Activation Energy of DC Hopping Conductivity of Lightly Doped Weakly Compensated Crystalline Semiconductors

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A model is proposed for calculating the thermal activation energy ε_3 of direct current hopping conductivity via nearest neighbors in lightly doped and weakly compensated crystalline semiconductors with hydrogen-like impurities. The temperature region is considered in which hops of single holes occur only between acceptors randomly distributed over the crystal (or hops of single electrons only between donors). The model is based on the idea of the Coulomb blockade of charge carriers by the field of compensating impurities (trap impurities). The hopping length of a hole between acceptors (or an electron between donors) is assumed to be equal to the critical (percolation) radius of the spherical region per a majority (doping) impurity atom. At a critical radius, an infinite cluster connecting ohmic contacts is formed in the crystal, along which charge carriers move in a hopping manner via majority impurities. The value of ε_3 is defined as average work on overcoming the electrostatic Coulomb blockade by a charge carrier and its hopping via the electrically conducting cluster to "infinity". The results of calculating ε_3 by the proposed model of the Coulomb blockade for the most well-studied bulk germanium and silicon *p*- and *n*-type crystals are consistent with known experimental data.

1. Introduction

At low temperatures, the direct current (DC) electrical conductivity of a crystalline *p*-type semiconductor with the hydrogen-like impurity concentration corresponding to the insulator side of the insulator–metal phase transition has the following form (see, e.g., refs. [1,2]):

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

where the electrical conductivity σ_1 is due to the transitions of holes from acceptors in the charge state (0) to the *v*-band, σ_2 is determined by the transitions of single holes between electrically neutral acceptors with the formation of a pair of ions in the charge states $(+1)$ and (-1), σ_3 is associated with the phonon-assisted hops of single holes from acceptors in the charge state (0) to the nearest acceptors in the charge state (-1), formed due to the introduction of compensating donors into a semiconductor, σ_{01}, σ_{02}, and σ_{03} are the weakly temperature-dependent prefactors (compared with 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 of holes in the vicinity of temperatures where the aforementioned mechanisms of electrical conductivity dominate; k_B is the Boltzmann constant; T is the absolute temperature. (The charge states of acceptors $|a,-1\rangle$ and donors $|d,+1\rangle$ are given in units of the elementary charge *e*.) Note, that the electrical ε_2-conductivity appears in weakly compensated semiconductors in the range of doping levels by majority impurities from "moderate" to "heavy" (see, e.g., ref. [3]).

We will be interested in the mechanism of hopping electrical conductivity $\sigma_3 = \sigma_h$. Historically, following the two higher temperature thermal activation energies (transitions from the impurity energy level to the *v*- or *c*-band and transitions between electrically neutral impurities), it is assigned the index "3". At a low doping level, i.e., far from the Mott transition (insulator–metal phase transition) at low temperatures, DC hopping electrical conductivity has the following form:[1,2]

$$\sigma_h = \sigma_3 = \sigma_{03}\exp\left(-\frac{\varepsilon_3}{k_B T}\right) \quad (2)$$

The most important electrophysical parameters of a semiconductor that determine its properties are the doping level (the concentration of the majority impurity) and the compensation ratio K (the ratio of the concentration of compensating impurities to the concentration of the majority impurities). Further we consider only lightly doped weakly compensated (LDWC) crystalline semiconductors, in which the doping level is much lower than that corresponding to the insulator–metal transition, and the value of $K \ll 1$.

The dependence $\ln(1/\sigma)$ versus $1/T$ according to Equation (1) for such semiconductors, as well as their energy band diagram on the example of *p*-type semiconductors are illustrated in **Figure 1**. At a certain characteristic temperature T_j, the

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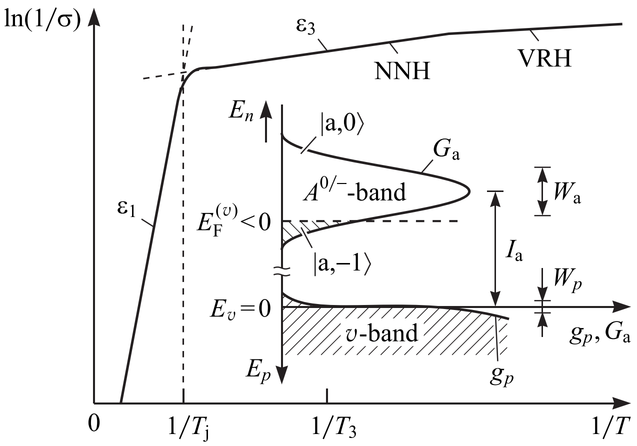

Figure 1. Scheme of the dependence of the natural logarithm of the reciprocal DC electrical conductivity $\ln(1/\sigma)$ of LDWC semiconductor on the reciprocal temperature $1/T$. At $T = T_j$, the observed values of the minimum band electrical conductivity with the thermal activation energy ε_1 and the maximum hopping electrical conductivity with the thermal activation energy ε_3 are equal. Nearest neighbor hopping (NNH) is the region of phonon-assisted tunnel hops of holes between the nearest acceptors in the charge states (0) and (−1) with the activation energy $\varepsilon_3 \ll \varepsilon_1$ (in the vicinity of temperature T_3); variable range hopping (VRH) is the region of hole hops optimized by both the activation energy and the length. The inset shows the energy diagram for the acceptor $A^{0/-}$-band of LDWC p-type semiconductor at low temperatures (the energy axis is broken). Here, E_p and E_n are the energies of a hole and an electron, respectively, $E_\nu = 0$ is the top of the ν-band of an undoped semiconductor (the electron-filled ν-band states are hatched), g_p is the density of single-electron states in the ν-band of LDWC semiconductor, G_a is the distribution density of acceptor energy levels in $A^{0/-}$-band [the energy levels of acceptors vacant for holes are hatched, i.e., those in the charge states (−1)]; I_a is the ionization energy of a single (isolated) acceptor, $E_F^{(\nu)} < 0$ is the Fermi level, W_a is the width of the acceptor band, W_p is the root-mean-square fluctuation of the potential energy of ν-band holes.

minimum observed band conductivity with the activation energy ε_1 is equal to the maximum hopping conductivity with the activation energy $\varepsilon_3 \ll \varepsilon_1$ (see, e.g., refs. [4–6]). Note that, according to ref. [5], at the hole concentration in the ν-band $p \ll K(1-K)N_a$, where N_a is the concentration of acceptors, K is the ratio of the donor concentration to the acceptor concentration, the inequality $W_p \ll W_a$ is satisfied. The quantity $K(1-K)N_a$ is the effective concentration of holes hopping via acceptors in the $A^{0/-}$-band.[4]

The study of the thermal activation energy ε_3 is of key importance, since its results are used in the creation of cryothermal resistances and photodetectors based on the crystalline semiconductors operating in the range from infrared to terahertz radiation (see, e.g., refs. [7,8]).

There are quite a lot of experimental data[1,2,9–20] on the thermal activation energy ε_3 of the DC hopping electrical conductivity of LDWC crystalline semiconductors with hydrogen-like impurities. These data were compared with calculations based on mathematical and computer models[13,14,21–26] known at that time. Let us briefly discuss these models (some of which were considered earlier, for example, in refs. [24,27]).

Historically, the first model for describing the dependence of the activation energy ε_3 on the concentration of the majority impurities in LDWC semiconductors is the Mott model[21] (see also ref. [23]). This model gives a correct assessment of the role of compensating impurities, which is fundamental for the low-temperature electrical conductivity. Charge carriers in the Mott model are charged hole vacancies on acceptors or electron vacancies on donors in p- or n-type materials, respectively. The quantity ε_3 in it is defined as the average energy required to overcome the Coulomb blockade of charge carriers in the field of the attractive potential of an oppositely charged compensating impurity and transfer them to infinity. According to refs. [28,29], the Coulomb blockade of electron (or hole) vacancies on the majority impurities by the field of compensating impurity ions leads to the formation of a Coulomb gap at the Fermi level. This gap determines both the migration of electron (or hole) vacancies and their spin exchange at low temperatures, which manifests itself in macroscopic electrical and magnetic properties near the insulator–metal concentration phase transition. At the same time, in the Mott model the Coulomb correlations in the random (Poisson) distribution of oppositely charged ions of the majority and compensating impurities are not taken into account and the dependence of ε_3 on the compensation ratio K is not fully described, more precisely, the result is obtained for vanishingly small values of K, close to zero.

In the Miller–Abrahams model[22] (see also ref. [23]), the current via majority impurities is carried out by charge carriers hopping between them. In this case, each hop corresponds to its own resistor, and together they form a three-dimensional equivalent resistance network. Then the exponent of the resistance network is calculated for a Poisson (random) distribution of impurities. However, the Coulomb interaction between oppositely charged ions of donors and acceptors is not taken into account in this model. A significant advance is the ability to analytically describe the dependence $\varepsilon_3(K)$. However, the derived values of ε_3 are on an average 10% greater than those observed in germanium crystals,[1,2,9–15] and 35% greater than in silicon crystals.[16–20]

The next step toward a more accurate calculation of the dependences of ε_3 on the doping level of the majority impurities and their compensation is associated with the Shklovskii–Efros model,[24] which develops Miller–Abrahams approach taking into account the percolation theory. This model introduces the concept of impurity complexes associated with a compensating impurity and expands the number of complexes under consideration from one to three. Thus, in a p-type semiconductor, the 0-, 1-, and 2-complexes represent an ionized donor, next to which there is no ionized acceptor, or there are 1 or 2 ionized acceptors, respectively. From the electrical neutrality of the set of charged 0- and 2-complexes, the position of the Fermi level in the zero-temperature limit is determined by numerical simulation. After that, long-range fluctuations of the electric potential are taken into account and the dependence of the activation energy ε_3 on the compensation ratio and the concentration of doping impurities is determined within the framework of the percolation theory. Thus, the dependence of the thermal activation energy $\varepsilon_3 = \varepsilon_{3(\mathrm{SE})}$ according to the Shklovskii–Efros model (index SE) on the compensation ratio $K = N_d/N_a$ of acceptors with the concentration N_a by donors with the concentration

$N_d = KN_a$ for a p-type LDWC semiconductor is determined as a correction to the difference between the positions of the Fermi level and the maximum density of hole states in the acceptor band. Approximation of numerical calculations (by the Monte Carlo method) of the value $\varepsilon_{3(SE)}$ over a limited array (up to 1600) of coordinates of acceptors and donor ions, energies and numbers of hole occupations of acceptors gives[24]

$$\varepsilon_{3(SE)} = 0.61 \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 R_a}\left(1 - 0.29K^{1/4}\right) \tag{3}$$

where e is the elementary charge, ε_r is the relative static permittivity (determined by v-band electrons on the background of the ionic cores of the crystal matrix), ε_0 is the electric constant; $R_a = \left(4\pi N_a/3\right)^{-1/3}$ is the distance between acceptors in a p-type semiconductor.

When obtaining relation (3), the validity is not completely clear: (i) long-range chaotic electrostatic potential in LDWC semiconductors; (ii) representation of the value of ε_3 as a difference of energy positions of the Fermi level and the maximum of the density of states in the impurity band at zero absolute temperature; (iii) use of a limited data array in computer modeling by the Monte Carlo method at extremely low compensation ratios of the majority impurities.

Note that Ginzburg[25] obtained an expression for the activation energy ε_3 by considering only the pairs "majority impurity ion–electrically neutral majority impurity", i.e., without taking into account compensating impurities. But this approach is rather applicable for moderately doped weakly compensated semiconductors, when ε_3 starts to decrease with an increasing concentration of the majority impurity.

Subsequently, Tkach and Chenskii[26] proposed an analytical expression for the dependence of the Fermi level on the compensation ratio of LDWC semiconductors based on the Shklovskii–Efros model and Markov chains. The results of calculations of the Fermi level E_F at zero absolute temperature by the model[26] practically do not differ from the calculations of E_F by the Shklovskii–Efros model.

The purpose of this work is to obtain a more rigorous analytical expression for the activation energy ε_3 of the stationary hopping electrical conductivity based on Mott's idea about the important role of the Coulomb blockade in determining it. The energy ε_3 is defined as the work required to overcome the Coulomb blockade of the charge states (-1) of acceptors by the field of mutually nearest fixed donors in the charge states $(+1)$ in a p-type material [or to overcome the Coulomb blockade of the charge states $(+1)$ of donors by the field of mutually nearest fixed acceptors in the charge states (-1) in an n-type material]. The result is an analytical expression for ε_3 in the form of a definite integral. The calculations performed according to this expression are compared with the experimental data known in the literature[1,2,9–20] and with the results of numerical simulation[24] of ε_3 for LDWC crystalline semiconductors with hydrogen-like impurity atoms.

Note that we present a comparison with the experimental data for the most well-studied LDWC covalent semiconductors. These data have stood the test of time. Unfortunately, there are no new experimental data on the value of ε_3 for the well-characterized LDWC semiconductor materials with hydrogen-like impurities.

2. Theoretical Model for Calculating ε_3

Let us consider a three-dimensional crystalline p-type semiconductor lightly doped with acceptors with the concentration $N_a = N_{a,0} + N_{a,-1}$ and weakly compensated by donors with the concentration N_d. Here $N_{a,0}$ and $N_{a,-1}$ are the concentrations of acceptors in the charge states (0) and (-1), respectively. The compensation ratio of hydrogen-like acceptors by hydrogen-like donors in a weakly compensated semiconductor is $0 < K(= N_d/N_a) < 5\%$. It is assumed that in a lightly doped semiconductor the concentration of the majority (doping) impurity is less than 5% of the concentration corresponding to the insulator–metal phase transition (Mott transition) at low temperatures. This corresponds to the doping level, starting from which there is a violation of the theoretically predicted increase in the value of ε_3 with an increasing concentration of the majority impurity.[30] All compensating donors are in the charge state $(+1)$, i.e., $N_{d,+1} = N_d = KN_a$. The average over the crystal volume electrical neutrality has the form:

$$N_{a,-1} = N_d = KN_a \tag{4}$$

Further, the hopping migration of holes is considered within the framework of the one-particle approximation, i.e., one hole is considered and it is assumed that it hops between acceptors in the averaged field of all holes and all impurity ions. At the hopping electrical ε_3-conductivity, thermally phonon-assisted tunneling transitions of holes occur between acceptors in the charge state (0) and acceptors nearest to them in the charge state (-1). This means that these charge states migrate through the crystal in an appropriate manner.[4]

Based on the virial theorem, in refs. [5,6] the characteristic temperature T_j of the transition from band migration of holes via the v-band states to hopping migration of holes via acceptors in the charge states (0) and (-1) at the concentration of v-band holes $p \ll K(1-K)N_a$ is determined as follows:

$$T_j \approx \frac{0.728}{k_B}\frac{e^2}{4\pi\varepsilon_r\varepsilon_0}\left(KN_a\right)^{1/3} \tag{5}$$

where ε_r is the relative static permittivity; at low temperatures $\varepsilon_r = 15.4$ for germanium crystals[31] and $\varepsilon_r = 11.47$ for silicon crystals;[32] $N_{a,-1} = KN_a$.

Note that at temperature $T \geq T_j$ there is no correlation in the location of all impurity ions and they are randomly (Poissonian) distributed over the crystal. At temperature $T < T_j$, the electrical conductivity of free holes via the v-band states is negligible compared to the hopping electrical conductivity. The concentration of localized holes in the acceptor band is $N_{a,0} = (1-K)N_a$. According to,[33,34] the maximum concentration of holes hopping between acceptors in the charge states (0) and (-1) is $N_h = K(1-K)N_a$, i.e., $N_h = N_{a,0}N_{a,-1}/N_a$. The ratio of the concentration of holes hopping via acceptors N_h to the concentration of holes on acceptors $N_{a,0} = (1-K)N_a$ is $N_h/(1-K)N_a = K$. The hopping electrical conductivity $\sigma_h = \sigma_3 = eN_hM_h$, where M_h is the drift hopping mobility, which determines the temperature dependence of σ_h.

Next, we take into account that a hole localized near one impurity atom is affected by the other impurity ions. As a result, the energy level of the impurity shifts (due to local fluctuations of concentration, the shift is random in different parts of the crystal). Instead of discrete local energy levels, an impurity band appears in the band gap of a semiconductor (see the $A^{0/-}$-band in Figure 1). In this case, we cannot know exactly where the hole energy level is located in the impurity band. Then, under the assumption that the distribution density of acceptor energy levels in the band gap is Gaussian, we can find the average concentration of electrically neutral and negatively charged acceptors by integrating over all possible values of acceptor energy levels in the $A^{0/-}$-band.

Thus, 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) [is electrically neutral] or in the charge state (-1) [is a singly negatively charged ion] are[4,5,35]

$$\begin{aligned}\langle f_0 \rangle &= \frac{N_{\mathrm{a},0}}{N_\mathrm{a}} = \int_{-\infty}^{+\infty} G_\mathrm{a} f_0 \, \mathrm{d}(E_\mathrm{a} - I_\mathrm{a}) = 1 - K \\ \langle f_{-1} \rangle &= \frac{N_{\mathrm{a},-1}}{N_\mathrm{a}} = \int_{-\infty}^{+\infty} G_\mathrm{a} f_{-1} \, \mathrm{d}(E_\mathrm{a} - I_\mathrm{a}) = K\end{aligned} \tag{6}$$

where G_a is a Gaussian distribution of density of hole states in the acceptor band ($A^{0/-}$-band), $f_0 = 1 - f_{-1} = \left\{1 + \beta_\mathrm{a}^{-1} \exp\left[-\left(E_\mathrm{F}^{(v)} + E_\mathrm{a}\right)/k_\mathrm{B} T\right]\right\}^{-1}$ is the probability of filling a state with the energy level E_a by a hole; $E_\mathrm{a} = E_{\mathrm{a},-1} - E_{\mathrm{a},0} > 0$ is the ionization energy of an electrically neutral acceptor from the ground state (a hole detachment from a neutral acceptor and its transition to the top of the v-band of an undoped crystal); $I_\mathrm{a} = I_{\mathrm{a},-1} - I_{\mathrm{a},0} = e^2/8\pi\varepsilon_\mathrm{r}\varepsilon_0 a_p > 0$ is the thermal ionization energy of an isolated (single) acceptor in the charge state (0); a_p is the Bohr radius of a hole on the acceptor; $E_\mathrm{F}^{(v)} < 0$ is the Fermi level; T is the absolute temperature; the top of the v-band ($E_v = 0$) of an undoped crystal is chosen as the reference point for $E_\mathrm{F}^{(v)}$, I_a, and E_a; β_a is the degeneracy factor of the energy level E_a of a hydrogen-like acceptor. For the case $T < T_\mathrm{j}$ it is assumed that $\beta_\mathrm{a} = 4$ (cf. ref. [36]) and the degeneracy factor of the hydrogen-like donor is $\beta_\mathrm{d} = 2$.[37–39] The magnetic moment of the acceptor (donor) atom nucleus is not taken into account.[40]

Let us assume that the distribution density of acceptor energy levels E_a in the band gap (see Figure 1) has a normal (Gaussian) distribution:[41,42]

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

where W_a^2 is the variance of acceptor energy levels E_a relative to I_a in the semiconductor band gap; $\int_{-\infty}^{+\infty} G_\mathrm{a} \mathrm{d}(E_\mathrm{a} - I_\mathrm{a}) = 1$.

The rms fluctuation of acceptor energy levels (the effective width of the acceptor band) W_a taking into account the Coulomb interaction of randomly (Poissonian) located in the crystal nearest impurity ions is equal to[4,5,43]

$$W_\mathrm{a} \approx 2.64 \frac{e^2}{4\pi\varepsilon_\mathrm{r}\varepsilon_0} (2KN_\mathrm{a})^{1/3} \tag{8}$$

where $2KN_\mathrm{a} = N_{\mathrm{a},-1} + N_\mathrm{d}$ is the concentration of all impurity ions in the crystal.

To take into account the effect of the electrostatic potential $\varphi(r) = e/4\pi\varepsilon_\mathrm{r}\varepsilon_0 r$ created by donor in the charge state (+1), at distance r from it, on the concentration of acceptors in the charge state (-1) it is necessary to find the position of the Fermi level $E_\mathrm{F}^{(v)}(r)$:

$$E_\mathrm{F}^{(v)}(r) = E_\mathrm{F}^{(v)} - e\varphi(r) = E_\mathrm{F}^{(v)} - e^2/4\pi\varepsilon_\mathrm{r}\varepsilon_0 r \tag{9}$$

where $E_\mathrm{F}^{(v)} < 0$ is found from the solution of the electrical neutrality Equation (4) taking into account Equation (5)–(8) at $\varphi(r) = 0$.

Note that in Equation (9) and further the purely Coulomb potential $\varphi(r)$ of the interaction of the mutually nearest donor and acceptor ions is taken into account without screening of this potential by holes hopping between acceptors.[44]

From Equation (6) and (9) follows that

$$\begin{aligned}N_{\mathrm{a},-1}(r) &= N_{\mathrm{a},-1}(\varphi(r)) \\ &= N_\mathrm{a} \int_{-\infty}^{+\infty} \frac{G_\mathrm{a} \mathrm{d}(E_\mathrm{a} - I_\mathrm{a})}{1 + \beta_\mathrm{a} \exp\left(\left[E_\mathrm{a} + E_\mathrm{F}^{(v)} - e\varphi(r)\right] \middle/ k_\mathrm{B} T\right)}\end{aligned} \tag{10}$$

Further, following ref. [5], we introduce the concept of mutually nearest positively charged donors and negatively charged acceptors. The donor ion and the acceptor ion are considered to be mutually nearest in the crystal if the donor ion is the nearest to the acceptor ion, and the acceptor ion is the nearest to the donor ion. Then the probability density function $P_\mathrm{cor}(r)$ to find a mutually nearest pair "acceptor ion – donor ion" in the range of distances $(r, r + \mathrm{d}r)$ between them taking into account the Coulomb attraction of the acceptor in the charge state (-1) to the donor ion is (see Appendix A):

$$\begin{aligned}P_\mathrm{cor}(r) &= 4\pi r^2 \left[N_{\mathrm{a},-1}(r) + KN_\mathrm{a}\right] \\ &\times \exp\left(-4\pi \int_0^r l^2 [N_{\mathrm{a},-1}(l) + KN_\mathrm{a}] \mathrm{d}l\right)\end{aligned} \tag{11}$$

where $\int_0^\infty P_\mathrm{cor}(r) \mathrm{d}r = 1$, $N_{\mathrm{a},-1}(r) \equiv N_{\mathrm{a},-1}(\varphi(r))$ is the concentration of acceptors in the charge state (-1), which by Equation (6) taking into account Equation (9) depends on r through the dependence of the Coulomb potential $\varphi(r)$; the position of the donor ion is chosen as the reference point for distances $(r = 0)$.

Note that without taking into account the Coulomb interaction between the donor ion and the acceptor ion, the probability density function by Equation (11) transforms into a purely geometric (Poisson) probability density function to find the mutually nearest impurity ion in the distance range $(r, r + \mathrm{d}r)$ providing that there are no other ions in the ball of radius r, i.e., $P_\mathrm{rnd}(r) = 4\pi r^2 N_\mathrm{ch} \exp(-4\pi r^3 N_\mathrm{ch}/3)$, where $N_\mathrm{ch} = N_{\mathrm{a},-1} + N_\mathrm{d} = 2KN_\mathrm{a}$ is the concentration of impurity ions.[5,45] This probability density function is used in refs. [4,5,43] to obtain Equation (8), which describes the rms fluctuation of acceptor energy levels.

Note that in refs. [46–49] the distribution of distances between mobile ions in liquid and solid crystals is considered and it is assumed that $N_{\mathrm{a},-1}(r) = N_\mathrm{a} \exp(e^2/4\pi\varepsilon_\mathrm{r}\varepsilon_0 r k_\mathrm{B} T)$. Then, as the donor ion approaches the acceptor ion, i.e., at $r \to 0$, the value of $N_{\mathrm{a},-1}(r)$ increases indefinitely; the value of $N_{\mathrm{a},-1}(r)$

becomes divergent due to the use of the Maxwell–Boltzmann distribution.[50] When writing Equation (10) for the probability of finding an acceptor in the charge state (-1) at distance r from the nearest donor in the charge state $(+1)$, the grand canonical Gibbs distribution[51,52] is used and the specified problem with the concentration $N_{a,-1}(r)$ does not arise.

According to numerical calculations,[24–26] 97.4% of the donors in a p-type semiconductor (or acceptors in an n-type semiconductor) participate in 1-complexes; see also ref. [53].

Further, when calculating the activation energy ε_3 for lightly doped weakly compensated semiconductors, the following assumptions simplifying the subsequent calculation are used: (i) The distance between the mutually nearest "electrically bound" ions of the donor–acceptor pair is assumed to be equal to the critical (percolation) radius R_{per} of the spherical region per acceptor, taking into account the donors that compensate them, at which end-to-end electrically conducting channels of acceptors are formed in the crystal. (ii) At the critical radius R_{per} the charge state (-1) of the acceptor, being "detached" as a result of activation, from the mutually nearest donor ion, without changing its nearest and farthest surroundings can migrate in a hopping manner via acceptors through the entire crystal, moving away from this donor to infinity. In fact, during this migration, subsequent captures by other distant donors are possible $(K \ll 1)$, after which the process is repeated. (iii) The restoration time of the initial local equilibrium state, when the donor and acceptor ions become again mutually nearest neighbors, is determined by the overall migration rate, i.e., ultimately by the temperature. (iv) The energy source of the magnitude ε_3 for activating hops is acoustic phonons (phonon assisted hopping).

It is assumed that the charge state (-1) of the acceptor belongs to an "infinite" cluster of acceptors connecting electrodes to the sample when the NNH-conductivity is realized in it.[24] Ionization equilibrium ensures the fulfillment of the local and global electrical neutrality of the crystal sample.

Note that the stationary hopping conductivity involves the charge states (-1) of acceptors which due to thermal fluctuations migrate in the acceptor band from the mutually nearest donor (located at distance R_{per}) to infinity. Here $R_{\text{per}} = B_c^{1/3}[4\pi(1+K)N_a/3]^{-1/3} \approx 0.867[(1+K)N_a]^{-1/3}$ is the distance between acceptors (majority impurities), equal to the percolation radius of the spherical region per acceptor taking into account the compensation of acceptors by donors; $B_c \approx 2.735$ is a dimensionless parameter, the average number of hopping bonds per atom of the majority impurity.[24,54–57] At the percolation radius R_{per} the charge state (-1) of the acceptor, being activated and "detached" from the donor ion, is able to migrate in a hopping manner via acceptors states through the entire crystal [more precisely, holes migrate, hopping from the acceptor in the charge state (0) to the acceptor in the charge state (-1)]. Note that the value of R_{per} takes into account the effect of the excluded fraction of self-avoiding walks (according to the terminology of ref. [58]) of holes via acceptors.

We define the thermal activation energy ε_3 of hopping migration of holes between acceptors and donors randomly (Poissonian) distributed over the crystal as the average work in the Coulomb field of the donor ion $E(\rho) = e/4\pi\varepsilon_r\varepsilon_0\rho^2$ necessary for hopping migration of the charge state (-1) of the acceptor from the mutually nearest donor in the charge state $(+1)$ from the point with coordinate $\rho = r = R_{\text{per}}$ to infinity $\rho = \infty$ (cf. ref. [23]):

$$\varepsilon_3 = \frac{1}{C_3}\int_{R_{\text{per}}}^{\infty} P_{\text{cor}}(r)\left(\int_r^{\infty} eE(\rho)\,\mathrm{d}\rho\right)\mathrm{d}r = \frac{1}{C_3}\frac{e^2}{4\pi\varepsilon_r\varepsilon_0}\int_{R_{\text{per}}}^{\infty}\frac{P_{\text{cor}}(r)}{r}\,\mathrm{d}r; \tag{12}$$

$$C_3 = \int_{R_{\text{per}}}^{\infty} P_{\text{cor}}(r)\,\mathrm{d}r = \exp\left(-4\pi\int_0^{R_{\text{per}}} l^2[N_{a,-1}(l) + KN_a]\,\mathrm{d}l\right)$$

where C_3 is the normalizing factor; the probability $P_{\text{cor}}(r)\mathrm{d}r$ is determined by Equation (11) taking into account $N_{a,-1}(l) = N_{a,-1}(r)$ by Equation (10); $E(\rho) = -\mathrm{d}\varphi/\mathrm{d}\rho$ is the Coulomb electric field strength created by the donor ion at distance ρ from it; $\varphi(\rho) = e/4\pi\varepsilon_r\varepsilon_0\rho$ is the electrostatic potential created by the donor in the charge state $(+1)$ at distance ρ from it.

Note that the value of ε_3 by Equation (12) corresponds to the activation energy of hopping migration of an average hole of the acceptor band from "infinity" to $R_{\text{per}} \approx 0.867[(1+K)N_a]^{-1/3}$.

In order to extend the obtained equations to n-type semiconductors with hydrogen-like donors in all equations the index "a" [acceptors in the charge states (0) and (-1)] should be replaced by the index "d" [donors in the charge states (0) and $(+1)$].

3. Calculation Results and Their Comparison with Experimental Data

Table 1 shows the results of calculations of ε_3 by Equation (12), taking into account Equation (4)–(11) at the temperature $T_3 = T_j/3$ determined by Equation (5), and their comparison with the experimental data[1,2,9–20] for bulk germanium and silicon crystals of n- and p-type doped with various hydrogen-like impurities. The thermal ionization energies of a single majority impurity atom in the charge state (0) used in calculations for n-type and p-type germanium crystals are:[59,60] $I_d = 10.32$ meV (n-Ge:Sb), $I_d = 14.17$ meV (n-Ge:As), $I_d = 12.89$ meV (n-Ge:P), and $I_a = 11.32$ meV (p-Ge:Ga); for n-type and p-type silicon crystals: $I_d = 45.58$ meV (n-Si:P) and $I_a = 44.39$ meV (p-Si:B).

From the experimental data for LDWC crystals of Ge and Si we selected such samples in which the compensation ratio $K < 5\%$ and the concentration of the doping impurity $N_{d(a)} < 0.05N_M$, where N_M is the concentration of the majority impurity corresponding to the Mott transition (see ref. [61] and references therein). For n-type and p-type germanium crystals: $N_M \approx 1.68 \times 10^{17}$ cm^{-3} (n-Ge:Sb, $K < 0.1$), $N_M \approx 3.61 \times 10^{17}$ cm^{-3} (n-Ge:As, $K \approx 0$), $N_M \approx 2.53 \times 10^{17}$ cm^{-3} (n-Ge:P, $K \approx 0$), and $N_M \approx 1.85 \times 10^{17}$ cm^{-3} (p-Ge:Ga, $K \approx 0.35$); for n-type and p-type silicon crystals: $N_M \approx 3.81 \times 10^{18}$ cm^{-3} (n-Si:P, $K \approx 0.1$) and $N_M \approx 4.1 \times 10^{18}$ cm^{-3} (p-Si:B, $K \approx 0.1$). As it was established on the example of Ge and Si,[62,63] at weak compensation ratios K the value of N_M is practically independent of compensation, which makes it possible to use the above data on N_M in the entire considered range of weak compensations.

Table 1. Parameters of hydrogen-like doping impurities in semiconductor crystals of Ge and Si and the thermal activation energy ε_3 of the hopping electrical conductivity calculated by Equation (12), taking into account Equation (4)–(11) at the temperature $T_3 = T_j/3$ by Equation (5), and by Shklovskii–Efros model $\varepsilon_{3(\mathrm{SE})}$ [Equation (3)] in comparison with the experimental data.[1,2,9–20]

Material	Sample	$N_{d(a)}$ [cm^{-3}]	K [%]	T_j [K] Calculation	ε_3 [meV] Experiment	ε_3 [meV] Calculation	$\varepsilon_{3(\mathrm{SE})}$ [meV] Calculation	Experimental data refs.
n-Ge:Sb	−5	1.6×10^{15}	≈3	2.87	0.99	0.96	0.95	[2]
	−7	2.3×10^{15}	≈3	3.24	1.1	1.08	1.07	
	−8	3×10^{15}	≈3	3.54	1.2	1.18	1.17	
	−10	5.2×10^{15}	≈3	4.25	1.5	1.42	1.40	
	–	6×10^{15}	≈3	4.46	1.76	1.49	1.47	[9]
	E3	6.7×10^{15}	4	5.09	1.62	1.58	1.51	[10]
	–	6.7×10^{15}	≤3	4.62	1.75	1.55	1.52	[11,12]
	–	6.8×10^{15}	≤3	4.65	1.45	1.55	1.53	
	–	6.8×10^{15}	2–4	4.06	1.3	1.52	1.55	
n-Ge:As	–	2×10^{16}	≈2	5.82	1.89	2.17	2.22	[9]
n-Ge:P	1	3.7×10^{15}	≈3	3.79	1.25	1.27	1.25	[13,14]
	2	4.3×10^{15}	≈3	3.99	1.39	1.33	1.31	
	3	4.9×10^{15}	≈3	4.17	1.47	1.39	1.37	
	4	6.3×10^{15}	≈3	4.53	1.56	1.51	1.49	
	5	6.9×10^{15}	≈3	4.67	1.60	1.56	1.54	
	6	1.1×10^{16}	≈3	5.46	1.74	1.82	1.80	
p-Ge:Ga	–	2.66×10^{15}	2–4	3.74	1.45	1.16	1.11	[15]
	–	4.4×10^{15}	≈2	3.66	1.40	1.32	1.34	[1]
n-Si:P	215A	1.1×10^{17}	0.73	9.85	5	5.07	5.41	[16]
p-Si:B	–	2.3×10^{16}	0.1	3.01	3.89	3.50	3.33	[17,18]
	–	2.49×10^{16}	0.1	3.09	4.15	3.59	3.42	
	–	2.74×10^{16}	0.1	3.20	3.99	3.71	3.53	
	–	3.06×10^{16}	0.1	3.31	4.29	3.84	3.66	
	–	3.1×10^{16}	0.1	3.33	4.09	3.86	3.68	
	–	3.6×10^{16}	0.1	3.50	4.22	4.06	3.87	
	–	3.6×10^{16}	0.04	2.58	4.79	4.29	3.91	
	–	3.6×10^{16}	0.06	2.95	4.47	4.21	3.89	
	–	3.6×10^{16}	0.08	3.25	4.37	4.13	3.88	
	–	3.6×10^{16}	0.18	4.26	4.12	3.84	3.83	
	–	3.6×10^{16}	0.34	5.26	3.97	3.63	3.79	
	–	3.6×10^{16}	0.62	6.43	3.73	3.51	3.74	
	–	3.6×10^{16}	0.89	7.25	3.65	3.49	3.71	
	11	4.5×10^{16}	0.22	4.90	4.3	4.06	4.12	[19]
	12	5.2×10^{16}	0.11	4.08	4.4	4.55	4.36	
	13	6×10^{16}	0.078	3.82	4.7	4.91	4.60	
	14	7.8×10^{16}	0.03	3.03	5.2	5.59	5.07	
	B-977	8.94×10^{16}	1.4	11.42	4.5	4.74	4.97	[20]
	15	9×10^{16}	0.2	5.99	5.2	5.16	5.19	[19]
	B-171	1.07×10^{17}	3.4	16.30	5.1	5.27	5.13	[20]
	16	1.2×10^{17}	0.03	3.50	6.2	6.46	5.86	[19]

Table 1 shows that the results of calculations of the thermal activation energy ε_3 of the hopping electrical conductivity by Equation (12) taking into account Equation (4)–(11) at the temperature $T_3 = T_j/3$ by Equation (5) are generally quantitatively consistent with the experimental data for Ge and Si. The calculations of $\varepsilon_{3(\mathrm{SE})}$ by Equation (3) proposed by

Shklovskii and Efros[13,14,24] for the zero-temperature limit agree approximately equally well for Ge and somewhat worse for Si with the experimental data.

Although the analytical calculations according to our Equation (12) practically coincide with the numerical calculations of Shklovskii–Efros [see Equation (3)], there are nevertheless the following reasons for their deriving: (i) to avoid the unjustified introduction of long-range chaotic electrostatic potential in LDWC semiconductors; (ii) to avoid the unjustified assumption that the value ε_3 is equal to the difference between energy position of the Fermi level, obtained from the equality of the concentrations of 0- and 2-complexes, and the maximum of the density of states in the impurity band at zero absolute temperature; (iii) to avoid the necessity to calculate the coefficients in evaluation of ε_3 by numerical simulation by the Monte Carlo method using a limited data array; (iv) to take into account the influence of temperature on the value of ε_3.

Thus, comparison of calculation results (see also ref. [64]) using both models with experiment gives almost equally good results and does not allow us to make a final choice between them. Nevertheless, it shows the realism of our model, based on Mott's idea about the relation of the activation energy of hopping migration in the doped semiconductors with overcoming the Coulomb blockade of charge carriers in the impurity band by the field of compensating impurities.

4. Conclusions

An electrostatic model is constructed to calculate the thermal activation energy of the hopping electrical ε_3-conductivity via the nearest neighbors in lightly doped weakly compensated semiconductors with hydrogen-like impurities. This model allowed to obtain an analytical expression (in the form of a definite integral) for the value of ε_3. The model is based on the idea that the mechanism of the electrical ε_3-conductivity is realized by the thermally activated charge carriers overcoming the Coulomb blockade in the impurity band. The Coulomb blockade is created by a field of compensating trap impurities. A subsequent hopping migration of charge carriers via the states of the majority impurities is considered within the framework of the percolation theory. In fact, we propose a model of "detachment" of the charge state of the doping impurity from the mutually nearest ion of the compensating impurity, i.e., in some sense an analogue of the Mott model for ε_3.

It is assumed that donors and acceptors are randomly (Poissonian) distributed over a crystal, and hops of single holes occur only between acceptors in the charge states (0) and (−1) in a *p*-type semiconductor (or electrons between donors in the charge states (0) and (+1) in an *n*-type semiconductor). Among the three possible types of impurity complexes, only "1-complexes" (mutually nearest donor ion and acceptor ion) are considered. The distance between "electrically bound" majority impurities is assumed to be equal to the critical (percolation) radius $R_{\text{per}} \approx 0.867\left[(1+K)N_{\text{a(d)}}\right]^{-1/3}$, where $(1+K)N_{\text{a(d)}}$ is the total concentration of impurities in the crystal with the compensation ratio K (index "a" for *p*-type or index "d" for *n*-type). At the hopping length R_{per} of charge carriers between the atoms of the majority impurity in the crystal sample, an end-to-end (i.e., from anode to cathode) electrically conducting channel is formed. As a result of thermal activation at the characteristic temperature T_3, the charge state (−1) of the acceptor "detaches" from the mutually nearest donor ion in a *p*-type semiconductor at the critical radius R_{per} and starts to migrate in a hopping manner through the crystal. Hence, in *p*-type semiconductors, the activation energy ε_3 is defined as the work of electrostatic field forces required for the hopping migration of a hole from infinity to the acceptor ion located at a distance R_{per} from the compensating donor ion. Similarly, the value of ε_3 is calculated for *n*-type semiconductors.

We compared calculations based on our model [Equation (12) at the absolute temperature $T_3 = T_{\text{j}}/3$] and the Shklovskii–Efros model [Equation (3) at zero absolute temperature] against the known experimental data for bulk covalent crystals (*n*- and *p*-Ge; *n*- and *p*-Si). Both theories describe the experimental values of the activation energy ε_3 almost equally well. Nevertheless, this comparison demonstrates the realism of our model, and the physical picture of hopping migration on which the model is based. The key role in this picture is played by the activation effect of overcoming the Coulomb blockade of charge carriers in the impurity band by the field of compensating impurities.

Appendix A. Probability of Distribution of Oppositely Charged Mutually Nearest Impurity Ions in Electrically Neutral Crystal

Let hydrogen-like acceptors and compensating donors are randomly distributed in the crystal matrix of a *p*-type semiconductor, which are considered as a gas of point particles. Each acceptor can be in one of two charge states (−1) and (0), while all donors are in the charge state (+1). In contrast to the fixed states of donor ions, the charge states (−1) of acceptors can migrate through the crystal accordingly to the thermally activated hole hopping from acceptors in the charge state (0) to acceptors in the charge state (−1). Let $N_{\text{d},+1}$ be the donor concentration, and $N_{\text{a},-1}(r)$ be the local concentration of acceptors in the charge state (−1) located in the Coulomb field of mutually nearest donors, where r is the distance from the donor to the acceptor ion. [The acceptor and donor ions are called mutually nearest neighbors if the acceptor ion is the acceptor in the charge state (−1) nearest to this donor ion, and the donor ion is the donor in the charge state (+1) nearest to this acceptor ion.]

The stationary probability that in a chosen volume V of a crystal matrix there are k point particles (acceptor ions or donor ions) does not depend on the shape of V and its location in the matrix and is given by the Poisson distribution (see ref. [5] and references therein, as well as ref. [65]):

$$\mathcal{P}(k,\mathcal{N}_{iV}) = \frac{(\mathcal{N}_{iV})^k \exp(-\mathcal{N}_{iV})}{k!} \qquad \text{(A1)}$$

where $\mathcal{N}_{iV}$ is the average number of particles of the type $i=1$ (acceptor ions) or $i=2$ (donor ions) in the volume V; $\mathcal{N}_{1V} = \int_V N_{\text{a},-1}(l)\,\mathrm{d}^3\mathbf{l}$ is the average number of acceptors in the charge state (−1) enclosed in the volume V, which are affected by the Coulomb field of donor ion of the mutually nearest donor–acceptor ion pair; $\mathcal{N}_{2V} = \int_V N_{\mathrm{d},+1}\,\mathrm{d}^3\mathbf{l} = VN_{\mathrm{d},+1}$ is the average number of donors in the charge state $(+1)$ enclosed in the volume V; for a spherical region the element of volume $\mathrm{d}^3\mathbf{l} = 4\pi l^2 \mathrm{d}l$.

Let us consider the probability space consisting of particle pairs $(|\mathrm{d},+1\rangle, |\mathrm{a},-1\rangle)$, where $|\mathrm{d},+1\rangle$ is a positively charged hydrogen-like donor and $|\mathrm{a},-1\rangle$ is a negatively charged hydrogen-like acceptor. Let event A_r consists of the pairs $(|\mathrm{d},+1\rangle, |\mathrm{a},-1\rangle)$ in which the ionized donor and the ionized acceptor are mutually nearest neighbors and the distance $|\mathbf{r}_{\mathrm{d},+1} - \mathbf{r}_{\mathrm{a},-1}|$ between these donor and acceptor ions lies within the range $[r, r + \mathrm{d}r)$ (see **Figure A1**).

Let us find the probability of detecting the mutually nearest pair "acceptor ion – donor ion", taking into account the Coulomb attraction between them and the distance from r to $r + \mathrm{d}r$ in the pair. Let us place the origin of coordinates at the donor ion and find the distribution of distances from the donor ion to the nearest acceptor ion. For this purpose, let us consider a ball of volume $V_{\mathrm{ball}} = 4\pi r^3/3$ with center at the donor ion and a ball of volume $4\pi r^3/3$ with center at the nearest acceptor ion (see Figure A1). In order for the donor ion placed at the coordinate origin to have the acceptor in the charge state (-1) as its nearest neighbor, and in turn this acceptor ion to have this donor ion as its nearest neighbor, it is necessary, that in region I there are no acceptors in the charge states (-1), in region II there are no donors in the charge states $(+1)$, in region III there are neither acceptor ions nor donor ions, and in region $S_{\mathrm{d},+1}$ there are at least one acceptor in the charge state (-1).

Let us calculate the probability $\mathcal{P}_{-1}(A_r)$ of the event A_r. For the donor ion, consider a random event $A_{r\mathrm{d}} \subset A_r$, consisting of all pairs from A_r that contain this donor ion. The random event $A_{r\mathrm{d}}$ is the intersection of four independent events (the area notations are shown in Figure A1)): there are no acceptors in the charge states (-1) in region I (event A_1), there are no donors in the charge states $(+1)$ in region II (event A_2), there are neither acceptor ions nor donor ions in region III (event A_3), and there are at least one acceptor in the charge state (-1) in region $S_{\mathrm{d},+1}$ (event A_4). Taking into account Equation (A1) we obtain

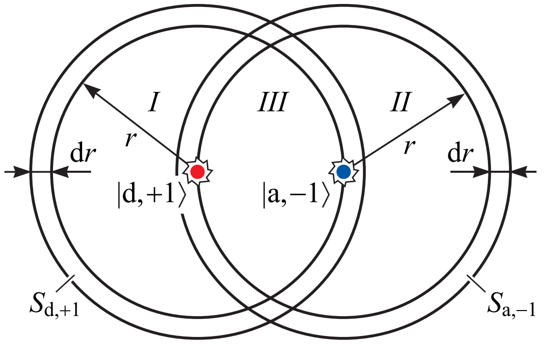

Figure A1. Balls of radius r with centers at the donor ion $|\mathrm{d},+1\rangle$ (at a point with radius vector $\mathbf{r}_{\mathrm{d},+1}$) and at the acceptor ion $|\mathrm{a},-1\rangle$ (at a point with radius vector $\mathbf{r}_{\mathrm{a},-1}$) forming a mutually nearest pair "donor ion – acceptor ion" with distance range $[r, r + \mathrm{d}r)$ between them. At the center of each ball, an infinitesimal neighborhood of the donor ion $|\mathrm{d},+1\rangle$ or the acceptor ion $|\mathrm{a},-1\rangle$ is excluded, $S_{\mathrm{d},+1}$ is the spherical layer with thickness dr of the ball with the center on the donor ion $|\mathrm{d},+1\rangle$, more precisely $S_{\mathrm{d},+1} = \{\mathbf{r} \in \mathbb{E}^3 | r < |\mathbf{r} - \mathbf{r}_{\mathrm{d},+1}| < r + \mathrm{d}r\}$, $S_{\mathrm{a},-1}$ is the spherical layer with thickness dr of the ball with the center on the acceptor ion $|\mathrm{a},-1\rangle$, more precisely $S_{\mathrm{a},-1} = \{\mathbf{r} \in \mathbb{E}^3 | r < |\mathbf{r} - \mathbf{r}_{\mathrm{a},-1}| < r + \mathrm{d}r\}$, where $\mathbb{E}^3$ is the three-dimensional Euclidean space. Here it is taken into account that in region I there are no acceptor ions, in region II there are no donor ions, and in region III there are neither acceptor ions nor donor ions.

$$\mathcal{P}_{-1}(A_{r\mathrm{d}}) = \mathcal{P}(A_1)\mathcal{P}(A_2)\mathcal{P}(A_3)\mathcal{P}(A_4),$$

$$\mathcal{P}(A_1) = \mathcal{P}(0, \mathcal{N}_{1V_I}) = \exp(-\mathcal{N}_{1V_I}), \quad \mathcal{N}_{1V_I} = \int_{V_I} N_{\mathrm{a},-1}(l)\mathrm{d}^3\mathbf{l};$$

$$\mathcal{P}(A_2) = \mathcal{P}(0, \mathcal{N}_{2V_{II}}) = \exp(-\mathcal{N}_{2V_{II}}), \quad \mathcal{N}_{2V_{II}} = V_{II}N_{\mathrm{d},+1};$$

$$\mathcal{P}(A_3) = \mathcal{P}(0, \mathcal{N}_{1V_{III}})\mathcal{P}(0, \mathcal{N}_{2V_{III}}) = \exp(-\mathcal{N}_{1V_{III}})\exp(-\mathcal{N}_{2V_{III}}),$$

$$\mathcal{N}_{1V_{III}} + \mathcal{N}_{2V_{III}} = \int_{V_{III}} [N_{\mathrm{a},-1}(l) + N_{\mathrm{d},+1}]\mathrm{d}^3\mathbf{l};$$

$$\mathcal{P}(A_4) = 1 - \mathcal{P}(0, \mathcal{N}_{1S_{\mathrm{d},+1}}) \approx 4\pi r^2 N_{\mathrm{a},-1}(r)\mathrm{d}r$$

Then the probability $\mathcal{P}_{-1}(r)$ to find the acceptor ion at distance r from the donor ion taking into account their Coulomb interaction is

$$\begin{aligned}\mathcal{P}_{-1}(r) = {} & 4\pi r^2 N_{\mathrm{a},-1}(r)\mathrm{d}r \times \exp(-\mathcal{N}_{1V_I}) \\ & \times \exp(-\mathcal{N}_{2V_{II}})\exp[-(\mathcal{N}_{1V_{III}} + \mathcal{N}_{2V_{III}})]\end{aligned} \tag{A2}$$

The probability $\mathcal{P}_{+1}(r)$ to find the donor ion at distance r from the acceptor ion taking into account their Coulomb interaction is similarly written:

$$\begin{aligned}\mathcal{P}_{+1}(r) = {} & 4\pi r^2 N_{\mathrm{d},+1}\mathrm{d}r \times \exp(-\mathcal{N}_{2V_{II}})\exp(-\mathcal{N}_{1V_I}) \\ & \times \exp[-(\mathcal{N}_{1V_{III}} + \mathcal{N}_{2V_{III}})]\end{aligned} \tag{A3}$$

Let us take into account that the entering of the acceptor ion and the donor ion to the origin of coordinates are incompatible events. Then from Equation (A2) and (A3) we obtain the probability of finding the mutually nearest acceptor in the charge state (-1) and donor in the charge state $(+1)$ in the form:

$$\begin{aligned}\mathcal{P}_{\mathrm{cor}}(r) &= \mathcal{P}_{-1}(r) + \mathcal{P}_{+1}(r) \\ &= \frac{1}{C_{\mathrm{cor}}} 4\pi r^2 [N_{\mathrm{a},-1}(r) + N_{\mathrm{d},+1}]\mathrm{d}r \exp(-\mathcal{N})\end{aligned} \tag{A4}$$

where C_{cor} is the normalization factor obtained from the normalization condition $\int_0^\infty \mathcal{P}_{\mathrm{cor}}(r) = 1$; $\mathcal{N} = \mathcal{N}_{1V_I} + \mathcal{N}_{2V_{II}} + \mathcal{N}_{1V_{III}} + \mathcal{N}_{2V_{III}}$ is the average number of acceptors in the charge state (-1) in the volume $V_I + V_{III}$ and the average number of donor ions in the charge state $(+1)$ in the volume $V_{II} + V_{III}$ taking into account their Coulomb interaction.

The average number of ions $\mathcal{N}$ in two balls (see Figure A1) included in Equation (A4) is calculated as follows:

$$
\begin{aligned}
\mathcal{N} &= \mathcal{N}_{1V_I} + \mathcal{N}_{2V_{II}} + \mathcal{N}_{1V_{III}} + \mathcal{N}_{2V_{III}} \\
&= \int_{V_I} N_{\mathrm{a},-1}(l)\mathrm{d}^3\mathbf{l} + V_{II} N_{\mathrm{d},+1} \\
&\quad + \int_{V_{III}} N_{\mathrm{a},-1}(l)\mathrm{d}^3\mathbf{l} + V_{III} N_{\mathrm{d},+1} \\
&= \int_{V_{\mathrm{ball}}} N_{\mathrm{a},-1}(l)\mathrm{d}^3\mathbf{l} + (V_{II} + V_{III}) N_{\mathrm{d},+1} \\
&= \int_{V_{\mathrm{ball}}} N_{\mathrm{a},-1}(l)\mathrm{d}^3\mathbf{l} + V_{\mathrm{ball}} N_{\mathrm{d},+1} \\
&= 4\pi \int_0^r l^2 N_{\mathrm{a},-1}(l)\mathrm{d}l + \frac{4\pi r^3}{3} N_{\mathrm{d},+1}
\end{aligned}
\tag{A5}
$$

where the last transformation is obtained by the transition from the Cartesian coordinate system to the spherical coordinate system.

Then from Equation (A5) we obtain the normalized to unity desired probability $\mathcal{P}_{\mathrm{cor}}(r)$ to find the mutually nearest acceptor in the charge state (-1) and the donor ion in the charge state $(+1)$ at distance $[r, r + \mathrm{d}r)$ in the following form:

$$
\begin{aligned}
\mathcal{P}_{\mathrm{cor}}(r) = P_{\mathrm{cor}}(r)\mathrm{d}r &= 4\pi r^2 [N_{\mathrm{a},-1}(r) + N_{\mathrm{d},+1}]\mathrm{d}r \\
&\times \exp\left(-4\pi \int_0^r l^2 N_{\mathrm{a},-1}(l)\mathrm{d}l - \frac{4\pi r^3}{3} N_{\mathrm{d},+1}\right)
\end{aligned}
\tag{A6}
$$

where $P_{\mathrm{cor}}(r)$ is the probability density function normalized to unity due to the relation [see Equation (A4)]:

$$
\begin{aligned}
C_{\mathrm{cor}} &= \int_0^\infty \mathcal{P}_{\mathrm{cor}}(r) = \int_0^\infty P_{\mathrm{cor}}(r)\mathrm{d}r \\
&= \int_0^\infty 4\pi r^2 [N_{\mathrm{a},-1}(r) + N_{\mathrm{d},+1}] \\
&\quad \times \exp\left(-4\pi \int_0^r l^2 [N_{\mathrm{a},-1}(l) + N_{\mathrm{d},+1}]\mathrm{d}l\right)\mathrm{d}r \\
&= -\int_0^\infty \frac{\mathrm{d}}{\mathrm{d}r} \exp\Bigg(-4\pi \int_0^r l^2 [N_{\mathrm{a},-1}(l) \\
&\quad + N_{\mathrm{d},+1}]\mathrm{d}l\Bigg)\mathrm{d}r = 1
\end{aligned}
\tag{A7}
$$

If $N_{\mathrm{a},-1}$ does not depend on r, i.e., there is no Coulomb correlation between the location of fixed donors [all in the charge state $(+1)$] and migrating charge states (-1) of acceptors (due to hole hopping between acceptors), then the resulting Equation (A6) transforms into the Equation from ref. [5] for mutually nearest randomly distributed ions in the charge states $(+1)$ and (-1).

Note that the average distance r_{cor} between the mutually nearest fixed donor in the charge state $(+1)$ and the mobile charge state (-1) of the acceptor, taking into account their purely Coulomb attraction, is less than the average distance r_{rnd} between the mutually nearest donor and acceptor ions randomly distributed over the crystal:

$$
r_{\mathrm{cor}} = \int_0^\infty r\mathcal{P}_{\mathrm{cor}}(r) < r_{\mathrm{rnd}} \approx 0.554[(N_{\mathrm{d},+1} + N_{\mathrm{a},-1})]^{-1/3}
\tag{A8}
$$

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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/x94zzmdcdx, ref. [64].

Keywords

Coulomb blockade of charge carriers, doping and compensating hydrogen-like impurities, hopping thermal activation energy, hops of holes or electrons via majority impurities, nearest neighbor hopping conductivity

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