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Maximum hopping direct current conductivity via hydrogen-like impurities in semiconductors

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A quasi-classical model for calculating DC (direct current) electrical conductivity in crystalline semiconductors with hydrogen-like impurities is developed at the transition from band conduction to impurity hopping conduction with decreasing temperature. This transition from the minimum band conductivity to the maximum hopping conductivity via impurities has the form of a characteristic „kink" in the temperature dependence of the electrical resistivity. The idea of the calculation is to preliminarily determine the transition temperature T_j using the standard approach within the framework of the two-band model. The shift of the top of the v-band (the bottom of the c-band) into the depth of the band gap due to the formation of a quasi-continuous band of allowed energy values from the excited states of acceptors (donors) is taken into account. This leads to a decrease in the value of a thermal ionization energy of the majority shallow impurities due to a decrease in the maximum localization radius of a hole on an acceptor (an electron on a donor) with increasing impurity concentration. The values of the observed maximum hopping conductivity and drift hopping mobility corresponding to the temperature T_j are calculated. The numerical calculation within the framework of the proposed model is consistent with the known experimental data on the electrical conductivity and Hall coefficient of moderately compensated p-Ge crystals doped by neutron transmutation and non-intentionally compensated metallurgically doped n-Ge, as well as n- and p-Si crystals on the insulator side of the Mott insulator–metal concentration phase transition.

Keywords: bulk crystals of germanium and silicon, hydrogen-like acceptors and donors, holes and electrons, band and hopping motion of charge carriers.

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1. Introduction

When using lightly doped and moderately compensated semiconductor materials as working substances of various low-temperature conversion devices, it is important to know the characteristic temperature T_j, below which the dependence of their DC resistivity ρ sharply „hits a plateau" (see Fig. 1,a). This feature of $\rho(T)$ is taken into account in the development of cryothermal resistances and photodetectors (from infrared to terahertz wavelengths) based on crystalline semiconductors (see, for example, [1–3]).

The dependences $\ln\rho$ vs. $1/T$ for lightly doped and moderately compensated semiconductors, for certainty of the p-type, as well as their energy band diagram are illustrated in Fig. 1.

In homogeneous three-dimensional semiconductors, on the insulator side of the insulator–metal concentration phase transition there are (see, for example, [4–7]) two regimes (mechanisms) of DC extrinsic conductivity $\sigma = 1/\rho$ (see Fig. 1): *band-like conduction* (or BC) and *hopping conduction* (or HC). Let us introduce, following the data of papers [8,9], the temperature T_j at which the electrical conductivity σ_{bj} with thermal activation energy ε_b in the BC regime is equal to the electrical conductivity σ_{hj} with thermal activation energy $\varepsilon_h \ll \varepsilon_b$ in the HC regime.

The BC regime is realized at temperatures ($T > T_j$), when the average v-band hole most of the time moves „freely" between scattering events on impurity ions and phonons in the crystal matrix. In the HC regime (at $T < T_j$) the hole most of the time is localized on the acceptor. Hopping electrical conductivity σ_h is carried out by holes tunneling via the nearest acceptors in the charge states (0) and (-1) assisted by phonons, so that σ_h decreases with temperature decreasing (NNH regime). At the lowest temperatures, electrical conductivity is carried out by hole hops via acceptors in the charge states (0) and (-1), which are no longer the nearest ones, but with an optimized ratio of the length and activation energy of the hop (the so-called regime with a variable hop length, or VRH regime). In the VRH regime, the thermal activation energy of hole hops via acceptors $\varepsilon_h \propto T^{1/2}$ in the presence of the Coulomb gap at the Fermi level [10] and $\varepsilon_h \propto T^{3/4}$ in its absence [11]. Identification of the experimentally observed behavior $\varepsilon_h(T)$ for the VRH regime is a separate task (see, for example, [12]).

Previously, the dependence of the concentration of delocalized v-band holes on the concentration of impurities at the temperature T_j was calculated for p-Ge : Ga [9] and p-Dia : B [13] crystals. Here we are mainly interested

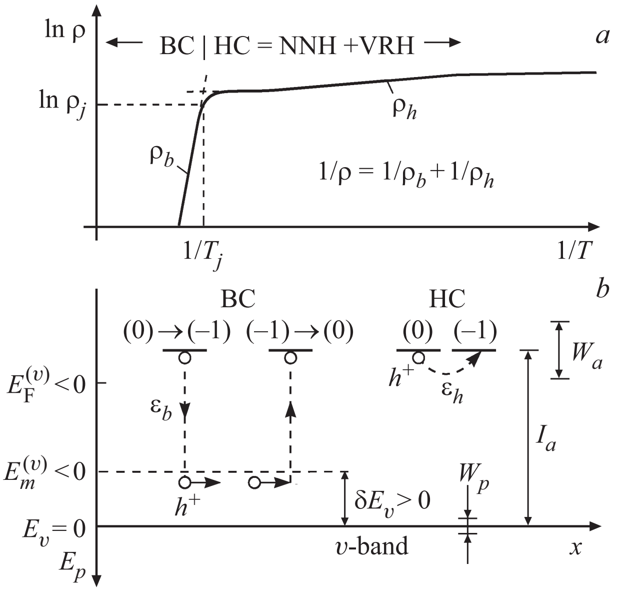

Figure 1. a — dependence of the natural logarithm of DC resistivity $\ln\rho$ of a lightly doped crystalline semiconductor on the reciprocal temperature $1/T$; at $T = T_j$, the band $\sigma_{bj} = 1/\rho_{bj}$ and hopping $\sigma_{hj} = 1/\rho_{hj}$ conductivities are equal. b — scheme of hole (h^+) transitions along the coordinate axis x at their band (BC; activation energy ε_b) and hopping (HC) migration in p-type semiconductor; NNH stands for the phonon-assisted tunnel hops of holes via the nearest acceptors in the charge states (0) and (-1) with activation energy $\varepsilon_h \ll \varepsilon_b$; VRH denotes the hole hops optimized by activation energy and length; E_p is the hole energy, $E_m^{(v)} < 0$ is the mobility edge for v-band holes, $E_v = 0$ is the top of the v-band of an undoped semiconductor, I_a is the ionization energy of a single acceptor, W_a is the width of the acceptor band, W_p is the rms fluctuation of the potential energy of v-band holes.

in the DC resistivity $\rho = \rho_j$ and the Hall coefficient R_{H} at $T \approx T_j$.

The quantitative calculation of the hopping electrical conductivity via hydrogen-like impurities is still an urgent problem (see, for example, [14,15]). However, if we are talking about the maximum hopping conductivity observed near the break point („kink") of the $\ln\rho(1/T)$ temperature dependence, then within the framework of the standard two-band model it is possible to estimate the value of the maximum hopping conductivity, knowing the value of the minimum band conductivity. The main obstacle on this path — the calculation of the temperature T_j vs. the dopant concentration and its compensation ratio — was overcome earlier [8,9].

The purpose of the paper is to obtain a relation for calculating the DC conductivity and the Hall coefficient in covalent semiconductors of p- and n-type at a transition temperature from v-band holes (or c-band electrons) dominance in conductivity to the dominance of hopping conductivity via hydrogen-like impurities, as well as comparison of calculation results with experimental data for germanium and silicon crystals.

2. General relationships

As an example, let us consider a lightly doped p-type crystalline semiconductor on the insulator side far from the Mott insulator–metal concentration phase transition [16,17]. Let the concentration of hydrogen-like acceptors is equal to $N_a = N_0 + N_{-1}$ in the charge states (0) and (-1), and the concentration of donors being completely in the charge states $(+1)$ is equal to $N_d = N_{+1} < N_a$; the charge states of impurities are expressed in units of elementary charge. The charge states of the acceptors migrate over the crystal, i.e., they are mobile, while the charge states of the donors are strictly localized. Further, crystals of p- and n-types are considered, in which the concentration of doping (majority) impurities is up to $0.25N_{\mathrm{M}}$ for $K < 0.1$ and up to $0.45N_{\mathrm{M}}$ for $0.25 < K < 0.5$, where N_{M} is the critical concentration corresponding to the Mott transition.

The electrical neutrality equation for p-type crystalline semiconductor relates, among other things, at a temperature $T \approx T_j$ the concentration of v-band holes $p(T_j) = p_j$ to the concentration of impurity ions [8]:

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

where $K = N_d/N_a = N_{+1}/N_a$ is the compensation ratio for compensation of acceptors by donors $(0 < K < 1)$.

Based on the virial theorem, in the papers [8,9] an analytic expression for the temperature T_j at $p_j \ll K(1-K)N_a$ was obtained in the form

$$T_j \approx \frac{0.728}{k_{\mathrm{B}}} \frac{e^2}{4\pi\varepsilon_r\varepsilon_0} (KN_a)^{1/3}, \tag{2}$$

where k_{B} is the Boltzmann constant, e is the elementary charge, ε_r is the relative permittivity (determined by v-band electrons against the background of ion cores of the crystal matrix), ε_0 is the electric constant.

To calculate the concentration of v-band holes at $T = T_j$, it is necessary to find the value of their drift mobility edge $E_m^{(v)} = -\delta E_v$ and the position of the Fermi level $E_{\mathrm{F}}^{(v)}$ (see Fig. 1, b).

Let us calculate the shift of the top of the v-band $\delta E_v > 0$ into the depth of the band gap (energy gap) of the semiconductor due to the formation of a quasi-continuous energy spectrum due to the overlap of the excited states of acceptors with their concentration increasing. Drift mobility edge for v-band holes $E_m^{(v)} = -\delta E_v = E_{\mathrm{per}} + E_{\mathrm{res}}$, where $E_{\mathrm{per}} < 0$ is the threshold of diffusion percolation of v-band holes, $E_{\mathrm{res}} < 0$ is the decrease in the thermal ionization energy of the acceptor due to the confinement of the maximum radius of the hole orbit on the acceptor due to the presence of both acceptors and donors in the crystal (see Fig. 1, b). Note that in a lightly doped p-type semiconductor, the contribution of the exchange energy of v-band holes to $E_m^{(v)}$ can be neglected (see, for example, [18]).

To find $E_m^{(v)}$, we estimate E_{per} and E_{res} separately and compare their values at $T = T_j$.

The energy level (threshold) of the diffusion percolation of v-band holes in a three-dimensional crystalline sample in the quasi-classical approximation is (see, for example, [14,19])

$$E_{\text{per}} \approx -0.955 W_p < 0, \tag{3}$$

where W_p is the amplitude of Gaussian fluctuations of the potential energy of the v-band hole.

When taking into account the Coulomb interaction of only nearest point charges (impurity ions and v-band holes) and „smoothing“ of the potential relief in a crystal by an average hole at its de Broglie wavelength at $T = T_j$, according to the data of papers [9,18], the quantity W_p is

$$W_p \approx 0.77 \frac{e^2}{4\pi\varepsilon_r\varepsilon_0}\left(\frac{p_j}{N_{\text{ch}}}\right)^{1/2} N_{\text{ch}}^{1/3}, \tag{4}$$

where $N_{\text{ch}} = N_{-1} + KN_a + p_j = 2N_{-1} \approx 2KN_a$ is the concentration of all point charges (Poisson-distributed [20] in the crystal) satisfying the electrical neutrality condition (1) when the concentration of holes in v-band is limited to $p_j \ll K(1-K)N_a$. It follows from relations (2)−(4) that at temperature T_j the inequality $W_p/k_{\text{B}}T_j \ll 1$ is satisfied.

The decrease in the thermal ionization energy of the hydrogen-like acceptor due to the confinement of the maximum Bohr radius of the hole orbit on the acceptor is given by the formula [21,22]

$$E_{\text{res}} = -I_a a_p / R_{\text{im}} < 0, \tag{5}$$

where $a_p = e^2/8\pi\varepsilon_r\varepsilon_0 I_a$ is the radius of the Bohr orbit of hole on a single acceptor with the thermal ionization energy I_a from the ground (unexcited) state to v-band (to the energy level $E_v = 0$) due to thermal fluctuations; $R_{\text{im}} = [4\pi(1+K)N_a/3]^{-1/3} = 0.62[(1+K)N_a]^{-1/3}$ is the average radius of the spherical region per one impurity atom (including acceptors and donors) in the crystal matrix.

At the temperature T_j, when $p(T_j) = p_j \ll K(1-K)N_a$, the estimate E_{per} and E_{res} according to (3) and (5) gives $|E_{\text{per}}| \ll |E_{\text{res}}|$, so $E_m^{(v)} = -\delta E_v \approx E_{\text{res}}$. Then from (5) we have

$$E_m^{(v)} \approx E_{\text{res}} = -I_a \frac{a_p}{R_{\text{im}}} < 0, \tag{6}$$

where I_a is the thermal ionization energy of a single acceptor in the charge state (0); $2R_{\text{im}} = d_{\text{im}} = 1.24[(1+K)N_a]^{-1/3}$ is the average diameter of the spherical region inside a semiconductor sample, all points of which are closer to the same impurity than to any other. Note that the value d_{im} is by $\approx 3\%$ less than the average distance between the nearest impurities in the crystal matrix $d_{\text{VD}} = 1.28[(1+K)N_a]^{-1/3}$ (determined in paper [23] by the method of Voronoi−Dirichlet polyhedra).

The first ideas about the „shift“ of the bottom of the c-band into the depth of the band gap due to the formation of quasi-continuous band of allowed energy values for c-band electrons from the excited states of donors in the charge state (0) are contained in paper [24] and, in particular, were used in papers [25,26]. However, these papers did not take into account the influence of donor compensation by acceptors on the value of the donor ionization energy (see δE_v value for acceptors in Fig. 1, b). Also note the analogy between the decrease in the thermal ionization energy of donors with their concentration in semiconductors and the decrease in the energy of „cold ionization“ of metal vapors with the concentration of metal atoms, when the incipience of the c-band appears [27] (see also [28,29]).

The concentration of v-band holes $p(T_j)$ for the case $p(T_j) \ll K(1-K)N_a$, taking into account (6), can be represented (see Fig. 1, b) as a standard relation from the theory of nondegenerate semiconductors [30,31]:

$$p(T_j) \equiv p_j = p_v(T_j)\exp\left(\frac{E_{\text{F}}^{(v)}(T_j) - E_m^{(v)}}{k_{\text{B}}T_j}\right), \tag{7}$$

where

$$p_v(T_j) = 2(2\pi m_{pd} k_{\text{B}} T_j)^{3/2}/(2\pi\hbar)^3,$$

m_{pd} is the density of states effective mass for v-band holes, $\hbar = h/2\pi$ is the reduced Planck's constant, $|E_{\text{F}}^{(v)} - E_m^{(v)}| > 0$ is the energy gap between the Fermi level $E_{\text{F}}^{(v)} < 0$ and the mobility edge $E_m^{(v)} < 0$ for v-band holes, $E_m^{(v)} = -\delta E_v \approx E_{\text{res}} = -I_a a_p/R_{\text{im}}$ for $W_p \ll k_{\text{B}}T_j$; $\delta E_v > 0$ is the shift of the v-band top into the band gap; $\delta E_v = 0$ for an undoped crystalline semiconductor. The position of the Fermi level $E_{\text{F}}^{(v)}(T_j) < 0$ with respect to $E_v = 0$ is determined from the electrical neutrality condition $N_{-1}(E_{\text{F}}^{(v)}) = KN_a$ under the condition $p(T_j) \ll K(1-K)N_a$ taking into account the finite width of the acceptor band $W_a \gg W_p$.

The concentration of negatively charged acceptors taking into account the Gaussian distribution G_a of energy levels in the acceptor band E_a (relative to I_a) with an effective width W_a, according to the data of paper [13], is equal to

$$N_{-1} = N_a \int\limits_{-\infty}^{+\infty} f_{-1} G_a \, d(E_a - I_a)$$

$$\equiv \frac{N_a}{W_a\sqrt{2\pi}} \int\limits_{-\infty}^{+\infty} f_{-1} \exp\left[-\frac{(E_a - I_a)^2}{2W_a^2}\right] d(E_a - I_a), \tag{8}$$

where $f_{-1} = \{1 + \beta_a \exp[(E_{\text{F}}^{(v)} + E_a)/k_{\text{B}}T]\}^{-1}$ is the probability of filling the acceptor state with energy level E_a by a hole, $\beta_a = 4$ is the degeneracy factor of the energy level of a single hydrogen-like acceptor in the crystalline semiconductor with degenerate v-band extremum (the top of the valence band) at the center of the Brillouin zone, $I_a = e^2/8\pi\varepsilon_r\varepsilon_0 a_p$ is the thermal ionization energy of a single acceptor relative to $E_v = 0$.

The effective width of the acceptor band W_a, taking into account the interaction of only nearest ions at

$p(T_j) \ll K(1-K)N_a$, when $N_{-1} = KN_a$, is equal to [9,18]

$$W_a = 2.64\,\frac{e^2}{4\pi\varepsilon_r\varepsilon_0}\,(2KN_a)^{1/3}. \tag{9}$$

Comparison of formulas (4) and (9) gives $W_a \gg W_p$ for $p(T_j) \ll K(1-K)N_a$.

Note that, according to (9) and (2), the ratio of the acceptor band width W_a to the thermal energy $k_\mathrm{B}T$ at temperature $T = T_j$ is equal to $W_a/k_\mathrm{B}T_j \approx 4.57$ and does not depend on the concentration of acceptors and their compensation ratio. As a consequence, the acceptor band cannot be considered narrow for temperature T_j.

So, the concentration of v-band holes at the temperature $T = T_j$ is determined from (7) taking into account the mobility edge $E_m^{(v)}$ by (6) and the Fermi level $E_\mathrm{F}^{(v)}(T_j)$, calculated from the electrical neutrality equation $N_{-1} = KN_a$ taking into account (8).

To calculate the electrical conductivity $\sigma(T_j) \equiv \sigma_j = \sigma_{bj} + \sigma_{hj} = 2\sigma_{bj}$ at temperature $T \approx T_j$ along with the hole concentration p_j by (7) it is necessary to know their drift mobility μ_{pj}. In the quasi-classical approximation of quantum mechanics the drift mobility of the nondegenerate gas of v-band holes, limited by their elastic scattering by impurity ions, at temperature T_j is described by the expression [32,33]

$$\mu_p(T_j) \equiv \mu_{pj} = \frac{5}{2}\left(\frac{4\pi}{3}\right)^{1/3}\frac{\hbar(4\pi\varepsilon_r\varepsilon_0)^2k_\mathrm{B}T_j}{e^3m_{p\sigma}N_i^{2/3}}\,\frac{1}{\ln(1+\gamma)}, \tag{10}$$

where $N_i \equiv N_\mathrm{ch}$ is the concentration of ions of hydrogen-like impurities (acceptors and donors); $N_i = 2KN_a$ at hole concentration $p \ll K(1-K)N_a$; dimensionless parameter $\gamma = (3/4\pi N_i)^{2/3}(20\pi\varepsilon_r\varepsilon_0k_\mathrm{B}T_j/e^2)^2$.

Note that formula (10) takes into account the minimum possible scattering angle, according to Conwell–Weiskopf [34], as well as the finite time of interaction between hole and one impurity ion (see also [35]). When calculating the drift mobility of holes (and electrons) for temperature T_j we can neglect the decrease in their mobility due to scattering on vibrations of atoms of the crystal matrix (see, for example, [36–38]) of the studied samples of germanium and silicon (see Figs. 2–7).

Electrical conductivity of v-band holes at temperature T_j, when $\sigma_{bj} = \sigma_{hj}$, is

$$\sigma_b(T_j) \equiv \sigma_{bj} = ep_j\mu_{pj} = 1/\rho_b(T_j), \tag{11}$$

where p_j is determined by formula (7), and μ_{pj} — by (10).

According to the definition of temperature T_j (see Fig. 1, a), the electrical resistivity $\rho_j = 1/\sigma_j$ at $T = T_j$ is equal to

$$\rho_j = \frac{1}{\sigma_{bj}+\sigma_{hj}} = \frac{1}{2\sigma_{bj}} = \frac{1}{1/\rho_{bj}+1/\rho_{hj}} = \frac{\rho_{bj}}{2}, \tag{12}$$

where the maximum value of DC hopping conductivity $\sigma_{hj} = ep_j\mu_{pj} = 1/2\rho_j$ at temperature T_j is determined by the concentration of v-band holes p_j and by their drift mobility μ_{pj}.

Along with the electrical conductivity at temperature T_j, the Hall effect is also often studied, the difficulties of its measuring in the case of a low doping level occur at lower temperatures. The relation that takes into account the contribution of the band (σ_{bj}) and hopping (σ_{hj}) electrical conductivities to the experimental value of the Hall coefficient $R_\mathrm{H}(T_j)$ at temperature T_j has the usual form for two-band model [30,39]:

$$R_\mathrm{H}(T_j) = \frac{R_{bj}\sigma_{bj}^2 + R_{hj}\sigma_{hj}^2}{(\sigma_{bj}+\sigma_{hj})^2} \approx \frac{R_{bj}\sigma_{bj}^2}{(\sigma_{bj}+\sigma_{hj})^2} = \frac{r_b}{4ep_j}, \tag{13}$$

where $R_{bj} = r_b/ep_j > 0$ is the Hall coefficient for v-band holes, p_j is the concentration of v-band holes by (7), r_b is the Hall factor ($r_b \approx 1$ at low temperatures in a sufficiently strong magnetic field [40]), R_{hj} is the Hall coefficient for holes hopping via acceptors ($|R_{hj}| \ll R_{bj}$).

According to the data of papers [9,18], the high-temperature (at $T = T_j$) concentration of holes hopping via acceptors is equal to $N_{hj} = K(1-K)N_a$. Then, from the equality of the maximum hopping $\sigma_{hj} = eN_{hj}M_{hj}$ and the minimum band conductivities $\sigma_{bj} = ep_j\mu_{pj}$, one can find the maximum drift hopping mobility of holes migrating via acceptors in the charge states (0) and (-1) at $T = T_j$:

$$M_h(T_j) \equiv M_{hj} = \frac{p_j\mu_{pj}}{K(1-K)N_a}. \tag{14}$$

Let us calculate the maximum drift hopping mobility of holes M_{hj} using formula (14) for p-Ge:Ga crystals (see Table 1) for $K = 0.4$ on the insulator side of the Mott transition ($N_a < N_\mathrm{M} = 1.85\cdot10^{17}\,\mathrm{cm}^{-3}$). For the concentration of gallium atoms $N_a = 3\cdot10^{15}\,\mathrm{cm}^{-3}$ we have $M_{hj} = 0.14\,\mathrm{cm}^2/(\mathrm{V\cdot s})$; for $N_a = 3\cdot10^{16}\,\mathrm{cm}^{-3}$ we have $M_{hj} = 93\,\mathrm{cm}^2/(\mathrm{V\cdot s})$.

Note that both the measurements of the Hall effect and their interpretation in the region of hopping electrical conductivity are still unsolved problem (see, for example, [41,42]). Therefore, to clarify the approaches to this problem, the dependence of the high-temperature (maximum) drift hopping mobility on the doping impurity concentration and its compensation ratio according to (14) is of interest.

Note that for n-type semiconductors with hydrogen-like donors in all formulas 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 ($+1$)], and symbols „p“ and „v“ (for p-type) — by symbols „n“ and „c“ (for n-type).

3. Comparison of calculation results with experimental data

To plot the theoretical (calculated from (12) and (13)) dependences of the electrical resistivity $\rho(T_j) \equiv \rho_j$

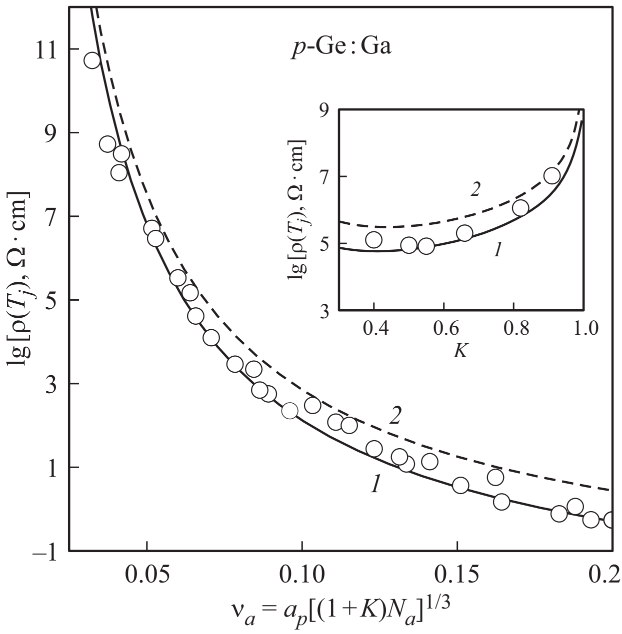

Figure 2. Decimal logarithm of DC resistivity ρ at temperature T_j vs. Mott parameter ν_a for neutron-transmutation gallium-doped p-type germanium crystals. Points are the experiment [43–50], lines are the calculation by formula (12) for the compensation ratio $K = 0.4$. The insert shows the dependence ρ_j on the compensation ratio K at constant gallium concentration $N_a = 2.66 \cdot 10^{15}\,\mathrm{cm}^{-3}$: points are the experiment [44], lines are the calculation by formula (12). Solid lines *1* are the calculation for $E_m^{(v)}$ by (6), dashed lines *2* — for $E_m^{(v)} = 0$.

and the Hall coefficient $R_{\mathrm{H}}(T_j)$ for temperature T_j on the Mott parameter generalized for the case of nonzero compensation $\nu_a = a_p[(1+K)N_a]^{1/3}$ for acceptors and $\nu_d = a_n[(1+K)N_d]^{1/3}$ for donors, the following relations were used:

$$\frac{a_{p(n)}}{R_{\mathrm{im}}} = 1.612\nu_{a(d)}; \quad \frac{k_{\mathrm{B}}T_j}{I_{a(d)}} = 1.456\left(\frac{K}{1+K}\right)^{1/3}\nu_{a(d)},$$

obtained from formulas (2) and (6).

To plot the calculated dependences of $\rho(T_j)$ and $R_{\mathrm{H}}(T_j)$ on $\nu_a = a_p[(1+K)N_a]^{1/3}$ and $\nu_d = a_n[(1+K)N_d]^{1/3}$ in Figs. 2–7 the parameters of germanium of p-type [43–50], n-type [51,52] and silicon of n-type [53–55] and p-type [54,55], specified in Tables 1 and 2 were used (see also [36–38,56,57]). The parameter $\nu_{a(d)}$ takes into account both the concentration of the doping (majority) hydrogen-like impurity (N_a or N_d) and its compensation ratio $0 < K < 1$ by minority (compensating) impurity.

Experimental data and calculations are presented for semiconductors with acceptor concentrations $N_a < 0.45N_{\mathrm{M}}$ (for p-Ge : Ga), $N_a < 0.25N_{\mathrm{M}}$ (for p-Si : B) and donors $N_d < 0.25N_{\mathrm{M}}$ (for n-Ge and n-Si), where N_{M} is the concentration of the majority impurity corresponding to the Mott transition (see paper [17] and references therein). For compensated germanium crystals of p- and n-type $N_{\mathrm{M}} = 1.85 \cdot 10^{17}\,\mathrm{cm}^{-3}$ (p-Ge : Ga, $K \approx 0.4$); $N_{\mathrm{M}} \approx 1.68 \cdot 10^{17}\,\mathrm{cm}^{-3}$ (n-Ge : Sb, $K < 0.1$); for weakly compensated silicon crystals of p- and n-type ($K \approx 0.1$): $N_{\mathrm{M}} = 3.81 \cdot 10^{18}\,\mathrm{cm}^{-3}$ (n-Si : P); $N_{\mathrm{M}} = 7.8 \cdot 10^{18}\,\mathrm{cm}^{-3}$ (n-Si : As); $N_{\mathrm{M}} = 3 \cdot 10^{18}\,\mathrm{cm}^{-3}$ (n-Si : Sb); $N_{\mathrm{M}} = 4.1 \cdot 10^{18}\,\mathrm{cm}^{-3}$ (p-Si : B).

Figs. 2–7 show calculations for such degrees of doping and compensations of semiconductors, in which the energy gap between the Fermi level and the mobility edge for the majority charge carriers exceeds $3k_{\mathrm{B}}T_j/2$; for p-type semiconductors $|E_{\mathrm{F}}^{(v)} - E_m^{(v)}| > 3k_{\mathrm{B}}T_j/2$ or for n-type semiconductors $|E_{\mathrm{F}}^{(c)} - E_m^{(c)}| > 3k_{\mathrm{B}}T_j/2$ (see also Fig. 1, *b*).

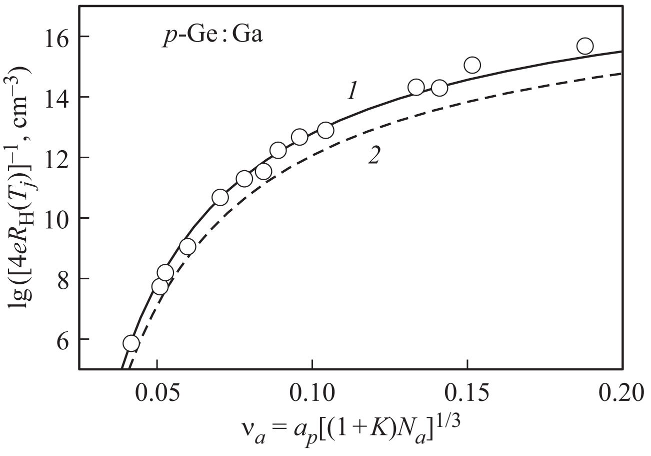

Figure 3. Reciprocal value of the Hall coefficient R_{H} at temperature T_j vs. Mott parameter ν_a for neutron-transmutation gallium-doped p-type germanium crystals. Points are the experiment [43,47], lines are the calculation for the Hall factor $r_b = 1$ by formula (13) taking into account (7) for the compensation ratio $K = 0.4$. Solid line *1* is the calculation for $E_m^{(v)}$ by (6), dashed line *2* — for $E_m^{(v)} = 0$.

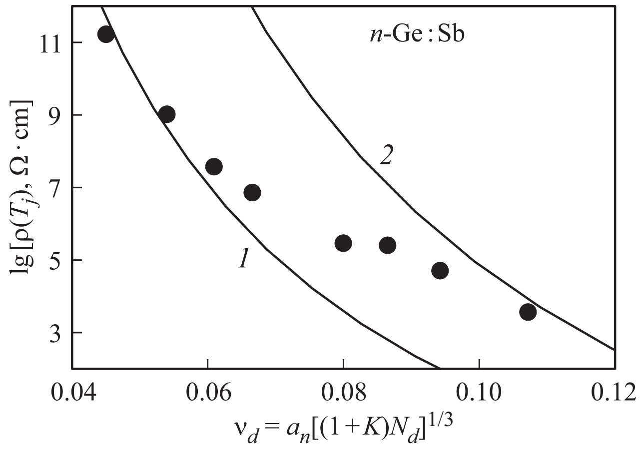

Figure 4. Logarithm of DC resistivity ρ at temperature T_j vs. Mott parameter ν_d for antimony-doped n-type germanium crystals. Points are the experiment [51,52], lines are the calculation by formula (12) for the compensation ratios: $K = 0.05$ (*1*) and 0.01 (*2*).

Table 1. Parameters of *p*- and *n*-type germanium crystals

Semiconductor	I_a, meV	a_p, nm	β_a	ε_r	m_{pd}/m_0	$m_{p\sigma}/m_0$	K	References
p-Ge : Ga	11.32	4.13	4	15.4	0.35	0.26	0.4 0.35 0.3 0.35 0.4	[43,44] [45] [46] [47,48] [49,50]
Semiconductor	I_d, meV	a_n, nm	β_d	ε_r	m_{nd}/m_0	$m_{n\sigma}/m_0$	K	References
n-Ge : Sb	10.32	4.53	2	15.4	0.553	0.119	0.02–0.06	[51,52]

Table 2. Parameters of *p*- and *n*-type silicon crystals

Semiconductor	I_d, meV	a_n, nm	β_d	ε_r	m_{nd}/m_0	$m_{n\sigma}/m_0$	K	References
n-Si : P	45.58	1.38	2	11.47	1.062	0.259	0.01–0.02 $\sim$ 0.1	[53] [54]
n-Si : As	53.76	1.17					$\sim$ 0.01 0.04, 0.06	[54] [55]
n-Si : Sb	42.74	1.47					$\sim$ 0.1 0.02–0.05	[54] [55]
Semiconductor	I_a, meV	a_p, nm	β_a	ε_r	m_{pd}/m_0	$m_{p\sigma}/m_0$	K	References
p-Si : B	44.39	1.41	4	11.47	0.584	0.397	$\sim$ 0.01 0.1–0.3	[54] [55]

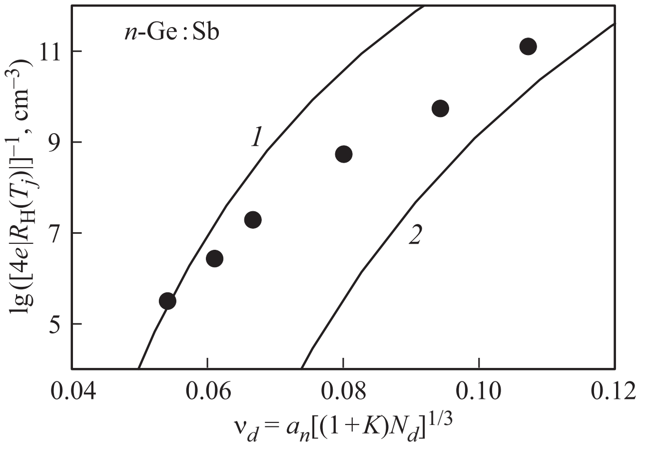

Figure 5. Reciprocal value of Hall coefficient $|R_H|$ at temperature T_j vs. Mott parameter ν_d for *n*-type germanium crystals doped with antimony. Points are the experiment [51], lines are the calculation for the Hall factor $r_b = 1$ by formula (13) taking into account (7) for the compensation ratios: $K = 0.05$ (*1*) and 0.01 (*2*).

Experimental dependences $\rho(T_j)$ and $R_H(T_j)$ for moderately compensated *p*-Ge samples (Figs. 2 and 3) and non-intentionally compensated samples of *n*-Ge (Figs. 4 and 5) and *n*-Si and *p*-Si (Figs. 6 and 7) qualitatively coincide with the calculated values. For neutron-transmutation doped *p*-type germanium crystals, where the compensation ratio of the doping impurity (acceptors, gallium atoms) in the

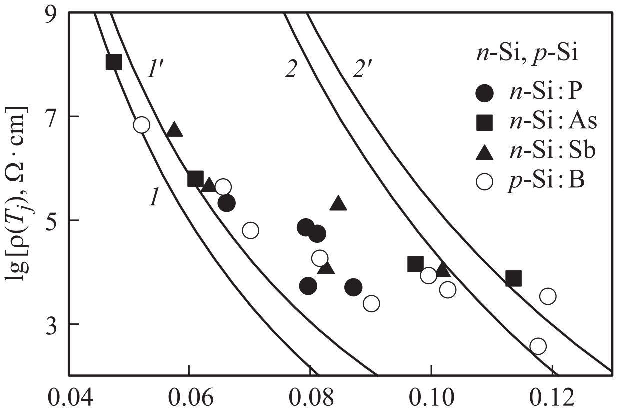

Figure 6. Logarithm of DC resistivity ρ at temperature T_j vs. Mott parameters ν_d and ν_a for *n*-type silicon crystals doped with donors (P, As and Sb) and *p*-type silicon crystals doped with acceptors (B). Points are the experiment [53–55], lines are the calculation by formula (12) with the compensation ratios: $K = 0.1$ (*1* — *n*-type, *1'* — *p*-type) and 0.01 (*2* — *n*-type, *2'* — *p*-type).

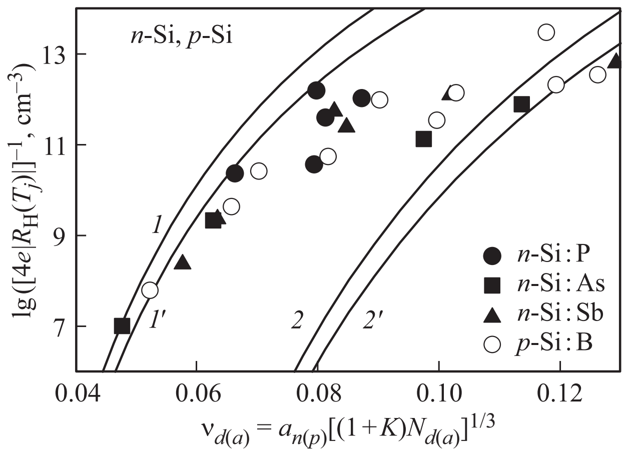

Figure 7. Reciprocal value of the Hall coefficient $|R_{\mathrm{H}}|$ at temperature T_j vs. Mott parameters ν_d and ν_a for *n*-type silicon crystals doped with donors (P, As and Sb) and *p*-type doped with acceptors (B). Points are the experiment [53–55], lines are the calculation for the Hall factor $r_b = 1$ by formula (13) taking into account (7) for the compensation ratios: $K = 0.1$ (*1* — *n*-type, *1'* — *p*-type) and 0.01 (*2* — *n*-type, *2'* — *p*-type).

entire range of their concentration varied only within the range from 0.3 to 0.4 and depended on the hardness of the neutron spectrum [58], there is a good agreement with our calculation. On the contrary, in crystals of *n*-type germanium and *n*- and *p*-type silicon obtained by metallurgical doping with hydrogen-like donors, as comparison with calculation shows, the compensation ratio expectedly decreases from ≈ 5 to 1% (for germanium) and from ≈ 10 to 1% (for silicon) with increasing of the doping impurity concentration. Note that at $\nu_d > 0.12$ and $K < 0.1$, along with the D^0-band of donors formed by the charge states (0) and (+1), a D^--band formed by the the charge states (−1) and (0) of donors is also possible (see, for example, [59]).

It can be seen from Figs. 2 and 3 (on the example of *p*-type germanium crystals with the compensation ratio ≈ 40%) that taking into account according to (6) the shift $\delta E_v = -E_m^{(v)}$ of the top of the v-band into the band gap is fundamentally important for describing the dependence of the electrical resistance $\rho(T_j)$ and the Hall coefficient $R_{\mathrm{H}}(T_j)$ on the concentration of acceptors: at $\delta E_v = -E_m^{(v)} = 0$ the calculated values differ noticeably from the experimental ones. The same remark applies to *n*-Ge crystals, as well as to *p*- and *n*-Si.

4. Conclusion

A quantitative description of the DC conductivity and Hall coefficient is given in the framework of a two-band model that takes into account the band of allowed energy values for the majority charge carriers and the band of hydrogen-like doping (majority) impurities separated from it in the energy gap of crystalline semiconductors. Formulas are derived that describe the electrical conductivity $1/\rho(T_j)$ and the Hall coefficient $R_{\mathrm{H}}(T_j)$ of semiconductors with hydrogen-like impurities at temperatures T_j, when the contributions to the electrical conductivity from the band and hopping electrical migration of holes (for *p*-type semiconductor) and electrons (for *n*-type semiconductor) are equalized. It is taken into account that the confinement of the maximum localization radius of the hole on an acceptor (electron on donor) on the impurity ion core with increase in the concentration of impurity atoms leads to a shift of the edge of the allowed energy band into the depth of the energy gap of the semiconductor. The high-temperature (at $T = T_j$) concentration of holes hopping via acceptors is equal to $K(1-K)N_a$, where K is the compensation ratio for compensation of acceptors with concentration N_a by donors; the concentration of electrons hopping via donors is equal to $K(1-K)N_d$, where K is the compensation ratio for compensation of donors with concentration N_d by acceptors. The obtained formulas allow to plot the dependences $\rho(T_j)$ and $R_{\mathrm{H}}(T_j)$ on the concentration of doping impurity atoms for the given compensation ratio $K < 0.5$ on the insulator side of the phase electronic (or hole) insulator–metal transition (Mott transition).

Comparison of $\rho(T_j)$ and $R_{\mathrm{H}}(T_j)$ calculations with experimental data at the Hall factor equal to 1 for *p*-Ge crystals with fixed compensation ratio $K = 0.3{-}0.4$ shows their good agreement in a wide range of acceptor (gallium atoms) concentrations. Estimates are made of the maximum drift hopping mobility of holes as a function of the concentration of gallium atoms N_a at a concentration of hopping holes $K(1-K)N_a$. For non-intentionally compensated *n*-Ge, *n*-Si, and *p*-Si crystals the procedure of fitting the calculated curve to the experimental data allows to estimate the unknown compensation ratio of material and, in particular, it shows the expected decrease in the compensation ratio (in the range from 10 to 1%) with doping level increasing.

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Conflict of interest

The authors declare that they have no conflict of interest.

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