Model of DC Tunneling Conductivity via Hydrogen-Like Impurities in Heavily Doped Compensated Semiconductors

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Herein, a theoretical model is proposed for the weakly temperature-dependent electrical conductivity of compensated crystalline semiconductors with hydrogen-like impurities near the insulator–metal concentration phase transition (Mott transition). The model uses a simple non-stoichiometric cubic "impurity lattice" formed by the doping and compensating impurities in crystal matrix. A shift of the *c*-band bottom (*v*-band top) into the bandgap due to overlap of the excited states of neighboring impurities is considered. The distribution of electron (and hole) density of states in the band of ground (unexcited) states of impurities is assumed to be Gaussian. Tunneling transitions of electrons between nearest donors in the charge states (0) and (+1), and tunneling transitions of holes between acceptors in the charge states (0) and (−1) are considered. It is shown that, at low temperatures, transitions of electrons (holes) near the Fermi level in the impurity band lead to electrical conductivity that weakly depends on temperature (in the form of a characteristic plateau). The results of calculating electrical resistivity in the zero-temperature limit for the plateau region agree with the known experimental data for moderately compensated *n*- and *p*-type Ge, Dia, Si, ZnSe, GaAs, InSb, and InP crystals.

1. Introduction

The existing ideas about the insulator–metal phase transition with increasing concentration of hydrogen-like impurities and the related mathematical description still do not allow to calculate the value of electrical conductivity quantitatively consistent with experimental data on heavily doped compensated *n*- and *p*-type semiconductors in the close proximity of the Mott transition (on its insulating side; see, e.g., refs. [1–4]). Thus, the theory of quantum corrections (to the Drude–Lorentz formula for DC electrical conductivity) contains uncertain parameters with the dimension of length.[5,6] Therefore, in the practice of calculations, dimensionless ratios of these parameters are used, which describe the temperature dependence of electrical conductivity only qualitatively. In addition, the theory of quantum corrections to the low-temperature features of transport phenomena does not always find experimental support on the metallic side near the Mott transition either. This fact (by the example of *n*-Ge:Sb) was noted in ref. [7], where it was shown that the electron impurity states near the Mott transition are quasi-localized.

In bulk (3D) semiconductors, the main mechanisms of electrotransfer on the insulating side of the transition are (see, e.g., refs. [8,9]) band conduction (BC) and hopping conduction (HC) regimes of DC electrical conductivity; see **Figure 1** for an *n*-type semiconductor with the concentrations of doping impurity (donors) N_d and compensation impurity (acceptors) N_a. At the temperature T_j, the electrical resistivity ρ_b with thermal activation energy ε_b in BC regime is equal to the electrical resistivity ρ_h in HC regime. The HC regime corresponds to the electrical resistivity ρ_h, which at sufficiently low temperatures is characterized by a decrease in thermal activation energy $\varepsilon_h \ll \varepsilon_b$ with decreasing temperature (see, e.g., ref. [10]).

Near the insulator–metal transition, the temperature dependence of electrical resistivity (see Figure 1) has the form[5–7]

$$\rho_t(T) = \rho_t(0) + \gamma T^{\delta} \tag{1}$$

where quantities $\rho_t(0)$ and γ depend on the concentrations of majority and minority impurities; γ and $|\delta| < 1$ are the parameters of the theory of quantum corrections to the electrical resistance; $\rho_t(0) = \rho_t$ for $T \to 0$ K; $|\gamma T^{\delta}| < \rho_t(0)$.

The stationary electrical conductivity of an *n*-type semiconductor in the zero absolute temperature limit (at $T \to 0$ K) is due either to *c*-band electrons, or donor band electrons, depending on which of them contains the Fermi level. The migration of electrons via quasi-stationary states of donors whose energy levels are close to the Fermi level[11,12] leads to fluctuations in time of their energy levels. Due to the hopping charge exchange of donors, their energy levels are quasi-stationary. If the donor energy levels do not fluctuate in time (i.e., they are stationary), then at $T \to 0$ K in the absence of illumination, the stationary migration of electrons via donors in such a sample disappears.[13] On the contrary, according to Mott,[14] *c*-band electrons with an energy greater than the mobility edge $E_m^{(c)}$ are responsible for stationary electrical conductivity at arbitrarily low temperatures even in the absence of illumination (see **Figure 2**). Further, Mott (see ref. [1] and references therein),

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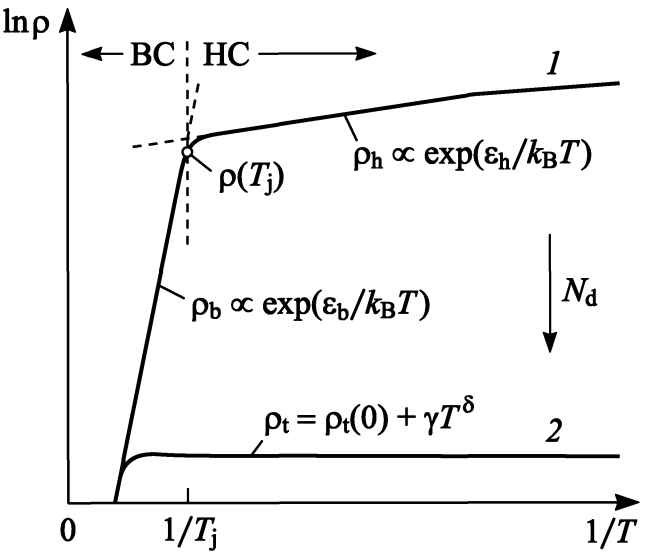

Figure 1. Scheme of the change in the form of the dependence of the logarithm of the DC electrical resistivity $\ln \rho$ of a moderately compensated n-type crystalline semiconductor on the inverse temperature $1/T$ with increasing the concentration N_d of a hydrogen-like doping impurity (donors) and a fixed compensation ratio $K = N_a/N_d$; ε_b $(= \varepsilon_1)$ is the thermal activation energy of electron transitions from ground states of donors to the c-band; ε_h $(= \varepsilon_3)$ is the activation energy of hopping migration of electrons via donors with the participation of phonons; k_BT is the thermal energy. Curve *1* corresponds to $N_d \ll N_M$, curve *2* to $N_d \approx N_M$, where N_M is the critical donor concentration corresponding to the insulator–metal transition (N_M increases with K); $\gamma = \text{const}$, parameter $|\delta| < 1$.

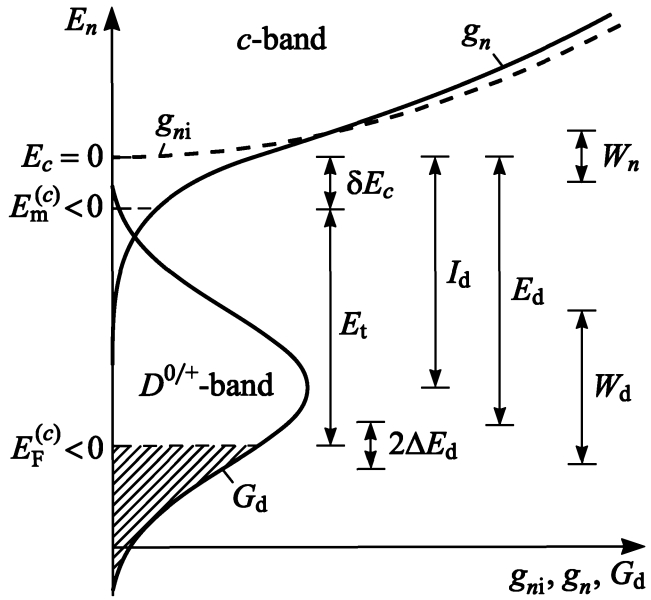

Figure 2. Energy band diagram of a compensated n-type semiconductor at low temperatures. The bottom of the c-band of the undoped crystal ($E_c = 0$) is set as the origin of the electron energy E_n; g_{ni} and g_n are the densities of single-electron states in the c-band for ideal (undoped) and doped semiconductors, respectively, G_d is the distribution density of donor energy levels E_d (relative to the ionization energy of a single donor I_d) in the donor band ($D^{0/+}$-band), $E_m^{(c)} = -\delta E_c < 0$ is the drift mobility edge for c-band electrons, $E_F^{(c)} < 0$ is the Fermi level, $E_t = E_m^{(c)} - E_F^{(c)} > 0$ is the energy level of electron tunneling transitions between donors (the energy required for the thermal transfer of an electron from the energy level of the donor to the mobility edge); $2\Delta E_d > 0$ is the interval of values of donor energy levels in the charge states (0) and (+1) between which electrons tunnel; W_n is the rms fluctuation of c-band electron energy; and $W_d \gg W_n$ is the effective width of the donor band.

based on the experimental data of Alexander and Holcomb,[15] concluded that in semiconductors near the insulator–metal transition, the impurity band is separated by the energy gap from the c-band (or the v-band). In other words, the Fermi level on the insulating side is located in the impurity band.

Since the early 1970s, the single-electron phenomenological gapless model of Anderson localization has been widely used to describe the insulator–metal phase transition in heavily doped compensated semiconductors,[16,17] in which the transition condition is the coincidence of the Fermi level with the mobility edge. Based on the experimentally established effect of the Coulomb gap collapse at the Fermi level as the insulator–metal phase transition is approached, one of the authors proposed[18] and developed[19] a gap model of the transition. This model describes the approach to the transition from the insulating side as the effect of the collapse of the Coulomb gap. However, in the case of close proximity to the insulator–metal transition and finite temperatures, the Coulomb gap does not manifest itself, since its width turns out to be less than the thermal energy k_BT. The absence of the Anderson metal–insulator transition in bulk samples of a number of metal alloys with increasing structural disorder and temperature in them, as well as the possibility of overcoming the Mott limit of the minimum electrical conductivity in them, was discussed in ref. [20].

Note that in inhomogeneously disordered strongly compensated samples ($1 - K \ll 1$), the formation of quasi-1D conducting channels, for example, of a dislocation nature, electrically connecting the electrodes (anode and cathode) to the sample is possible. These channels may comprise a small fraction of the volume of a semiconductor sample, but still shunt its conductivity (see, e.g., refs. [19,21]). Next, we consider only homogeneously disordered crystalline semiconductors with a moderate compensation ratio in which the formation of such channels can be neglected.[22]

So, theoretically and practically important question is to study the conditions under which in semiconductor systems with quasi-localized states of electrons on hydrogen-like donors (some of which are filled with electrons, and some are empty) in the limit $T \to 0$ K, the DC electrical conductivity via donors is not equal to zero.

We are interested in the possibility of a quantitative description of stationary electrical conductivity (similar to the Drude–Lorentz approach[23]) due to tunneling transitions of electrons (or holes) via doping impurities near the insulator–metal transition. According to (1), this corresponds to the quantity $\rho_t(T)$ at $T \to 0$ K, that is, $\rho_t(0)$. In accordance with Figure 2, for moderately compensated semiconductors, the migration of electrons (or holes) occurs in the region of $2\Delta E_d$ (or $2\Delta E_a$) width of the impurity band in the vicinity of the Fermi level $E_F^{(c)}$ (or $E_F^{(v)}$) via states of donors (or acceptors). In this case, the migration of electrons via the c-band states or of

holes via the v-band states does not occur. (On the contrary, in heavily doped weakly compensated semiconductors, stationary electrical conductivity is realized via the c- or v-band states.[24])

The purpose of this work is (i) to obtain a formula for calculating the DC tunneling electrical resistivity $\rho_t(0) = 1/\sigma_t(0)$ at low temperatures ($T < T_j$) corresponding to a plateau in the dependence of $\ln\rho$ versus $1/T$, for n- and p-type crystalline semiconductors heavily doped and moderately compensated by hydrogen-like impurities (see Figure 1, curve *2*); and (ii) to compare the calculations with the known experimental data for bulk semiconductor materials located near the Mott phase transition.

2. The Main Relationships of the Proposed Model

Let us consider a homogeneous bulk crystalline n-type semiconductor containing per unit volume $N_d = N_0 + N_{+1}$ hydrogen-like donors in the charge states (0) and (+1), between which tunneling transitions of electrons occur. (The charge states of impurities are given in units of elementary charge e.) We assume that at low temperatures in the vicinity of the Fermi level of the compensated semiconductor, the electron states in the donor band are quasi-localized. The compensation ratio of donors by hydrogen-like acceptors is $0 < K = N_a/N_d < 1$, where $N_a = N_{-1} = KN_d$ is the concentration of acceptors that are completely in the charge states (−1).

The quantity T_j (see Figure 1), determined from the virial theorem, has the form[8,25]

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

where k_B is the Boltzmann constant, e is the elementary charge, $\varepsilon_r\varepsilon_0$ is the static permittivity of intrinsic (undoped) semiconductor, ε_r is the relative permittivity (determined by v-band electrons on the background of the ionic cores of the crystal matrix), and ε_0 is the electric constant.

In the low-temperature region (for $T < T_j$), the concentration of c-band electrons is $n \ll K(1-K)N_d$. In this case, the electrical neutrality condition for a semiconductor doped with hydrogen-like donors and compensated with hydrogen-like acceptors has the form

$$N_{+1} = n + N_{-1} \approx KN_d = N_a \tag{3}$$

All acceptors in the studied temperature range do not directly participate in the tunneling migration of electrons via donors, but only block some migration sites. Following ref. [26], we assume that the doping impurity (donors) with the concentration $N_d = N_0 + N_{+1}$ and compensating impurity (acceptors) with the concentration $N_a = KN_d$ form a non-stoichiometric simple cubic "lattice" within the crystal matrix of the semiconductor with a translation period $d_{im} = 2R_{im} \approx 1.24[(1+K)N_d]^{-1/3}$, where $N_d + N_a = (1+K)N_d$ is the concentration of all impurities. The d_{im} value is equal to the diameter of a spherical region in a crystal per impurity atom or ion (both donor and acceptor). In the impurity lattice, each impurity has six nearest neighbors (the first coordination sphere). The fraction of electrically neutral donors in the impurity lattice is $(1-K)/(1+K)$, and the fraction of positively charged donors is $K/(1+K)$. For certainty, let us assume that the edge of the cubic unit cell of the impurity lattice is oriented parallel to the x-axis of the Cartesian coordinate system, that is, in the direction of the external electric field strength vector. We assume that the electron tunneling transitions occur only between the nearest donors in the charge states (0) and (+1), that is, an electron tunneling length is fixed and equal to d_{im}. Note that d_{im} value is close to the average distance between impurities determined in ref. [27] by the method of Voronoi–Dirichlet polyhedra. The crystal matrix is considered as a homogeneous isotropic medium with the static permittivity $\varepsilon_r\varepsilon_0$.

The mobility edge $E_m^{(c)}$ (see Figure 2), for the concentration of c-band electrons $n \ll K(1-K)N_d$, is[28,29]

$$E_m^{(c)} = -\delta E_c = E_{per}^{(c)} + E_{res} < 0 \tag{4}$$

where $E_{per}^{(c)} = -0.955W_n < 0$ is the percolation threshold (energy level) for the diffusion of c-band electrons; W_n is the root-mean-square (rms) fluctuation of the potential energy of c-band electron; $E_{res} = -I_d a_n/R_{im} < 0$ is the decrease of donor thermal-ionization energy due to the confinement of the maximum radius of "optical" electron orbit around donor-ion core due to the presence of other impurities in crystal; $I_d = e^2/8\pi\varepsilon_r\varepsilon_0 a_n$ is the ionization energy of a single (isolated) donor with the Bohr radius a_n of electron orbit in n-type crystal; $E_{res} \approx -1.612(e^2/8\pi\varepsilon_r\varepsilon_0)[(1+K)N_d]^{1/3}$. The quantity $\delta E_c > 0$ is due to the formation of a quasi-continuous band of delocalized electronic states from the excited states of donors below the bottom of the c-band.

The average over the crystal volume probabilities $\langle f_0\rangle$ and $\langle f_{+1}\rangle$ that the donor randomly selected in the crystal matrix is in the charge state (0) (is electrically neutral) or is in the charge state (+1) (is a singly positively charged ion) are (see, e.g., refs. [8,30])

$$\begin{aligned}\langle f_0\rangle &= \frac{N_0}{N_d} = \int_{-\infty}^{+\infty} G_d f_0\, d(E_d - I_d) = 1 - K\\ \langle f_{+1}\rangle &= \frac{N_{+1}}{N_d} = \int_{-\infty}^{+\infty} G_d f_{+1}\, d(E_d - I_d) = K\end{aligned} \tag{5}$$

where G_d is the Gaussian density of single-electron states in the donor band, $f_0 = \left\{1 + \beta_d^{-1}\exp\left[-\left(E_F^{(c)} + E_d\right)\Big/k_BT\right]\right\}^{-1}$ is the probability of an electron occupying the donor state; $f_{+1} = 1 - f_0$; $E_d = E_{+1} - E_0 > 0$ is the thermal-ionization energy of the electrically neutral donor (electron transition from the donor to the bottom of the c-band of an undoped crystal; Figure 2); $E_F^{(c)}$ is the Fermi level for electrons, T is the absolute temperature; (the bottom of the c-band ($E_c = 0$) of an undoped crystal is chosen as the origin of $E_F^{(c)} < 0$, I_d, E_d, and $E_m^{(c)} = -\delta E_c < 0$); β_d is the degeneracy factor of the energy level of a hydrogen-like donor in covalent and covalent-ionic crystalline semiconductors. For the case $T \to 0$ K, following refs. [31,32], it is assumed that $\beta_d = 2$, and the degeneracy factor of the hydrogen-like acceptor is $\beta_a = 4$ (cf. refs. [33–35]). The magnetic moment of the donor (acceptor) atom nucleus is not taken into account.[36]

Let us assume that the distribution density of donor energy levels in the bandgap (see Figure 2) has a normal (Gaussian) distribution[22,37]

$$G_d = \frac{1}{W_d\sqrt{2\pi}}\exp\left[-\frac{(E_d - I_d)^2}{2W_d^2}\right] \quad (6)$$

where W_d^2 is the dispersion of donor thermal-ionization energy levels E_d relative to I_d in the semiconductor bandgap; $\int_{-\infty}^{+\infty} G_d \mathrm{d}(E_d - I_d) = 1$ (see, e.g., ref. [38]).

The rms fluctuation of donor energy levels (the effective width of the donor band) W_d taking into account only the Coulomb interaction of a donor in the charge state (+1) with ions of the first coordination sphere of a notional impurity lattice with period d_{im} is equal to[39]

$$W_d = \left(\sum_{i=1}^{6} P_i U_i^2\right)^{1/2} = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 d_{im}}\left(\frac{12K}{1+K}\right)^{1/2} \quad (7)$$

where $P_i = 2K/(1+K) = 2K\Xi_d$ is the probability that any of the six sites of the impurity lattice in the first coordination sphere near the selected impurity ion occupied by an ionized donor or acceptor; $\Xi_d = 1/(1+K)$ is the fraction of donors at the impurity lattice sites; $|U_i| = e^2/4\pi\varepsilon_r\varepsilon_0 d_{im}$ is the modulus of the Coulomb energy of the interaction of the selected ion with the nearest ions located at the distance $d_{im} = 2R_{im} \approx 1.24[(1+K)N_d]^{-1/3}$ in a cubic lattice of doping and compensating impurities. When deriving formula (7), it was taken into account that the average energy of Coulomb interaction of the selected impurity ion with ions in the nearest six sites of the impurity lattice is equal to zero: $\sum_{i=1}^{6} P_i U_i = 0$.

The rms fluctuation of the potential energy of an average c-band electron W_n at $n \ll K(1-K)N_d$ is less than the rms fluctuation W_d of donor energy levels E_d owing to impurity ions (see, e.g., refs. [22,40]). This is a consequence of the "smoothing" of the potential relief W_d on scales of the order of magnitude of the average electron de Broglie wavelength (cf. refs. [25,35])

$$W_n \approx \left(\frac{n}{2N_{+1}}\right)^{1/2} W_d \quad (8)$$

where $n = N_{+1} - KN_d$ is the concentration of c-band electrons; $n + N_{+1} + KN_d \approx 2N_{+1}$ is the concentration of all point-charged particles in the crystal (i.e., c-band electrons and impurity ions); see Equation (3).

Note that expressions (7) and (8) give time-averaged rms fluctuations of the potential energy for point charges localized (W_d) and delocalized (W_n) in the crystal.

Further, we consider the dopant concentration, the degree of its compensation ratio K, and also the temperatures $T \ll T_j$, for which, according to (7) and (8), the rms fluctuations $W_d \gg k_B T$, $W_n \ll W_d$ and the concentration of c-band electrons $n(T) \ll K(1-K)N_d$, where $K(1-K)$ is the fraction of donor pairs that, according to the model,[41,42] limit the high-temperature region of hopping electron migration via them (see Figure 1, curve *2*). Under these conditions, we have $|E_{per}^{(c)}| \ll |E_{res}|$, and thus according to (4), the mobility edge is (see also Appendix A)

$$E_m^{(c)} = -\delta E_c \approx E_{res} = -I_d\frac{a_n}{R_{im}} < 0 \quad (9)$$

Note that the average over the crystal energy required for the transition of an electron from the energy level of a hydrogen-like donor to the c-band electron mobility edge (at $a_n < R_{im}$), according to ref. [35], is equal to $I_d + E_m^{(c)} \approx I_d + E_{res}$ (see Figure 2).

The fraction of donor pairs in the charge states (0) and (+1) whose energy levels E_d are separated from the Fermi level ($-E_F^{(c)} > 0$) by the value of $\pm\Delta E_d$, that is, $\left(-E_F^{(c)} - \Delta E_d - I_d\right) \le E_d - I_d \le \left(-E_F^{(c)} + \Delta E_d - I_d\right)$, is (see also ref. [39])

$$\Theta_t = \frac{1}{K(1-K)} \times \int_{-\infty}^{+\infty} G_d f_0(E_d + \Delta E_d) f_{+1}(E_d - \Delta E_d)\,\mathrm{d}(E_d - I_d) < 1 \quad (10)$$

where it is taken into account that the part $(1-K)$ of donors is occupied by electrons, and the part K is empty, G_d is the Gaussian density of distribution of energy levels E_d relative to the center of the donor band $I_d > 0$ (see Figure 2 and formula (6)); $f_0(E_d + \Delta E_d) = \left\{1 + \beta_d^{-1}\exp\left[-\left(E_F^{(c)} + E_d + \Delta E_d\right)\Big/ k_B T\right]\right\}^{-1}$ is the probability of an electron occupying a donor with an energy level $E_d + \Delta E_d$; $f_{+1}(E_d - \Delta E_d) = \left\{1 + \beta_d\exp\left[\left(E_F^{(c)} + E_d - \Delta E_d\right)\Big/ k_B T\right]\right\}^{-1}$; for $\Delta E_d \to 0$, one have $f_{+1} = 1 - f_0$ for all values of E_d.

Note that for $k_B T \ll W_d$ (formally, in the limit $T \to 0$ K), we can use the approximations: $f_0(E_d + \Delta E_d) \to H\left(E_F^{(c)} + \Delta E_d + E_d\right)$ and $f_{+1}(E_d - \Delta E_d) \to H\left(-E_F^{(c)} + \Delta E_d - E_d\right)$, where $H(\cdot)$ is the Heaviside step function. Then, from (10), we get

$$\Theta_t = \frac{1}{2K(1-K)} \times \left[\mathrm{erf}\left(\frac{E_F^{(c)} + \Delta E_d + I_d}{\sqrt{2}W_d}\right) - \mathrm{erf}\left(\frac{E_F^{(c)} - \Delta E_d + I_d}{\sqrt{2}W_d}\right)\right] < 1 \quad (11)$$

where $\mathrm{erf}(\cdot)$ is the error function; $E_F^{(c)}$ does not depend on temperature (see Equation (17)).

Further, following ref. [11], we assume that the contribution to the tunneling DC electrical conductivity $\sigma_t(0) = 1/\rho_t(0)$ according to (10) and (11) is made only by a set of quasi-resonant pairs of donors located at a distance d_{im} (donor energy levels E_d are in the range $\pm\Delta E_d$ in the vicinity of the Fermi level $-E_F^{(c)} > 0$). One of the donors is occupied by an electron (is in the charge state (0)), and the other, the donor nearest to it in the impurity lattice, is empty (is in the charge state (+1)).

Let us define the effective concentration of electrons that can migrate by means of tunneling between donors in the charge states (0) and (+1), as follows[30]

$$N_t = \frac{N_0 N_{+1}}{N_d} = K(1-K)N_d \quad (12)$$

where the index "t" denotes the tunneling mechanism of electron transfer.

Note that the quantity $K(1-K)N_d = N_t(K)$ determines the screening length (in the Debye–Hückel approximation) of the

stationary electric field[39,41] in an n-type semiconductor doped with hydrogen-like donors at the concentration of c-band electrons $n \ll K(1-K)N_d$. The concentration of tunneling electrons $N_t(K)$ reaches its maximum of $0.25N_d$ at the compensation of donors by acceptors $K = 0.5$. If, by analogy with the analysis of optical spectra, we take the full width of the function $N_t(K)$ at its half maximum, that is, at $K(1-K)N_d = 0.125N_d$, then we obtain the range of compensation ratios $0.15 < K < 0.85$. In general, this range of K values corresponds to moderate compensation of donors by acceptors.

Taking into account formula (12), the DC electrical conductivity σ_{tx} along the x axis in the case of tunneling transfer of electrons via donors is written as

$$\sigma_{tx} = eN_tM_t = eK(1-K)N_dM_t \tag{13}$$

where M_t is the drift tunneling electron mobility in the donor band.

Let us assume that in the vicinity of the Fermi level located in the donor band an electron tunnels between two neighboring donors in the charge states (0) and (+1) in the impurity lattice on average in time τ_t. In this case, the quasi-stationary[11,43] energy levels E_d of these donors are in the range $\left(-E_F^{(c)} - \Delta E_d\right) \le E_d \le \left(-E_F^{(c)} + \Delta E_d\right)$ in the vicinity of the Fermi level $-E_F^{(c)} > 0$. The average drift tunneling mobility of electrons M_t via donors by analogy with the Drude–Lorentz formula for c-band electrons and v-band holes (see, e.g., refs. [35,44,45]), we define as follows

$$M_t = \frac{e\tau_t}{m_{n\sigma}}\Xi_d\Theta_t \tag{14}$$

where τ_t is the average over the crystal duration of the electron tunneling transition between two donors in the charge states (0) and (+1) located at a distance d_{im} from each other, for $\left(-E_F^{(c)} - \Delta E_d - I_d\right) \le E_d - I_d \le \left(-E_F^{(c)} + \Delta E_d - I_d\right)$; $m_{n\sigma}$ is the conductivity effective mass of c-band electron; the quantity Θ_t according to (11) gives the probability that the donor energy levels E_d, between which the electron tunnels, are in the range $-E_F^{(c)} \pm \Delta E_d$; the quantity $\Xi_d = 1/(1+K)$ is the fraction of donors at the sites of a notional non-stoichiometric simple cubic lattice of donors and acceptors in the crystal matrix. (Note that in formula (14), the role of the quasi-momentum relaxation time of average c-band electron in the Drude–Lorentz scheme is played by the quantity $\tau_t\Xi_d\Theta_t$ for an electron tunneling between donors in the impurity lattice.)

We assume that the difference between the energy levels of two donors $2\Delta E_d$ in the charge states (0) and (+1), located at a distance d_{im} and responsible for the tunneling electrical conductivity (see Figure 2), is equal to the quantum splitting of the energy levels $\delta E_{0,+1}$ of these donors, that is, $2\Delta E_d = \delta E_{0,+1}$; see formula (16) later.

The tunneling transition time of an electron between an electrically neutral donor and a positively charged donor (located at a distance d_{im}) is determined as follows[46]

$$\tau_t = \frac{\pi\hbar}{\delta E_{0,+1}} \tag{15}$$

where $\hbar = h/2\pi$ is the reduced Planck constant, $\delta E_{0,+1} = 2\Delta E_d$ is the splitting of the energy levels of two donors in the charge states (0) and (+1). The quantity $\delta E_{0,+1}$ (by analogy with the splitting of electron energy levels in the molecular hydrogen ion H_2^+) is determined as follows[47,48]

$$\delta E_{0,+1} = 4E_t\frac{\rho_n(1+\rho_n)\exp(-\rho_n) - [1-(1+\rho_n)\exp(-2\rho_n)]S_n}{\rho_n(1-S_n^2)}$$

$$S_n = [1+\rho_n+(\rho_n^2/3)]\exp(-\rho_n); \quad \rho_n = d_{im}/a_n \tag{16}$$

where $E_t = E_m^{(c)} - E_F^{(c)} > 0$ is the energy level of electron tunneling transitions between donors in the charge states (0) and (+1); $d_{im} = 2R_{im} \approx 1.24[(1+K)N_d]^{-1/3}$ is the distance between the nearest neighbors in the "impurity lattice", assumed to be equal to the length of the electron tunneling transition between donors; $a_n = e^2/8\pi\varepsilon_r\varepsilon_0 I_d$ is the Bohr radius of electron orbit on a single donor in the charge state (0).

Note that the position of the Fermi level $E_F^{(c)} < 0$ in the bandgap should be below the mobility edge $E_m^{(c)} < 0$ of c-band electrons to exclude the possibility of their free electromigration in the crystal (from cathode to anode). This condition corresponds to semiconductors with such values of dopant concentration N_d and compensation ratio K, for which the following inequality is fulfilled: $E_t = E_m^{(c)} - E_F^{(c)} > 0$.

The quantity $E_F^{(c)} < 0$ according to the equation of electrical neutrality (3) taking into account (5) depends on temperature. At low temperatures ($k_BT \ll W_d$, formally for $T \to 0$ K), we have the relation (see, e.g., refs. [30,39])

$$2K = 1 - \mathrm{erf}\left(\frac{E_F^{(c)} + I_d}{\sqrt{2}W_d}\right) \tag{17}$$

where the Fermi level $E_F^{(c)}$ does not depend on temperature.

Next, we take into account all possible orientations of a randomly oriented non-stoichiometric cubic lattice of donors and acceptors, which determines the paths of tunneling migration of electrons in a macroscopic (3D) semiconductor sample, with respect to the direction of the external electric field strength along the x axis of the Cartesian coordinate system.[39,49] As a result, the DC tunneling electrical conductivity σ_t via donors is calculated by formula (13) taking into account (11)–(17) in the limit of zero temperature ($T \to 0$ K) as follows

$$\sigma_t(0) = \frac{\sigma_{tx}}{2} = \frac{e^2K(1-K)N_d\tau_t}{2m_{n\sigma}}\Xi_d\Theta_t = \frac{1}{\rho_t(0)} \tag{18}$$

where τ_t is determined by formula (15), Θ_t is given by (11), and $\Xi_d = 1/(1+K)$.

Formula (18) shows that, near the insulator–metal transition, the tunneling electrical resistivity $\rho_t(0) = 1/\sigma_t(0)$ decreases with the concentration of the majority (doping) impurity N_d at $K = \text{const}$. At a fixed value of the doping impurity concentration $N_d = \text{const}$, the value of $\rho_t(0)$ increases with the compensation ratio K. The quantity $\Xi_d\Theta_t = \Theta_t/(1+K)$ shows the fraction of doping impurities in the non-stoichiometric simple cubic

Table 1. Parameters of semiconductor crystals and hydrogen-like doping impurities at low temperatures.[51–55]

Material[a)]	ε_r	ν	$m^{(1)}_{n(p)}/m_0$	$m_{n(p)\sigma}/m_0$	$I_{d(a)}$ [meV]	$a_{n(p)}$ [nm]	$\beta_{d(a)}$
n-Ge:As	15.4	4	0.22	0.12	14.17	3.30	2
p-Ge:Ga	15.4	1	0.35	0.26	11.32	4.13	4
p-Dia:B	5.7	1	0.992	0.524	370	0.34	4
n-Si:P	11.47	6	0.322	0.26	45.58	1.38	2
n-ZnSe:Al	8.6	1	0.137	0.137	26.3	3.18	2
n-GaAs:Ge	12.4	1	0.0662	0.0662	5.98	9.71	2
n-GaAs:Sn	12.4	1	0.0662	0.0662	6	9.68	2
n-InSb	16.8	1	0.0136	0.0136	0.7	61.2	2
n-InP	12.22	1	0.08	0.08	7.3	8.07	2

[a)]Here ε_r is the relative permittivity, ν is the number of valleys in the *c*-band (*v*-band), $m^{(1)}_{n(p)}$ is the density of states effective mass of *c*-band electrons (*v*-band holes) in one valley, $m_{n(p)\sigma}$ is the conductivity effective mass of electrons and holes (in units of the electron mass in vacuum m_0), $I_{d(a)}$ is the thermal-ionization energy of a single donor (acceptor), $a_{n(p)}$ is the Bohr radius, and $\beta_{d(a)}$ is the degeneracy factor of the energy level of a hydrogen-like donor (acceptor).

impurity lattice that directly participates in the tunneling migration of electrons via donors.

The donor concentration $N_d = N_M$ at which the Mott phase transition occurs for an *n*-type semiconductor from the insulating state to the metallic state at the compensation ratio K is determined by the formula[50]

$$N_M^{1/3} a_n = \frac{0.542}{[(1-K)(\varepsilon_r+2)]^{1/3}} \tag{19}$$

where $a_n = e^2/8\pi\varepsilon_r\varepsilon_0 I_d$ is the electron Bohr radius of a single donor located in a pure crystal matrix with the relative permittivity ε_r.

Note that for the case of tunneling electromigration of holes via hydrogen-like acceptors in compensated *p*-type semiconductors near the hole Mott phase transition in all formulas, the index "d" (donors in the charge states (0) and (+1)) should be replaced by the index "a" (acceptors in the charge states (0) and (−1)), the index "*c*" should be replaced by the index "*v*", and the concentration of *c*-band electrons n and the index "*n*" should be replaced by the concentration of *v*-band holes p and the index "*p*".

3. Calculation Results and their Comparison with Experimental Data

To calculate the tunneling electrical resistivity $\rho_t(0)$ via impurities at temperatures T, corresponding to weak temperature dependence (i.e., plateau): $\rho_t(T) = \rho_t(0) + \gamma T^\delta$, where $\gamma =$ const and $|\delta| < 1$ (see Figure 1), the parameters of bulk semiconductor materials indicated in **Table 1** were used (see also refs. [51–55]). **Table 2** shows the results of calculating $\rho_t(0)$ using formula (18) and experimental data[56–71] obtained in the regime of linear hopping of electrons and holes (Ohm's law) near the insulator–metal transition. Semiconductors with moderate compensation ratios K and the concentration of the doping (majority) hydrogen-like impurity $N_{d(a)}$ are considered. Calculation of the

Table 2. Experimental data on electrical resistivity $\rho_t(T)$ of crystalline semiconductors at temperatures T, corresponding to a weak temperature dependence (plateau) in the curve $\ln\rho(1/T)$: $\rho_t(T) = \rho_t(0) + \gamma T^\delta$, where $\gamma =$ const, $|\delta| < 1$, and calculation results for $\rho_t(0)$, Mott concentration N_M, tunneling drift mobility M_t of electrons (holes), and splitting of impurity energy levels $\delta E_{0,+1}$ ($\delta E_{0,-1}$).

Material	Sample	T [K]	$N_{d(a)}$ [cm^{-3}]	K	$\rho_t(T)$ [Ω cm] Experiment	$\rho_t(0)$ [Ω cm] Calculation	N_M [cm^{-3}]	M_t [cm^2 V^{-1}s^{-1}]	$\delta E_{0,+1}$ ($\delta E_{0,-1}$) [meV]
n-Ge:As	–	<3.5	3.24×10^{18}	0.65	0.012[56]	0.016	7.18×10^{17}	0.105	8.180
	2	<2	6.28×10^{17}	0.28	0.043[57,58]	0.028	3.54×10^{17}	0.348	0.097
p-Ge:Ga	10-OR	<3	1.51×10^{17}	0.4	0.182[59]	0.178	2.16×10^{17}	0.193	0.389
	11-OR	<10	4.97×10^{17}	0.4	0.037[59]	0.080	2.16×10^{17}	0.130	0.436
	–	<16	2.5×10^{17}	0.4	0.095[60]	0.127	2.16×10^{17}	0.164	0.531
	–	<11	2.51×10^{17}	0.3	0.106[61]	0.115	1.86×10^{17}	0.206	0.224
	10	<6	1.98×10^{17}	0.35	0.191[62]	0.141	2×10^{17}	0.197	0.351
p-Dia:B	#6	<300	3×10^{20}	≈0.17	0.007[63,64]	0.005	6.26×10^{20}	0.006	3.430
	D	<310	1.2×10^{20}	≈0.17	0.008[65]	0.010	6.26×10^{20}	0.008	2.170
n-Si:P	A-63	<1.4	6.94×10^{18}	0.35	0.021[66]	0.018	6.96×10^{18}	0.045	1.460
	B-310	<1.4	1.07×10^{19}	0.5	0.031[66]	0.016	9.05×10^{18}	0.029	5.060
n-ZnSe:Al	675	<29	2.1×10^{17}	0.57	0.765[67]	0.174	1.08×10^{18}	0.139	1.040
	722	<35	5.8×10^{17}	0.26	0.144[67]	0.060	6.29×10^{17}	0.186	0.264
n-GaAs:Ge	0930	<7.5	5×10^{16}	0.6	0.250[68]	0.161	3.02×10^{16}	0.645	1.620
	0530	<3	5×10^{17}	0.63	0.014[68]	0.037	3.26×10^{16}	0.289	4.370
n-GaAs:Sn	6	<4.2	2.1×10^{16}	0.61	0.495[69]	0.293	3.13×10^{16}	0.852	0.902
n-InSb	2-14	<1.4	6.6×10^{14}	0.67	1.016[70]	0.513	1.12×10^{14}	16.7	0.545
n-InP	1002	<7.7	8.84×10^{16}	0.54	0.303[71]	0.121	4.63×10^{16}	0.470	1.320

N_M concentration using formula (19) shows that considered samples are near the electron (or hole) Mott phase transition.

For heavily doped crystalline semiconductors, moderate discrepancies between calculations using formula (18) and the experiment can be due to the dependence of the effective masses $m^{(1)}_{n(p)}$ and $m_{n(p)\sigma}$ of electrons (or holes) on the concentration of doping hydrogen-like impurities N_d (N_a) and their compensation ratios $K = N_a/N_d$ for n-type ($= N_d/N_a$ for p-type).[24] Also, the discrepancy between the calculations and the experiment for the neutron-transmutation-doped n-Ge:As sample from ref. [56] can be explained by incomplete annealing of radiation defects (see, e.g., refs. [72,73]). Finally, for the n-GaAs:Ge sample, the discrepancy between the experimental value of the electrical conductivity and the calculation using formula (18) can be associated with a value of the electron tunneling transition length larger than $d_{im} \approx 1.24[(1+K)N_d]^{-1/3}$. Here, we can point out to an analogy with the migration of c-band electrons under conditions of their dominant scattering on impurity ions in n-type gallium arsenide crystals. Due to the small value of the effective mass, a typical c-band electron can interact with several impurity ions simultaneously. This fact was noted in ref. [74] when calculating the low-temperature drift mobility of c-band electrons in n-GaAs.

The temperature values given in Table 2 correspond to the high-temperature plateau boundary in the dependence of $\ln\rho$ versus $1/T$; see Figure 1. From the known experimental data, such n- and p-type samples were selected in which the doping impurity concentrations met the conditions for the realization of moderate compensation (see Figure 2)

$$-1 < (|E_F^{(c)}| - I_d)/W_d < 1; \quad -1 < (|E_F^{(v)}| - I_a)/W_a < 1 \qquad (20)$$

Thus, for all n- and p-type semiconductors presented in Table 1, the calculation taking into account the equation of electrical neutrality (17) gives a range of compensation ratios $0.16 < K < 0.84$ that satisfies conditions (20). This agrees with the range $0.15 < K < 0.85$ given after formula (12). For such compensation ratios, the correlation between the location of hydrogen-like impurities and their energy levels can be generally neglected (see, e.g., refs. [10,75]). For details of our calculations see ref. [76].

4. Conclusion

A model of DC electrical conductivity of heavily doped moderately compensated semiconductors in the limit of zero absolute temperature near the insulator–metal phase transition is proposed. It is assumed that the doping and compensating impurities form a non-stoichiometric simple cubic impurity "lattice" in the crystal matrix. The translation period of this impurity lattice was assumed to be equal to the diameter of spherical region per impurity atom (ion). The tunneling of electrons (or holes) only between neighboring sites of the impurity lattice occupied by the majority impurity in semiconductors with a conditionally moderate compensation ratio, that is, for $0.15 < K < 0.85$, was considered. Also, we assumed a Gaussian distribution for fluctuation of the donor-ionization energy to c-band (acceptor to v-band). The widths of the donor and acceptor bands $W_{d(a)}$ were determined by Coulomb interaction of an impurity ion only with ions in the first coordination sphere of impurity lattice. For c-band electrons (or v-band holes) at low temperatures, the average de Broglie wavelength of an electron (or hole) is much larger than the period of the impurity lattice. Therefore, the rms fluctuation of the potential energy of c-band electrons (and v-band holes) $W_{n(p)}$ is much smaller than the impurity band width $W_{d(a)}$. We considered a shift $\delta E_{c(v)} > 0$ of the c-band bottom (the v-band top) into the semiconductor bandgap due to the formation of a quasi-continuous band of allowed energy values from the excited states of donors (or acceptors). In this case, the maximum possible radius of electron localization on the donor (or hole on the acceptor) is limited to half the translation period of the impurity lattice, and the thermal-ionization energy of the donor (or acceptor) is reduced.

In moderately compensated semiconductors, the Fermi level is in the impurity band and is separated by an energy gap from the mobility edge for c-band electrons (and v-band holes), so in the limit of zero temperature, they do not contribute to the DC electrical conductivity. Near the Mott transition at low temperatures, the electrical conductivity is determined by the tunneling migration of electrons (or holes) between the quasi-stationary states of neighboring donors (or acceptors) in the vicinity of the Fermi level.

The values of tunneling resistivity $\rho_t(0)$ of compensated semiconductors at low temperatures were calculated using the derived formulas and compared with known experimental data. The concentrations of the majority and compensating hydrogen-like impurities of the samples correspond to their location in the vicinity of the electron (or hole) Mott transition. Comparison of the results of calculations of tunneling electrical resistivity with experimental data for n- and p-type germanium, p-type diamond, as well as for crystals of n-type silicon, zinc selenide, gallium arsenide, indium antimonide, and indium phosphide, generally shows their quantitative agreement. In the region of low temperatures, these experimental data were previously beyond quantitative description.

Appendix A

The shift of the bottom of the c-band δE_c (the top of the v-band δE_v) into the depth of the bandgap according to (9) can be determined in an alternative way, taking into account the electrostatic screening of the Coulomb potential of impurity ions in the Debye–Hückel approximation. Thus, according to refs. [39,49] and references therein, the value $\delta E_c > 0$ for an n-type semiconductor is determined by the screening of a donor in the charge state $(+1)$ by a cloud of locally uncompensated negative-charged acceptors (taking into account the tunneling migration of electrons between donors) and is given by the formula

$$E_m^{(c)} = -\delta E_c \approx E_{cor} = -I_d \frac{3a_n}{2(\Lambda_{sc} + R_{im})} < 0 \qquad (A1)$$

where $\Lambda_{sc}^2 = \left(\sqrt{2\pi}\varepsilon_r\varepsilon_0 W_d/e^2 N_d\right)\exp\left\{\left[\left(E_F^{(c)} + I_d\right)\Big/\sqrt{2}W_d\right]^2\right\}$ is the square of the screening radius of the donor ion at low temperatures ($k_B T \ll W_d$), when c-band electron concentration $n \ll K(1-K)N_d$; the effective width of the donor band W_d

is determined by formula (7); the value of $\left(E_F^{(c)} + I_d\right)/W_d$ is found from the electroneutrality Equation (17); $R_{im} = [3/4\pi(1 + K)N_d]^{1/3}$ is the radius of the spherical Wigner–Seitz cell for impurities with concentration of $(1 + K)N_d$ in the crystal matrix. Similarly to (A1), the formula for the shift of the top of the v-band $\delta E_v > 0$ into the bandgap of a p-type semiconductor can be written.

The results of $\rho_t(0)$ value calculation by (18) taking into account the shift $\delta E_{c(v)}$ by (A1) give practically the same values (up to fractions of a percent) as the calculations of $\rho_t(0)$ taking into account the shift $\delta E_{c(v)}$ by (9).

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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/fn3cxdbnm8.

Keywords

DC tunneling conductivity, heavily doped compensated semiconductors, hydrogen-like donors and acceptors, low temperatures, Mott insulator–metal phase transition

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