\mathrm{a}}) = 1$ (see, e.g., ref. [53]).

The root-mean-square fluctuation of acceptor energy levels (the effective width of the acceptor $A^{0/-}$-band) W_{a} taking into account the Coulomb interaction of the acceptor in the charge state (-1) with ions of only the first coordination sphere of a nonstoichiometric simple cubic impurity lattice with a notional translation period d_{im} is equal to[44,45,54]

$$W_{\mathrm{a}} = \left(\sum_{i=1}^{6} P_i U_i^2\right)^{1/2} = \frac{e^2}{4\pi\varepsilon_{\mathrm{r}}\varepsilon_0 d_{\mathrm{im}}} \left(\frac{12K}{1+K}\right)^{1/2} \tag{8}$$

where $P_i = 2K/(1+K)$ is the probability that any of the six sites of the impurity lattice in the first coordination sphere near the selected impurity ion is occupied by an ionized donor or acceptor; $1/(1+K)$ is the fraction of acceptors at the impurity lattice sites; $|U_i| = e^2/4\pi\varepsilon_{\mathrm{r}}\varepsilon_0 d_{\mathrm{im}}$ is the modulus of the Coulomb energy of the interaction of the selected ion with the nearest ions located at the distance d_{im} in a cubic lattice composed of doping and compensating impurities. When deriving Formula (8), it is taken into account that the average energy of the Coulomb interaction of the selected impurity ion with ions in the nearest six sites of the impurity lattice is equal to zero: $\sum_{i=1}^{6} P_i U_i = 0$.

Note that Formula (8) is obtained in the approximation of the so-called "classical" impurity bands when the fluctuation shift of the impurity ion energy level is considered equal to the ion potential energy (the final state of an electrically neutral impurity after its ionization) created by the remaining impurity ions of the first coordination sphere of the impurity lattice.[49] Whereas, according to Formula (A3) from Appendix, the quantum mechanical splitting of energy levels $\delta E_{(0,-1)}$ in the acceptor $A^{0/-}$-band is significantly less than W_{a}; see also refs. [25,55,56].

The average over the crystal volume probabilities $\langle f_0 \rangle$ and $\langle f_{-1} \rangle$ that the acceptor randomly selected in the crystal matrix is in the charge state (0) or in the charge state (-1), providing $N_{\mathrm{a},+1} \ll N_{\mathrm{a},-1}$, are (see, e.g., ref. [44])

$$\begin{aligned} \langle f_0 \rangle &= \frac{N_{\mathrm{a},0}}{N_{\mathrm{a}}} = \int_{-\infty}^{+\infty} G_{\mathrm{a}} f_0 \mathrm{d}(E_{\mathrm{a}} - I_{\mathrm{a}}) \\ \langle f_{-1} \rangle &= \frac{N_{\mathrm{a},-1}}{N_{\mathrm{a}}} = \int_{-\infty}^{+\infty} G_{\mathrm{a}} f_{-1} \mathrm{d}(E_{\mathrm{a}} - I_{\mathrm{a}}) \end{aligned} \tag{9}$$

where $f_0 = \{1 + \beta_{\mathrm{a}}^{-1} \exp[-(E_{\mathrm{F}}^{(\nu)} + E_{\mathrm{a}})/k_{\mathrm{B}}T]\}^{-1}$ is the probability of filling a state with the energy level E_{a} by a hole; $f_{-1} \approx 1 - f_0$ for $N_{\mathrm{a},+1} \ll N_{\mathrm{a},-1}$; $E_{\mathrm{F}}^{(\nu)}$ is the Fermi level (measured from the top of the ν-band, $E_\nu = 0$, of the undoped crystal); $E_{\mathrm{F}}^{(\nu)} < 0$ if the Fermi level is in the band gap of the semiconductor; and $E_{\mathrm{a}} = E_{-1} - E_0 > 0$ is the thermal ionization energy of an acceptor in the charge state (0) in the $A^{0/-}$-band from the ground (unexcited) state to the top of the ν-band due to thermal fluctuations (hole detachment from a neutral acceptor and its transition to the ν-band). For boron-doped *p*-type silicon:[57] $\beta_{\mathrm{a}} = \beta_0/\beta_{-1} \approx 4$ (for phosphorus-doped *n*-type silicon and antimony-doped *n*-type germanium $\beta_{\mathrm{d}} = \beta_0/\beta_{+1} \approx 2$), β_Z is the number of quantum states of the acceptor (or donor) in the charge state Z (in units of elementary charge).

2.5. Correlation Energy of Acceptor Ions (−1) and (+1)

Let us assume that the transition of a hole in a nonstoichiometric simple cubic lattice of impurity atoms occurs between two neutral acceptors with the formation of an electric dipole from the

$A^{0/-}$-band acceptor in the charge state (-1) and the ν'-band acceptor in the charge state $(+1)$, located at the activation-free tunnel mobility edge $E_{\text{ta}}^{(\nu)}$. Let us assume that the ion in the charge state (-1) is located in the center of the first coordination sphere of the impurity lattice, and the ion in the charge state $(+1)$ is located on the surface of the second coordination sphere of the impurity lattice (see Figure 3). The distance between the pair of ions is $\sqrt{2}d_{\text{im}}$. Then the correlation energy of the Coulomb interaction of two acceptors in the charge states (-1) and $(+1)$ is equal to

$$U_{+1,-1} = -\frac{e^2}{4\pi\varepsilon_{\text{r}}\varepsilon_0 L_{+1,-1}} \tag{10}$$

where $L_{+1,-1} = \sqrt{2}d_{\text{im}} \approx 1.75[(1+K)N_{\text{a}}]^{-1/3}$ is the distance between acceptor ions in the charge states (-1) and $(+1)$; the ion (-1) is considered to be located in the center of the first coordination sphere and the ion $(+1)$—on the surface of the second coordination sphere of the lattice of impurity atoms.

It is clear that for a steady state and in a weak electric field, when a hole hops between electrically neutral acceptors located at a distance d_{im}, with the formation of two ions, the probability of a reverse hole hop is high. Therefore, we can assume the minimum hop length of a hole between acceptors in the charge states (0) equal to $L_{+1,-1} = \sqrt{2}d_{\text{im}}$, which corresponds to a hole hop from the center of the first coordination sphere to the surface of the second coordination sphere of the impurity lattice. Moreover, in strong electric fields, the probability of a reverse hole hop decreases, and then a region with a negative differential resistance is observed in the current–voltage characteristic (see, e.g., ref. [58]).

Note that the value $L_{+1,-1} \approx 1.75[(1+K)N_{\text{a}}]^{-1/3}$ is close to the doubled percolation radius $2R_{\text{per}} = 2B_{\text{c}}^{1/3}[4\pi(1+K)N_{\text{a}}/3]^{-1/3} \approx 1.73[(1+K)N_{\text{a}}]^{-1/3}$ of the spherical region per acceptor, taking into account the compensation of acceptors by donors. Here, the dimensionless parameter $B_{\text{c}} \approx 2.735$ means the average number of hopping bonds per atom of the majority impurity.[10,59–62] At the critical radius R_{per}, the charge state (-1) of the acceptor, being activated and "detached" from the donor ion, migrates in a hopping manner via the states of the acceptor $A^{0/-}$-band through the entire crystal.[10] In general, the value $2R_{\text{per}}$ takes into account the effect of self-avoiding walks (in the terminology of ref. [63]) of holes in two channels of electrical conductivity: (i) via the states of $A^{0/-}$-band and (ii) via the states on the top of the ν'-band.

The value of $U_{+1,-1}$ is similar to the contribution of the purely Coulomb interaction between acceptor and donor ions to the increase in the photon energy emitted in one act of radiative donor–acceptor recombination.[44]

Note that in the Debye–Hückel approximation (see refs. [47,50,54,64] and references therein), the total electrostatic energy of the acceptor in the charge state $(+1)$ and the cloud of screening charges located at a distance greater than $R_{\text{sc}} = d_{\text{im}}/2$ from this ion is given by the formula

$$U_{\text{sc}} = -I_{\text{a}}\frac{3a_{\text{pi}}}{2(\Lambda_{\text{sc}} + R_{\text{sc}})} < 0 \tag{11}$$

where $\Lambda_{\text{sc}} = (\varepsilon_{\text{r}}\varepsilon_0 k_{\text{B}}T\xi_{\text{h}}/e^2 N_{\text{h3}})^{1/2}$ is the screening radius of the acceptor Coulomb field, $N_{\text{h3}} = K(1-K)N_{\text{a}}$ is the concentration of holes hopping in the $A^{0/-}$-band, $(k_{\text{B}}T/e)\xi_{\text{h}}$ is the ratio of the hopping diffusion coefficient of holes via acceptors to their drift hopping mobility, and $\xi_{\text{h}} \geq 1$ is a dimensionless parameter

$$\frac{1}{\xi_{\text{h}}} = \frac{1}{K(1-K)}\int_{-\infty}^{+\infty} G_{\text{a}} f_0 f_{-1} \text{d}(E_{\text{a}} - I_{\text{a}}) \tag{12}$$

According to calculations in ref. [54], the value of $\xi_{\text{h}}T$ is practically independent of temperature for $T < T_{\text{j}}$, when $W_{\text{a}} \gg k_{\text{B}}T_2$ and the ν-band holes concentration $p \ll N_{\text{h3}}$.

The two-particle correlation energy of the interaction between the mobile charge state (-1) of the acceptor and the mobile charge state $(+1)$ of the acceptor is

$$E_{\text{cor}}^{(\text{a})} = -U_{+1,-1} > 0 \tag{13}$$

where $U_{+1,-1} < 0$ is given by Formula (10).

The multiparticle correlation energy of the acceptor ion and the cloud of screening charges in the Debye–Hückel approximation is $E_{\text{cor}}^{(\text{a})} = -U_{\text{sc}} > 0$, where $U_{\text{sc}} < 0$ is given by Formula (11).

We define the tunnel mobility edge for ν-band holes $E_{\text{ta}}^{(\nu)}$ as a shift into the band gap of the drift mobility edge of ν-band holes $E_{\text{m}}^{(\nu)} < 0$ by the Coulomb correlation energy $E_{\text{cor}}^{(\text{a})} > 0$ of the interaction between two acceptors in the charge states (-1) and $(+1)$ at a distance $L_{+1,-1}$

$$E_{\text{ta}}^{(\nu)} = E_{\text{m}}^{(\nu)} - E_{\text{cor}}^{(\text{a})} = -\frac{e^2}{4\pi\varepsilon_{\text{r}}\varepsilon_0}\left(\frac{1}{d_{\text{im}}} + \frac{1}{L_{+1,-1}}\right) < 0 \tag{14}$$

Note that holes migrate between the charge states $(+1)$ and (0) of acceptors lying near the tunnel mobility edge of the ν'-band;[19,20] see Figure 2. In this regime, the time of flight of a hole between acceptors in the charge states $(+1)$ and (0) is approximately equal in order of magnitude to the settling lifetime of a hole on the acceptor in the charge state $(+1)$. The holes at the tunnel mobility edge are much more mobile than the holes in the lower acceptor $A^{0/-}$-band, which migrate between the charge states (0) and (-1) of the $A^{0/-}$-band with the thermal activation energy ε_3. First, since the wave functions for the ν'-band states "overlap" more than for the $A^{0/-}$-band states,[23,55,65] the thermal activation energy for hole migration in the ν'-band is much less than ε_3. The average tunneling time of holes between acceptors in the charge states (0) → (-1) depends exponentially on the activation energy ε_3 (see, e.g., ref. [54]). Therefore, the tunneling (activation-free) transition of holes between acceptors according to the scheme $(+1)$ → (0) occurs much faster compared to the thermally activated transition (0) → (-1); see Appendix. Second, in the case of the hopping electrical ε_3-conduction, the effect of the Coulomb blockade of the hopping hole is enhanced by the field of a positively charged compensating donor, near which, as a rule, the target negatively charged acceptor is located. The migration of ν'-band holes is similar to the scattering of "free" holes by quasi-localized hole states on acceptors against the background of allowed ν-band states (see, e.g., ref. [66]).

The tunneling transition regime is realized for holes near the tunnel mobility edge $E_{\mathrm{ta}}^{(\nu)}$ in the upper acceptor band and is characterized by: (i) the absence of interference between the hole tunneling acts, in contrast to the propagation regime of "free" holes in the ν-band (band migration mechanism), (ii) the weak dependence on temperature due to hole tunneling without the assistance of phonons, in contrast to the hopping mechanism [with exponential dependence on the inverse temperature of the hopping frequency (average time of thermally activated tunneling) of holes via acceptors in the charge states (0) and (-1); see Appendix], and (iii) the localization time of holes on acceptors in the charge state $(+1)$ is much smaller than on acceptors in the charge state (0) in the $A^{0/-}$-band.

Note that the concentration $N_{\mathrm{h3}} = N_{\mathrm{a},0}N_{\mathrm{a},-1}/N_{\mathrm{a}}$ of holes hopping between acceptors in the charge states (0) and (-1) is much greater than the concentration $N_{\mathrm{h2}} = N_{\mathrm{a},+1}N_{\mathrm{a},0}/N_{\mathrm{a}}$ of holes tunneling between acceptors in the charge states $(+1)$ and (0); see, e.g., ref. [43].

Comparison of the drift mobility edge $E_{\mathrm{m}}^{(\nu)} < 0$ for free holes in the ν-band according to Formula (6) and the tunnel mobility edge of holes via acceptors $E_{\mathrm{ta}}^{(\nu)} < 0$ according to Formula (14) with the position of the center of the so-called $A^{+/0}$-band $I_{+1,0} = 0.055I_{\mathrm{a}} > 0$ (see, e.g., ref. [67]) shows that this band lies beyond the drift mobility edge in heavily doped weakly compensated semiconductors, i.e., $|E_{\mathrm{ta}}^{(\nu)}| > |E_{\mathrm{m}}^{(\nu)}| > I_{+1,0}$. In this case, the charge states $(+1)$ and (0) of the acceptors form quasi-resonant (in other words, quasi-localized[68,69]) states near the top of the ν'-band, separated from the mobility edge $E_{\mathrm{m}}^{(\nu)}$, as it is usually accepted.[12,67]

2.6. Thermal Activation Energy ε_2

We define the activation energy ε_2 as the difference between the Fermi level $E_{\mathrm{F}}^{(\nu)}$ and the tunnel mobility edge $E_{\mathrm{ta}}^{(\nu)}$ taking into account (2)–(14) (cf. refs. [12,39])

$$\begin{aligned}\varepsilon_2 &= -E_{\mathrm{F}}^{(\nu)} + E_{\mathrm{ta}}^{(\nu)} = -E_{\mathrm{F}}^{(\nu)} + E_{\mathrm{m}}^{(\nu)} - E_{\mathrm{cor}}^{(\mathrm{a})} \\ &= -E_{\mathrm{F}}^{(\nu)} - \frac{e^2}{4\pi\varepsilon_{\mathrm{r}}\varepsilon_0}\left(\frac{1}{d_{\mathrm{im}}} + \frac{1}{L_{+1,-1}}\right) \\ &\approx -E_{\mathrm{F}}^{(\nu)} - 1.376\frac{e^2}{4\pi\varepsilon_{\mathrm{r}}\varepsilon_0}[(1+K)N_{\mathrm{a}}]^{1/3} > 0\end{aligned} \tag{15}$$

where the Fermi level $E_{\mathrm{F}}^{(\nu)} < 0$ is found from the electrical neutrality Equation (2) taking into account (4), (7)–(9), the value of the mobility edge $E_{\mathrm{m}}^{(\nu)} < 0$ of ν-band holes is given by relation (6), the Coulomb correlation energy $E_{\mathrm{cor}}^{(\mathrm{a})} = -U_{+1,-1}$ of the interaction of the acceptor in the charge state (-1) in the center of the first coordination sphere with the acceptor in the charge state $(+1)$ on the surface of the second coordination sphere at the distance $L_{+1,-1} = 2\sqrt{2}R_{\mathrm{im}}$ is given by the relation (13) taking into account (10); $E_{\mathrm{m}}^{(\nu)} = \sqrt{2}U_{+1,-1}$.

Note that for n-type semiconductors with hydrogen-like donors in all formulas, the index "a" [acceptors in the charge states $(0,-1,+1)$] should be replaced by the index "d" [donors in the charge states $(0,+1,-1)$], and symbols "p" and "ν" (for p-type)—by symbols "n" and "c" (for n-type). A singly positively charged acceptor ion corresponds to a singly negatively charged donor ion.

3. Calculation Results and Discussion

As can be seen from Figure 1, the observation region of the ε_2-conductivity is centered approximately in the vicinity of the characteristic temperature $T_2 \approx T_{\mathrm{j}}/2$, where, according to refs. [20,21], the temperature T_{j} is determined from the equality of the contribution to the electrical conductivity of the holes of the valence and acceptor bands (electrons of the conduction and donor bands): $\sigma_1 = \sigma_2 + \sigma_3$. Thus, near the temperature T_2, in accordance with the concepts developed above, transitions of holes occur from the lower acceptor $A^{0/-}$-band to the tunnel mobility edge $E_{\mathrm{ta}}^{(\nu)}$ of holes between the charge states $(+1)$ and (0) of acceptors. Near the temperature T_2 transitions of electrons occur from the lower donor $D^{0/+}$-band to the tunnel mobility edge $E_{\mathrm{td}}^{(c)}$ of electrons between the charge states (-1) and (0) of donors. Taking into account (4), we obtain the relation (cf. ref. [48])

$$\frac{k_{\mathrm{B}}T_2}{I_{\mathrm{a(d)}}} \approx 0.677a_{p\mathrm{i}(n\mathrm{i})}(KN_{\mathrm{a(d)}})^{1/3} \tag{16}$$

where $a_{p\mathrm{i}(n\mathrm{i})}N_{\mathrm{a(d)}}^{1/3}$ is a dimensionless Mott parameter for hydrogen-like impurities; $a_{p\mathrm{i}} \propto 1/I_{\mathrm{a}}$ and $a_{n\mathrm{i}} \propto 1/I_{\mathrm{d}}$. Calculations of the value of $T_2 = T_{\mathrm{j}}/2$ according to (16) were used to find $E_{\mathrm{F}}^{(\nu)}$ from Equation (2) and substitute the value of $E_{\mathrm{F}}^{(\nu)}$ into Formula (15). For example, for p-Si:B with boron concentration $N_{\mathrm{a}} = 1\times10^{18}\ \mathrm{cm^{-3}}$ at $K \approx 0.01$ from (16), we obtain $T_2 \approx 11$ K, for n-Si:P with phosphorus concentration $N_{\mathrm{d}} = 1\times10^{18}\ \mathrm{cm^{-3}}$ at $K \approx 0.1$, we obtain $T_2 \approx 23$ K, and for n-Ge:Sb with antimony concentration $N_{\mathrm{d}} = 5\times10^{16}\ \mathrm{cm^{-3}}$ at $K \approx 0.05$, we obtain $T_2 \approx 5$ K.

From known experimental data, we selected p-Si:B, n-Si:P, and n-Ge:Sb crystals with a sufficiently weak compensation ratio $K < 10\%$ and the concentration of the doping impurity in the range $0.1N_{\mathrm{M}} < N_{\mathrm{a(d)}} < N_{\mathrm{M}}$, where N_{M} is the concentration corresponding to the Mott transition (see refs. [64,70] and references therein). Such a choice of K values is due to the fact that the region of the electrical ε_2-conductivity (see Figure 1) is clearly observed only in weakly compensated samples.[10,34] For weakly compensated boron-doped p-type silicon crystals $N_{\mathrm{M}} \approx 4.1\times10^{18}\ \mathrm{cm^{-3}}$ (p-Si:B, $K \approx 0.1$), for phosphorus-doped n-type silicon crystals $N_{\mathrm{M}} \approx 3.81\times10^{18}\ \mathrm{cm^{-3}}$ (n-Si:P, $K \approx 0.1$), and for antimony doped n-type germanium crystals $N_{\mathrm{M}} \approx 1.68\times10^{17}\ \mathrm{cm^{-3}}$ (n-Ge:Sb, $K < 0.1$).

Figure 4 shows the calculation results of the Fermi levels $E_{\mathrm{F}}^{(\nu)}$ and $E_{\mathrm{F}}^{(c)}$ from the electrical neutrality (2) taking into account (4), (7)–(9) in units of the thermal ionization energies I_{a} and I_{d} as a function of the dimensionless Mott parameter $a_{p\mathrm{i}(n\mathrm{i})}N_{\mathrm{a(d)}}^{1/3}$ for p-Si:B at compensation ratio $K = 0.01$ (curve *1*), for n-Si:P at $K = 0.1$ (curve *2*), and for n-Ge:Sb at $K = 0.01$ (curve *3*) on the insulator side of the insulator–metal concentration phase transition (Mott transition when $a_{p\mathrm{i}(n\mathrm{i})}N_{\mathrm{a(d)}}^{1/3} < 0.25$). The parameters were used: $I_{\mathrm{a}} = 44.39$ meV[71,72] $\varepsilon_{\mathrm{r}} = 11.47$[73]

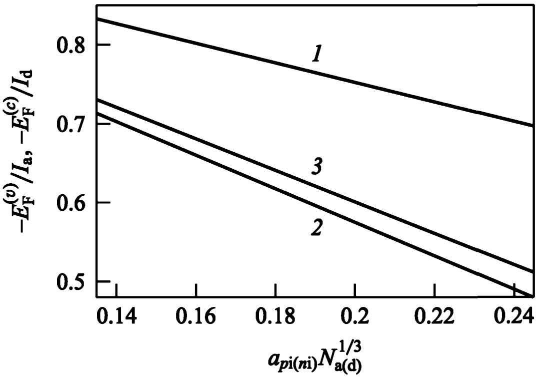

Figure 4. Dependences of the Fermi levels $E_F^{(v)} < 0$ and $E_F^{(c)} < 0$ in units of the thermal ionization energies I_a and I_d of impurities on the Mott parameter $a_{pi(ni)}N_{a(d)}^{1/3}$ for *p*-Si:B at $K = 0.01$ (curve *1*); for *n*-Si:P at $K = 0.1$ (curve *2*), and for *n*-Ge:Sb at $K = 0.05$ (curve *3*).

(for *p*-Si:B), $I_d = 45.58$ meV[71,72] $\varepsilon_r = 11.47$[73] (for *n*-Si:P), and $I_d = 10.29$ meV[71,72] $\varepsilon_r = 15.4$[74] (for *n*-Ge:Sb).

Note that in Figure 4, the values of the Fermi levels ($-E_F^{(v)} > 0$ and $-E_F^{(c)} > 0$) are calculated for wide impurity bands given by Formula (8), which depend on the concentrations of the majority impurities as $W_a \propto N_a^{1/3}$ and $W_d \propto N_d^{1/3}$. The Fermi levels for $K = \text{const}$ shift to the tunnel mobility edge for holes $E_{ta}^{(v)} < 0$ (the top of the v'-band) with increasing acceptor concentration N_a, and to the tunnel mobility edge for electrons $E_{ta}^{(c)} < 0$ (the bottom of the c'-band) with increasing donor concentration N_d.

Figure 5 shows the calculation by Formula (15) of the dependences of the activation energy ε_2 at the temperature $T_2 = T_j/2$, given by Formula (16), on the concentration of boron atoms N_a for the width W_a of the acceptor $A^{0/-}$-band by Formula (8) (curve *1*) and for the $A^{0/-}$-band of zero width ($W_a = 0$, curve *2*), as well as their comparison with the experimental data[26–29] for *p*-Si:B crystals at the compensation ratio of acceptors by donors $K = N_d/N_a = 0.01$ on the insulator side of the Mott transition.

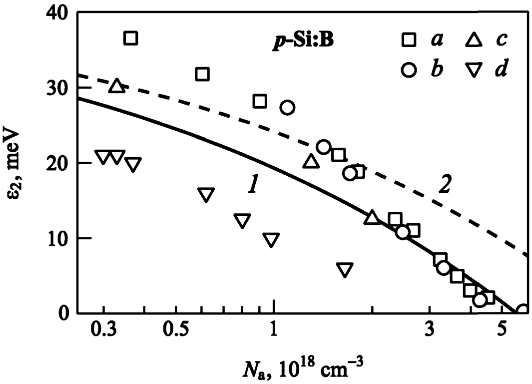

Figure 5. Dependences of the thermal activation energy ε_2 at the temperature $T_2 = T_j/2$, given by Formula (16), on the concentration N_a of B atoms (hydrogen-like acceptors) in *p*-type silicon crystals for the compensation ratio of acceptors by donors $K = 0.01$. Points are the experimental values obtained by: Gershenzon et al.[26] (*a*), Chroboczek et al.[27] (*b*), Ismagilova et al.[28] (*c*), and Bannaya et al.[29] (*d*); lines are the calculations by Formula (15) for W_a by Formula (8) (curve *1*) and for $W_a = 0$ (curve *2*).

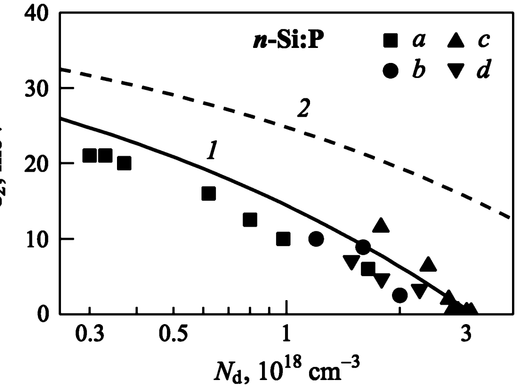

Figure 6. Dependences of the thermal activation energy ε_2 at the temperature $T_2 = T_j/2$ according to Formula (16), on the concentration N_d of P atoms (hydrogen-like donors) in *n*-type silicon crystals at the compensation ratio of donors by acceptors $K = 0.1$. Points are the experimental values obtained by: Bannaya et al.[29] (*a*), Toyotomi[30] (*b*), Liu et al.[31] (*c*), and Kajikawa and Sasaki[4,32] (*d*); lines are the calculations by Formula (15) for W_d by Formula (8) (curve *1*) and for $W_d = 0$ (curve *2*).

Figure 6 shows the calculation by Formula (15) of the dependences of the activation energy ε_2 at the temperature $T_2 = T_j/2$, given by Formula (16), on the concentration of phosphorus atoms N_d for the width W_d of the donor $D^{0/+}$-band by Formula (8) (curve *1*) and for the $D^{0/+}$-band of zero width ($W_d = 0$, curve *2*), as well as their comparison with the experimental data[4,29–32] for *n*-Si:P crystals at the compensation ratio of donors by acceptors $K = N_a/N_d = 0.1$ on the insulator side of the Mott transition.

Figure 7 shows the calculation by Formula (15) of the dependences of the activation energy ε_2 at the temperature $T_2 = T_j/2$,

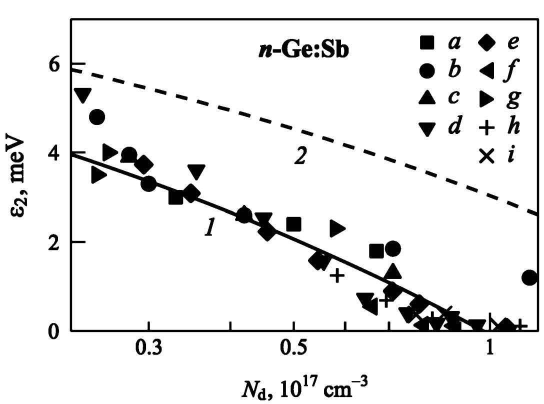

Figure 7. Dependences of the thermal activation energy ε_2 at the temperature $T_2 = T_j/2$ according to Formula (16), on the concentration N_d of Sb atoms (hydrogen-like donors) in *n*-type germanium crystals at the compensation ratio of donors by acceptors $K = 0.05$. Points are the experimental values obtained by: Gershenzon et al.[33–35] (*a*–*c*), Fritzsche[36,37] (*d*), Davis and Compton[38] (*e*), Agrinskaya et al.[39] (*f*), Kobayashi et al.[40] (*g*), Sadasiv[41] (*h*), and Yamanouchi[42] (*i*); lines are the calculations by Formula (15) for W_d by Formula (8) (curve *1*) and for $W_d = 0$ (curve *2*).

given by Formula (16), on the concentration of antimony atoms N_d for the width W_d of the donor $D^{0/+}$-band by Formula (8) (curve *1*) and for the $D^{0/+}$-band of zero width ($W_\mathrm{d} = 0$, curve *2*), as well as their comparison with the experimental data[33–42] for *n*-Ge:Sb crystals at the compensation ratio of donors by acceptors $K = N_\mathrm{a}/N_\mathrm{d} = 0.05$ on the insulator side of the Mott transition.

From the comparison of Figures 5–7, it can be seen that there is a good agreement for *n*-Ge:Sb, and a satisfactory agreement for *p*-Si:B and *n*-Si:P. A possible reason for the discrepancy in the latter case is the deviation of the real compensation of the studied samples from the values $K = 0.01$ for *p*-Si:B and $K = 0.1$ for *n*-Si:P used in the calculation. It is also seen that for the donor $D^{0/+}$-band (or the acceptor $A^{0/-}$-band) of finite width (curves *1*), the activation energy ε_2 is less than for the narrow impurity $D^{0/+}$-band (or $A^{0/-}$-band) (curves *2*).

Note that for the considered weak compensation ratios, the value of the distance $d_\mathrm{im} \approx 1.24[(1+K)N_{\mathrm{a(d)}}]^{-1/3}$ between impurity atoms is close to the value of the distance $d_\mathrm{a} = 2(4\pi N_\mathrm{a}/3)^{-1/3} \approx 1.24 N_\mathrm{a}^{-1/3}$ between acceptors only in uncompensated *p*-Si:B crystals or to the value of the distance $d_\mathrm{d} = 2(4\pi N_\mathrm{d}/3)^{-1/3} \approx 1.24 N_\mathrm{d}^{-1/3}$ between donors only in uncompensated *n*-Si:P and *n*-Ge:Sb crystals. Thus, for *p*-Si:B, *n*-Si:P, and *n*-Ge:Sb crystals, we have $d_\mathrm{a}/d_\mathrm{im} = (1+K)^{1/3} \approx 1.003$ at $K = 0.01$, $d_\mathrm{d}/d_\mathrm{im} \approx 1.032$ at $K = 0.1$, and $d_\mathrm{d}/d_\mathrm{im} \approx 1.016$ at $K = 0.05$, respectively.

If, from Formula (15), we determine the critical concentration N_M at which $\varepsilon_2 = 0$, then for the condition of insulator–metal transition (Mott transition), we have: $N_\mathrm{M}^{1/3} a_{p\mathrm{i}} = 0.25$ for *p*-Si:B at $K = 0.01$, $N_\mathrm{M}^{1/3} a_{n\mathrm{i}} = 0.2$ for *n*-Si:P at $K = 0.1$, and $N_\mathrm{M}^{1/3} a_{n\mathrm{i}} = 0.21$ for *n*-Ge:Sb at $K = 0.05$.

Note that the calculated curves in Figure 5–7 are plotted for fixed values of the temperature T_2. The question arises is the temperature dependence of these calculated curves weak enough with respect to T_2 in the range of experimental observation of the ε_2-conductivity in order not to contradict the constancy of its activation energy? To answer this question, we calculated in **Figure 8** dependences of the quantities $-E_\mathrm{F}^{(v)}/I_\mathrm{a} > 0$ and $-E_\mathrm{F}^{(c)}/I_\mathrm{d} > 0$ on the temperature ratio T_2/T_j for *p*-Si:B crystals with $N_\mathrm{a} = 3 \times 10^{17}\,\mathrm{cm}^{-3}$ (curve *1*) and $3 \times 10^{18}\,\mathrm{cm}^{-3}$ (curve *2*) as well as for *n*-Ge:Sb with $N_\mathrm{d} = 1 \times 10^{16}\,\mathrm{cm}^{-3}$ (curve *3*) and $7 \times 10^{16}\,\mathrm{cm}^{-3}$ (curve *4*). It can be seen that the changes of $E_\mathrm{F}^{(v)}/I_\mathrm{a}$ and $E_\mathrm{F}^{(c)}/I_\mathrm{d}$, and therefore ε_2 according to Formula (15), over a wide range of T_2 are really small, which allows us to answer the question. In *n*-Si:P crystals with $N_\mathrm{d} = 2.5 \times 10^{17}$–$4 \times 10^{18}\,\mathrm{cm}^{-3}$ and the compensation ratio $K = 0.1$, the calculation also gives a weak dependence of the Fermi level $E_\mathrm{F}^{(c)}$ on temperature T_2.

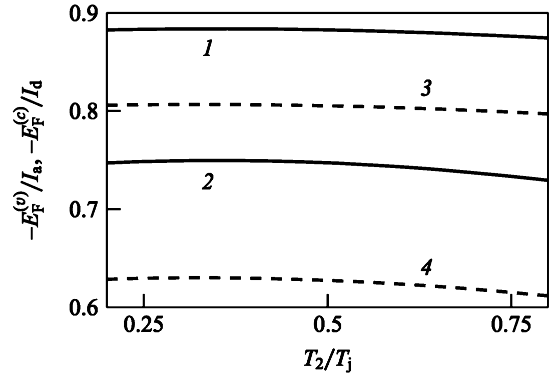

Figure 8. Dependences of the Fermi levels $E_\mathrm{F}^{(v)} < 0$ (solid lines) and $E_\mathrm{F}^{(c)} < 0$ (dashed lines) in units of the thermal ionization energies I_a and I_d of impurities on the temperature T_2 in units of the temperature T_j by Formula (4) for *p*-Si:B crystals with the concentration of B: $N_\mathrm{a} = 3 \times 10^{17}\,\mathrm{cm}^{-3}$ (curve *1*) and $3 \times 10^{18}\,\mathrm{cm}^{-3}$ (curve *2*) at $K = 0.01$ and for *n*-Ge:Sb with the concentration of Sb: $N_\mathrm{d} = 1 \times 10^{16}\,\mathrm{cm}^{-3}$ (curve *3*) and $7 \times 10^{16}\,\mathrm{cm}^{-3}$ (curve *4*) at $K = 0.05$.

Note that Figure 5–7 show the calculated values of ε_2 by Formula (15) with the correlation energy $E_\mathrm{cor}^{(\mathrm{a})} = -U_{+1,-1}$ (or $E_\mathrm{cor}^{(\mathrm{d})} = -U_{-1,+1}$), where $U_{+1,-1}$ (or $U_{-1,+1}$) is determined by (10). In comparison, calculations of ε_2 by Formula (15) with the correlation energy $E_\mathrm{cor}^{(\mathrm{a})} = -U_\mathrm{sc}$ (or $E_\mathrm{cor}^{(\mathrm{d})} = -U_\mathrm{sc}$), where U_sc is determined by (11), lead to values of ε_2 no more than 5% greater for *p*-Si:B crystals and no more than 1% greater for *n*-Si:P and *n*-Ge:Sb crystals.

4. Conclusions

For a quantitative description of the activation energy value of the electrical ε_2-conductivity of weakly compensated semiconductors on the basis of previous results,[18,23–25] an electrostatic model of tunneling (jumping) migration of charge carriers near the mobility edge via the neutral states of majority hydrogen-like impurities is developed. In contrast to the well-known Hubbard model, these states are assumed to be quasi-localized. However, the more fundamental difference lies in the different ways of calculating the position of this edge, the starting point of which is the precalculation of the drift mobility edge for charge carriers. This edge determines the value of the thermal ionization energy of the majority impurities $\varepsilon_1 > \varepsilon_2$ and is located near the edge of the conduction band or valence band in *n*- and *p*-type semiconductors, respectively. Its origin is due to the formation of the subband of the excited states of neutral majority impurities near this edge.

To simplify the calculations, it is assumed that the doping and compensating impurities form a single nonstoichiometric simple cubic lattice with a translation period equal to the diameter of the spherical region per one impurity in the crystal. The first coordination sphere of the impurity lattice contains six impurities at a distance d_im from an arbitrary lattice site, and the second coordination sphere (with a radius of $\sqrt{2}d_\mathrm{im}$) contains 12 impurities. It is also assumed that the width of the majority and compensating impurity bands is determined by the Coulomb interaction of the impurity ions of the first coordination sphere of the nonstoichiometric impurity lattice.

The position of the mobility edge for the ε_2-conductivity is determined by taking into account the Coulomb interaction of oppositely charged majority impurities in the charge states (-1) and $(+1)$, i.e., within the framework of the "molecular" approach, in contrast to the single-atom Hubbard gap. Here, we are dealing with the Coulomb interaction energy of a pair of oppositely charged the majority (doping) impurity ions $U_{+1,-1}$ for acceptors (or $U_{-1,+1}$ for donors) at a distance of $\sqrt{2}d_{\mathrm{im}}$. Such a pair of ions is formed at each act of thermally activated charge carrier transition between two electrically neutral majority impurities. The desired values of ε_2 are determined as the difference between the energy levels of the mobility edge for the ε_2-conductivity in the upper impurity subband and the Fermi level, which is located in the lower impurity subband. Since the values of ε_2 are determined at a certain temperature $T = T_2$, the independence of the obtained result from the choice of the value of T_2 was deliberately tested in the ε_2-conductivity observation region.

As a result, for the first time, we were able to quantitatively describe the behavior of the energy value ε_2 in the entire region of its observation on the insulator side of the insulator–metal phase transition (Mott transition) with increasing doping level of majority impurities for an almost constant compensation by minority impurities.

Numerical calculations of the ε_2 values using the obtained formulas are carried out for *p*-Si:B, *n*-Si:P, and *n*-Ge:Sb crystals in the range from 0.1 N_{M} to N_{M}, where N_{M} is the concentration of the majority impurity corresponding to the Mott transition. The experimental values of the compensation ratios are $K \leq 0.01$ for *p*-Si:B, $K \leq 0.1$ for *n*-Si:P, and $K \leq 0.05$ for *n*-Ge:Sb, i.e., they are really small. The results of calculations of the ε_2 values (without any fitting parameters) by our model of the multicenter (intersite) Coulomb correlations are consistent with the known experimental data for these semiconductors. This also means that the Hubbard single-center (intrasite) Coulomb correlations are not manifested. The question arises: why? We assume that the reason is in the increase of the degree of screening of the Coulomb potential when approaching the insulator–metal phase transition, which leads to the impossibility of localization of two electrons in it.

Appendix: Splitting of Energy Levels of Impurity Pairs

As the concentration of hydrogen-like impurities increases, "molecular" pairs are formed (in the terminology of ref. [16]) in the impurity lattice with a distance d_{im} between the atoms in the pair. In this case, the energy levels of impurity pairs are split by the value δE. For a *p*-type semiconductor, three types of molecular pairs from acceptors are realized: pairs with two holes $(0, 0)$, with one hole $(0, -1)$, and with three holes $(+1, 0)$. For an *n*-type semiconductor, three types of molecular pairs from donors are realized: pairs with two electrons $(0, 0)$, with one electron $(0, +1)$, and with three electrons $(-1, 0)$. The charge state $(+1)$ of the acceptor corresponds to the charge state (-1) of the donor, and the charge state (-1) of the acceptor corresponds to the charge state $(+1)$ of the donor. To extend the formulas below to *n*-type materials, the symbols "*p*" and "*v*" (for *p*-type) should be replaced by the symbols "*n*" and "*c*" (for *n*-type), and the index "a" should be replaced by the index "d."

(i) By analogy with the energy level difference between the triplet and singlet spin states of two electrons in a hydrogen molecule (H_2^0), we write the splitting of the energy levels of two acceptors [each in the charge state (0)] located at a distance $d_{\mathrm{im}} = \rho a_p$ in the form[75,76]

$$\delta E_{(0,0)} = \frac{2(QS^2 - A)}{1 - S^4} \tag{A1}$$

where

$$\begin{aligned}
Q &= 2\langle E_{\mathrm{a}}\rangle \frac{1}{\rho}\exp(-2\rho)\left(1 + \frac{5}{8}\rho - \frac{3}{4}\rho^2 - \frac{1}{6}\rho^3\right),\\
S &= \exp(-\rho)(1 + \rho + \rho^2/3),\\
A &= 2\langle E_{\mathrm{a}}\rangle \left\{\frac{S^2}{\rho}\left[1 + \frac{6}{5}(\gamma + \ln\rho)\right]\right.\\
&\quad - \exp(-2\rho)\left(\frac{11}{8} + \frac{103}{20}\rho + \frac{49}{15}\rho^2 + \frac{11}{15}\rho^3\right)\\
&\quad \left. + \frac{6M}{5\rho}\left[M\mathrm{Ei}(-4\rho) - 2S\mathrm{Ei}(-2\rho)\right]\right\},\\
\gamma &= 0.57722,\ M = \exp(\rho)(1 - \rho + \rho^2/3),\\
\mathrm{Ei}(x) &= -\int_{-x}^{\infty} t^{-1}\exp(-t)\mathrm{d}t,\\
d_{\mathrm{im}} &= 2R_{\mathrm{im}} \approx 1.24[(1 + K)N_{\mathrm{a}}]^{-1/3}
\end{aligned} \tag{A2}$$

$a_p = e^2/8\pi\varepsilon_{\mathrm{r}}\varepsilon_0\langle E_{\mathrm{a}}\rangle$ is the Bohr radius of a hole on an acceptor in the charge state (0) in a doped crystal; $\langle E_{\mathrm{a}}\rangle = I_{\mathrm{a}} + E_{\mathrm{m}}^{(v)} = I_{\mathrm{a}}(1 - a_{pi}/R_{\mathrm{im}})$ is the thermal ionization energy of an electrically neutral acceptor to the drift mobility edge $E_{\mathrm{m}}^{(v)}$ of *v*-band holes in a doped crystal (see Figure 2); $I_{\mathrm{a}} = I_{0,-1} = e^2/8\pi\varepsilon_{\mathrm{r}}\varepsilon_0 a_{pi}$ is the thermal ionization energy of a single acceptor in the charge state (0) [the electrically neutral acceptor passes to the charge state (-1), and the hole transfers to the top of the *v*-band of the ideal (undoped crystal)]; and a_{pi} is the Bohr radius (a measure of spatial extent of the ground quantum state of an electrically neutral acceptor).

According to (A1,A2), the value $\delta E_{(0,0)}$ is the energy difference between the triplet and singlet spin states of two holes on two electrically neutral acceptors. The value $\delta E_{(0,0)}$ determines[56,77] the time $\tau_{(0,0)} = \pi\hbar/\delta E_{(0,0)}$ of the tunnel exchange of holes between two acceptors in the charge states (0); $\hbar = h/2\pi$ is the reduced Planck constant. For example, for *p*-Si:B crystals with $N_{\mathrm{a}} = 1 \times 10^{18}\ \mathrm{cm}^{-3}$ at $K \approx 0.01$, we obtain $\tau_{(0,0)} \approx 1.1 \times 10^{-10}$ s. For *n*-Ge:Sb crystals with $N_{\mathrm{d}} = 5 \times 10^{16}\ \mathrm{cm}^{-3}$ at $K \approx 0.05$, the tunnel exchange time of electrons between two donors in the charge states (0) is $\tau_{(0,0)} \approx 5.1 \times 10^{-11}$ s.

Note that Formula (A1) was used[50] to quantitatively describe the behavior (the Curie–Weiss type) of the low-temperature paramagnetic susceptibility of hydrogen-like electrically neutral donors in germanium crystals.

(ii) By analogy with the energy level difference between the ground and excited states of the electron in a positively charged molecular hydrogen ion (H_2^+), we write the splitting of the energy levels of two acceptors in the charge states (0) and (-1), located at a distance $d_{\mathrm{im}} = \rho a_p$, in the form[56,75,78]

$$\delta E_{(0,-1)} = \frac{2(JS - B)}{1 - S^2} \tag{A3}$$

where $J = -2\langle E_{\mathrm{a}}\rangle[1 - \exp(-2\rho)(1 + \rho)]/\rho$; $B = -2\langle E_{\mathrm{a}}\rangle(1 + \rho) \times \exp(-\rho)$; and $S = \exp(-\rho)(1 + \rho + \rho^2/3)$.

The ratio of the value $\delta E_{(0,-1)}$ according to Formula (A3) to the width of the acceptor band W_{a} by (8) for *p*-Si:B with

$N_a = 1 \times 10^{18}$ cm^{-3} at $K \approx 0.01$ is $\delta E_{(0,-1)}/W_a \approx 0.2$, and for *n*-Ge:Sb with $N_d = 5 \times 10^{16}$ cm^{-3} at $K \approx 0.05$ is $\delta E_{(0,+1)}/W_a \approx 0.23$. The value $\delta E_{(0,-1)}$ by (A3) determines[56,77] the time $\tau_{(0,-1)} = \pi\hbar/\delta E_{(0,-1)}$ of hole tunneling from the acceptor in the charge state (0) to the acceptor in the charge state (−1). For example, for *p*-Si:B with $N_a = 1 \times 10^{18}$ cm^{-3} at $K \approx 0.01$, the tunneling time of a hole between acceptors in the charge states (0) and (−1) is $\tau_{(0,-1)} \approx 2.9 \times 10^{-12}$ s. For *n*-Ge:Sb with $N_d = 5 \times 10^{16}$ cm^{-3} at $K \approx 0.05$, the tunneling time of an electron from the donor in the charge state (0) to the donor in the charge state (+1) is $\tau_{(0,+1)} \approx 4.2 \times 10^{-12}$ s.

(iii) By analogy with the energy level difference between the excited and ground states of three electrons in a negatively charged molecular hydrogen ion (H_2^-), we write the splitting of the energy levels of two acceptors in the charge states (+1) and (0), located at a distance $d_{im} = \rho a_p$, in the form[16,79]

$$\begin{aligned} &\delta E_{(+1,0)} = E_g - E_u, \\ &E_g = 4.2\langle E_a\rangle \exp(-1.4886\rho); \\ &E_u = 0.0368\langle E_a\rangle\{\exp[-1.7773(\rho - 2.33)] \\ &\quad -2\exp[-0.88865(\rho - 2.33)]\} \end{aligned} \tag{A4}$$

According to (A4), the value $\delta E_{(+1,0)}$ is the energy level difference between the excited (even, *g*) and ground (odd, *u*) quantum states of three holes on two acceptors. The value $\tau_{(+1,0)} = \pi\hbar/\delta E_{(+1,0)}$ determines[56,77] the tunneling time of a hole from the acceptor in the charge state (+1) to the acceptor in the charge state (0). For example, for *p*-Si:B with $N_a = 1 \times 10^{18}$ cm^{-3} at $K \approx 0.01$, the tunneling time of a hole is $\tau_{(+1,0)} \approx 3.7 \times 10^{-11}$ s. For *n*-Ge:Sb with $N_d = 5 \times 10^{16}$ cm^{-3} at $K \approx 0.05$, the tunneling time of an electron from the donor in the charge state (−1) to the donor in the charge state (0) is $\tau_{(-1,0)} \approx 4.2 \times 10^{-11}$ s.

From comparison of the values $\delta E_{(0,-1)}$ by (A3) and $\delta E_{(+1,0)}$ by (A4) for a given concentration and compensation ratio of acceptors, it follows that $\tau_{(0,-1)}$ is smaller than $\tau_{(+1,0)}$ by about an order of magnitude. Let us take into account the thermal activation energy ε_3 of the tunneling transition of a hole between acceptors in the charge states (0) and (−1) in the temperature region centered at $T_3 \approx T_j/3$ (see Figure 1), where T_j is given by Formula (4). In this case, the average time of thermally activated tunneling of a hole is $\langle\tau_3\rangle = \tau_{(0,-1)} \exp(\varepsilon_3/k_B T_3) > \tau_{(+1,0)}$. For example, for *p*-Si:B with $N_a = 1 \times 10^{18}$ cm^{-3} at $K \approx 0.01$, the experimentally observed value of the activation energy is on average $\varepsilon_3 \approx 5.57$ meV.[27,29] Then the average time of thermally assisted (activated) tunneling $\langle\tau_3\rangle$ of a hole between acceptors in the charge states (0) and (−1) is $\langle\tau_3\rangle \approx 2.7 \times 10^{-8}$ s, which is ≈730 times greater than $\tau_{(+1,0)} \approx 3.7 \times 10^{-11}$ s. For *n*-Ge:Sb with $N_d = 5 \times 10^{16}$ cm^{-3} at $K \approx 0.05$, the experimentally observed value of the activation energy is $\varepsilon_3 \approx 1.25$ meV.[33] In this case, the average time of thermally activated tunneling $\langle\tau_3\rangle$ of an electron from the donor in the charge state (0) to the donor in the charge state (+1) $\langle\tau_3\rangle = \tau_{(0,+1)} \exp(\varepsilon_3/k_B T_3) \approx 3.3 \times 10^{-10}$ s. It can be seen that the value of $\langle\tau_3\rangle$ is ≈7.8 times greater than the tunneling time $\tau_{(-1,0)} \approx 4.2 \times 10^{-11}$ s of an electron from the donor in the charge state (−1) to the donor in the charge state (0).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in Mendeley Data at https://doi.org/10.17632/37zbwzcp8b, ref. [80].

Keywords

hydrogen-like impurities, *p*-type and *n*-type silicon and *n*-type germanium crystals, thermal activation energy of ε_2-conductivity, tunneling (jumping) regime of charge carrier migration, weakly compensated semiconductors

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