Drift-diffusion model of hole migration in diamond crystals via states of valence and acceptor bands

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Abstract
Ionization equilibrium and dc electrical conductivity of crystalline diamond are considered, for the temperature $T_j$ in the vicinity of which valence band ($v$-band) conductivity is approximately equal to hopping conductivity via acceptors. For the first time, we find explicitly (in the form of definite integrals) the fundamental ratio of diffusion coefficient to drift mobility for both $v$-band holes and holes hopping via hydrogen-like acceptors for the temperature $T_j$. The known ratios follow from the obtained ones as particular cases. The densities of the spatial distributions of acceptors and hydrogen-like donors as well as of holes are considered to be Poissonian and the fluctuations of electrostatic potential energy are considered to be Gaussian. The dependence of exchange energy of $v$-band holes on temperature is taken into account. The thermal activation energy of hopping conduction as a function of the concentration of boron atoms (as acceptors) is calculated for temperature $T_b \approx T_j/2$.

Without the use of any adjustable parameters, the results of calculations quantitatively agree with data obtained from the measurements of hopping conductivity of diamond with boron concentration from $3 \times 10^{17}$ to $3 \times 10^{20}$ cm$^{-3}$, i.e. on the insulating side of the Mott phase transition.

1. Introduction

The ionization equilibrium, e.g. between $v$-band (valence band) holes and acceptor impurity atoms in $p$-type semiconductor crystals, and the coexistence of $v$-band and hopping via acceptors migration of holes are considered separately (see, e.g., reviews [1–3]). However, at such a temperature $T_j$, when the dc $v$-band electrical conduction is approximately equal to the dc hopping electrical conduction via hydrogen-like acceptors it is necessary to consider jointly the ionization equilibrium and the drift-diffusion migration of holes. It is important for the wide bandgap semiconductors, like boron-doped crystalline diamond, for which $T_j$ is in the region from liquid nitrogen to room temperatures and higher. For the narrow bandgap semiconductors, like boron-doped crystalline silicon, temperature $T_j$ is usually in the region from liquid helium to liquid hydrogen temperatures [4]. Such a difference in temperatures $T_j$ between boron-doped diamond and boron-doped silicon is connected with that the thermal energy of ionization by electrically neutral boron atoms in diamond is eight times greater than the one in silicon. Let us note that the wide bandgap semiconductors (for which the energy of electron affinity is less than the band gap) are important for applications in high-temperature electronics and power optics [5]. In particular, heavily boron-doped diamonds are attractive for studies of superconductivity at liquid helium temperature and higher (see, e.g., [6, 7]) and application as electrodes for detection of neurochemicals in the human brain at room temperature [8].

The purpose of this article is to calculate theoretically (in the framework of the drift-diffusion model) the ratio of the diffusion coefficient to the drift mobility for both $v$-band holes and acceptor band holes in boron-doped diamond crystals of $p$-type ($p$-Dia:B). In contrast to other works we consider the temperature region where the contributions of free $v$-band holes and holes hopping via acceptor band are comparable.

Let us consider a bulk homogeneous diamond crystal that contains $v$-band holes with the average concentration $p$, a majority impurity—hydrogen-like acceptors (boron atoms) in the charge states (0) and (−1).
with the total average concentration \( N \), and a minority impurity—hydrogen-like donors, all in the charge state (+1), with the average concentration \( KN \), where \( 0 < K < 1 \) is the compensation ratio of acceptors by donors. The electrical neutrality condition at ionization equilibrium for a random distribution of impurity atoms and holes over the crystal volume is

\[
p + KN = N_{-1},
\]

where \( N_{-1} = N - N_0 \) is the average concentration of ionized acceptors, i.e. acceptors in the charge state \((-1)\), \( N_0 \) is the average concentration of electrically neutral acceptors.

Holes in the \( v \)-band with a total energy \( E_p \) above the threshold of drift-diffusion migration \( \delta E_r < 0 \) (see figure 1) are delocalized over the entire volume of the crystal (between scattering or recombination events) holes in the \( v \)-band. These completely free \( v \)-band holes characterize the dc electrical conductivity \( \sigma_v \) and the stationary Hall effect. We will denote their concentration as \( p_{\text{mob}} \). On the other hand, holes in the \( v \)-band with energy \( E_p < \delta E_r \) can only move within restricted regions of a crystal and are probably responsible for the increase of the macroscopic permittivity in doped semiconductors (see, e.g., [1, 9–11]). Let \( p_{\text{loc}} \) be the concentration of partially free \( v \)-band holes. The total concentration of \( v \)-band holes is \( p = p_{\text{mob}} + p_{\text{loc}} \). We will show that \( p_{\text{loc}}/p \ll 1 \) on the insulating side of the concentration transition insulator–metal (Mott transition) for \( K \leq 0.5 \) in the limit of zero temperature. In boron-doped moderately compensated \((K < 0.1)\) diamond of \( p \)-type the critical concentration of boron atoms corresponding to the Mott transition is \( N = N_{M} \approx 4 \times 10^{20} \text{cm}^{-3} \) [12]. Impurity atoms are assumed to be localized at sites of diamond crystal lattice. However, because holes can transfer from acceptors into the \( v \)-band and back, as well as hop between acceptors, the charge states of immobile acceptors \((0)\) and \((-1)\) migrate within crystal [13]. Conversely, all donors permanently remain in the charge state \((+1)\), so their charge states do not migrate.

At temperatures \( T < T_j \) the electrical conductivity is mainly determined by holes hopping from acceptors in the charge state \((0)\) to acceptors in the charge state \((-1)\): the HC regime in figure 1. Turbulent (jumping, relay) migration of holes is realized in the vicinity of the temperature \( T_j \), when the \( v \)-band \( \sigma_v \) and the hopping \( \sigma_h \) via acceptors electrical conductivities are approximately equal to each other (JC regime). At temperatures \( T > T_j \) the electrical conductivity is mainly determined by \( v \)-band holes, that move 'freely' in the crystal matrix between events of scattering on phonons and impurity atoms (BC regime).

The expression for the density of the stationary (direct) electric current of mobile ions and conduction electrons in solids taking into account drift and diffusion components of the current was first written by Wagner [14]; see also [15]. The expression for the density of stationary hopping current of electrons via hydrogen-like donors in the charge states \((0)\) and \((+1)\) in the drift-diffusion approximation was first obtained in [16, 17].

In a crystalline semiconductor of \( p \)-type the density \( J_p \) of a direct (stationary) current of \( v \)-band holes in the direction of the coordinate \( x \) axis has the form [14, 18, 19]:

\[
J_p = e p \mu_p \delta - e D_p \frac{dp}{dx} = \sigma_p \delta - e D_p \frac{dp}{dx},
\]

where \( e \) is the elementary charge, \( p \) is the concentration of \( v \)-band holes, \( \mu_p \) is the hole drift mobility, \( \delta = -d\varphi/dx \) is the value of the external electric field strength directed along \( x \) axis; \( \varphi \) is the electric potential, \( x \) is the coordinate, \( D_p \) is the diffusion coefficient, \( \sigma_p = e p \mu_p \) is the dc conductivity of \( v \)-band holes.

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**Figure 1.** The logarithm of the dc electrical conductivity \( \sigma \) as a function of the reciprocal temperature \( 1/T \) for a \( p \)-type crystalline semiconductor in the regime of hole migration in the \( v \)-band \( (\sigma_v) \) at the total ionization of acceptors for \( T \approx T_j \) and in the regime of hole hopping via nearest neighbor acceptors \( (\sigma_h) \) at \( T_j \approx T_j/2 \). In the region \( T_j \approx 3T_j/2 \) the energy of thermal ionization of acceptors is determined. Here \( \text{BC} \) is the conduction of holes in the valence band, \( \text{HC} \) is the conduction of holes in the acceptor band, \( \text{JC} \) is the jumping migration of holes—the mixture of the \( v \)-band and hopping conduction. Inset: \( E_p \) is the total energy of \( v \)-band hole; \( E_r = 0 \) is the top of the \( v \)-band of undoped crystal; \( E_r < 0 \) is the Fermi level (relative to \( E_r = 0 \)); \( W_p \) is the root-mean-square fluctuation of the \( v \)-band hole potential energy; \( \delta E_r \) is the shift of the valence band top into the band gap; \( E_r > 0 \) is the energy difference between \( E_r = 0 \) and the center of the acceptor band with effective width \( W_p \); \( E_s \) is the single-electron energy in a crystal.
Note that in the framework of the linear stationary theory of electron and hole transport in semiconductors it is assumed that in the expressions for the current densities the quantities that appear in front of the differentiation by coordinate operator do not depend on the coordinate \([18–20]\). We will use this approximation in the following.

From equation (2) at \(J_p = 0\), but \(\varphi \neq 0\), in the limit \(\varphi(x) \to 0\) for all \(x\) we get \([19–21]\):

\[
\frac{D_p}{\mu_p} = \frac{p \varphi}{\mu_p} = -\frac{p}{\mu_p} \frac{d\varphi}{dx} = \frac{p}{\mu_p} \frac{d\xi}{dx} = \frac{p}{\mu_p} \frac{dE}{dx},
\]

where \(\xi(x) = E_p - e\varphi(x)\) is the electrochemical potential of holes in the point with the coordinate \(x\); \(E_p\) is the Fermi level for holes (that is determined from the electroneutrality condition (1)).

From equations (1)–(3) follows the expression for the static electrical conductivity of \(\nu\)-band holes

\[
\sigma_v = \varepsilon^2 D_p \frac{dp}{d\xi} = \varepsilon^2 D_p \frac{dp}{dE_p},
\]

that is used for analyzing the conditions and quantitatively describing the insulated–metal transition in semiconductors for given doping and compensation levels \([22]\).

For an ‘ideal’ nondegenerate gas of holes, where the root–mean–square fluctuation of the potential energy of a \(\nu\)-band hole \(W_p\), is much smaller than the thermal energy \(k_0 T\), the shift of the \(\nu\)-band top \(\delta E_re\) = 0, and the Fermi level \(E_F < 0\), \([E_F] \gg k_0 T\), from equation (3) follows the Nernst–Einstein–Smoluchowski relation \([23]\) (see also \([15]\)):

\[
\frac{D_p}{\mu_p} = \frac{k_0 T}{\varepsilon},
\]

where \(k_0\) is the Boltzmann constant, \(T\) is the absolute temperature; \(k_0 T\) is the thermal energy.

For an ‘ideal’ degenerate gas of \(\nu\)-band holes, where \(W_p \ll k_0 T\), \(\delta E_re = 0\), and the Fermi level (energy) \(E_F \gg k_0 T\), from equation (3) we get (see, e.g., \([24]\)):

\[
\frac{D_p}{\mu_p} = \frac{2E_p}{3\varepsilon} \gg \frac{k_0 T}{\varepsilon}.
\]

Comparison of equations (4) and (5) shows that for degenerate gas of \(\nu\)-band holes the \(D_p/\mu_p\) ratio becomes greater than the one for nondegenerate gas of \(\nu\)-band holes. This is due to the fact that \(D_p \propto \frac{1}{2} \rho_m^2 / \tau_e = \tau_e v_F^2\) and \(\mu_p \propto \tau_e\), where \(\rho_m = \frac{1}{2} v_F\tau_e\) is the mean free path \([25]\) of hole in a crystal, \(\tau_e\) is the quasimomentum relaxation time of \(\nu\)-band hole, \(v_F \propto \sqrt{E_b}\) is the Fermi velocity \([19, 20]\). Thus, for degenerate gas, \(D_p/\mu_p \propto E_F\).

In a \(p\)-type semiconductor, the density of the stationary hopping current of holes via hydrogen-like acceptors along the \(x\) axis is \([13, 26]\):

\[
n_h \equiv \varepsilon N_h \left[ M_h \varphi - D_h \frac{d}{dx} \ln \left( \frac{N_0}{N_{-1}} \right) \right] = \sigma_h \varphi - eD_h \frac{dN_h}{dx},
\]

where \(N_h = N_0 N_{-1}/N\) is the effective concentration of holes hopping via acceptors in the charge states \((0)\) and \((-1)\); \(N_0/N\) is the fraction of electrically neutral acceptors that belong to the infinite cluster of acceptors ‘connecting’ the electrodes to the crystal under the conditions of stationary hopping electrical conduction, \(N_{-1}/N\) is the fraction of ionized acceptors that belong to the infinite cluster of acceptors providing hopping dc migration of holes between electrodes, \(M_h\) is the drift mobility of holes hopping via acceptors, \(\varphi = -d\varphi/dx\) is the value of the external electric field in the crystal, \(D_h\) is the diffusion coefficient of holes hopping along \(x\) axis, \(\sigma_h = eN_h M_h\) is the dc hopping electrical conductivity via states of the acceptor band.

It follows from equation (6) that at \(J_h = 0\), but \(\varphi \neq 0\), the drift and diffusion components of the hopping current density in the \(x\)-direction compensate each other. Taking into account that in crystal the external electric field strength \(\varphi = -d\varphi/dx \approx 0\) and that the electrochemical potential \(\xi(x) = E_F - e\varphi(x)\) in the limit \(\varphi(x) \to 0\) for all \(x\) we get

\[
\frac{D_p}{M_h} = -\frac{d\varphi}{d \ln (N_0/N_{-1})} \left/ \frac{d\xi}{d \ln (N_0/N_{-1})} \right.,
\]

where \(d\xi/dN_0 = dE_F/dN_{-1}\), by virtue of \(N_0(E_F) + N_{-1}(E_F) = N\) does not depend on \(E_F\).

In \([27]\) a nonlinear theory of hopping electron transport in bulk disordered materials has been proposed, where the drift hopping mobility and the diffusion coefficient depend on the external electric field strength. In this work in the weak electric field limit \((e\varphi d \ll k_0 T\), where \(d\) is the mean hop length of electron via localized states) and when the thermal energy is greater than the fluctuation dispersion of energy levels of localized states it is shown that the ratio of the diffusion coefficient to the drift mobility is equal to \(k_0 T/e\).

Finally, the values of effective hole or electron concentrations involved in hopping migration via hydrogen-like impurities in crystalline semiconductors are determined in \([11, 16, 17, 28–30]\). For example, for a \(p\)-type semiconductor with the average concentration of acceptors \(N_a = N_0 + N_{-1}\) in the charge states \((0)\) and \((-1)\), the concentration of holes hopping via acceptors is \(N_{hp} = N_0 N_{-1}/N_h\). For an \(n\)-type semiconductor with the
average concentration of donors \( N_d = N_0 + N_{i,1} \) in the charge states \((0)\) and \((+1)\) the concentration of electrons hopping via donors is \( N_{dn} = N_0 N_{i,1}/N_0 \). However, derivations of the relation \( D_h/M_b \) for holes hopping via acceptors and electrons hopping via donors in \([31–34]\) used particular forms of the expressions for \( N_{hp} \) and \( N_{bn} \) that are only suitable for limiting values of the compensation ratio \((K \ll 1 \) or \(1 - K \ll 1\)) of the majority impurity by the minority impurity. In this paper we will show how to lift this limitation for the example of \(p\)-Dia:B within the framework of the linear drift-diffusion model of hopping migration of holes via boron atoms.

### 2. Statistics of holes in valence and acceptor bands

In the thermodynamic equilibrium state for the concentration of \(v\)-band holes \(p\) averaged over the volume \(V\) of a bulk crystalline diamond sample according to \([30, 35–37]\) we obtain

\[
p = \frac{1}{V} \int_{-\infty}^{+\infty} g_p f_p dE_p, \tag{8}
\]

where \(g_p\) is the energy density of states of \(v\)-band holes (taking into account their spin that is equal to the electron spin), \(f_p = \{1 + \exp[(E_p - E_f)/k_B T]\}^{-1}\) is the Fermi–Dirac function, \(E_p = E_{kin} + U_p\) is the total energy of the hole, the sum of the kinetic energy \(E_{kin}\) and the potential energy \(U_p\) of its interaction with impurity atoms and other holes, \(E_f\) is the Fermi level (chemical potential for holes), \(k_B T\) is the thermal energy. Values of \(E_p\), \(E_f\), \(E_a\), \(\delta E/V\), and \(U_p\) are given relative to the top of the \(v\)-band \((E_0 = 0)\) of the undoped crystal (figure 1).

According to \([38, 39]\) the probability density function of potential energy \(U_p\) fluctuations of a hole in the \(v\)-band of a bulk crystal is Gaussian

\[
g_p(U_p) = \left(\frac{1}{\sqrt{2\pi} W_p}\right) \exp\left(-\frac{U_p^2}{2W_p^2}\right), \tag{9}
\]

where \(W_p\) is the root-mean-square fluctuation of the potential energy of the hole, see equation (18).

In the quasi-classical approximation \([38, 39]\), taking into account the probability density function \(g_p\) of potential energy \(U_p\) fluctuations given by equation (9), for the energy density of states of holes in the \(v\)-band we find

\[
g_p = \frac{V(2m_p)^{3/2}}{2\pi^2 \hbar^3} \int_{-\infty}^{E_p} (E_p - U_p)^{1/2} g_p dU_p, \tag{10}
\]

where \(m_p\) is the density-of-states effective mass of a hole in the \(v\)-band of undoped diamond, \(E_p - U_p = E_{kin}\) is the kinetic energy of the hole, and \(\hbar = h/2\pi\) is the Planck constant.

Note that in the ‘ideal’ diamond crystal, i.e. without fluctuations of the potential energy of \(v\)-band holes, when \(g_p \rightarrow \delta(U_p)\), where \(\delta(U_p)\) is the Dirac delta function, equation (10) takes the standard form \([18–20]\):

\[
g_p = \left(\frac{V(2m_p)^{3/2}}{2\pi^2 \hbar^3}\right) \sqrt{E_{kin}}, \tag{11}
\]

where \(E_{kin} = (\hbar k)^2/2m_p > 0\) is the kinetic energy of motion of a free \(v\)-band hole with the module of quasiwave vector \(|k| = k\).

Taking into account three subbands of the diamond valence band (heavy \((h)\) and light \((l)\) holes, as well as holes in the subband split-off due to the spin–orbit interaction \((so)\), the hole effective mass \(m_p\) is \([40]\):

\[
m_p = (m_{hh}^{3/2} + m_{lh}^{3/2} + m_{lo}^{3/2})^{2/3} = 0.992m_0, \tag{12}
\]

where \(m_{hh} = 0.78m_0\) is the heavy hole effective mass, \(m_l = 0.14m_0\) is the light hole effective mass, \(m_{lo} = 0.394m_0\) is the hole effective mass in the spin–orbit split-off subband of the \(v\)-band, and \(m_0\) is the electron mass in vacuum. (Further we assume that \(m_p\) does not depend on \(v\)-band hole concentration.)

The average concentration of the acceptors in the charge state \((-1)\), taking into account deviations of their energy levels \(E_a\) from the average value \(\bar{E}_a\), can be written as \([30]\):

\[
N_{-1} = N \int_{-\infty}^{+\infty} G_a f_{-1} d(E_a - \bar{E}_a) = N \bar{f}_{-1} = N (1 - \bar{f}_0), \tag{13}
\]

where \(G_a\) is the probability density function for the distribution of energy levels in the diamond band gap,

\[
f_{-1} = 1 - f_0 = \{1 + \beta \exp[(E_a + E_0)/k_B T]\}^{-1}, \tag{14}
\]

Excluding the excited states of all the acceptors, for \(f_{-1}\) we find \([19, 21]\):

\[
f_{-1} = 1 - f_0 = \{1 + \beta \exp[(E_a + E_0)/k_B T]\}^{-1}, \tag{14}
\]
where $\beta_s = 4 + 2 \exp(-\varepsilon_{so}/k_B T)$ is the degeneracy factor of energy level $E_s$ considering all three hole subbands in the diamond v-band, $\varepsilon_{so} = 6$ meV is the value of hole so-subband split-off from the degenerate heavy and light hole subbands. If the thermal energy $k_B T$ (e.g., at $T_J \approx 3 T_N/2$; figure 1) is substantially larger than $\varepsilon_{so}$ then $\beta_s \approx 6$. The reference point for the acceptor energy level $E_F > 0$ and the Fermi level $E_F < 0$ in equation (14) is chosen at $E_F = 0$. For calculation of $\bar{f}_{+} = 1 - \bar{f}_0$ by equation (13) in the exponent of the function $f_{+1}$ given by equation (14) the quantity $E_F$ should be replaced by $(E_F - E_s)$ and $E_F$ should be replaced by $(E_F + E_s)$.

Taking into account the excited states of electrically neutral acceptors, the quantity $\beta_s$ in equation (14) should be replaced by [13, 41]:

$$\beta_{am} \approx \beta_s \left(1 + \int_1^\infty \frac{d}{\sqrt{k_B T}} \exp \left[ \frac{1 - l^2}{l k_B T} \right] dl \right),$$

(15)

where $l_m = (d_m^2/2a_0^3)^{1/2} \approx 0.526(8\pi \varepsilon I_s/e^2)^{1/2}(1 + K)N^{-1/6} \geq 1$ is the largest number of possible excited states of the average acceptor in the charge state $(0), d_m \approx 0.554[(1 + K)N^{-1/3}]$ is the average distance between the nearest impurity atoms considered as point particles (Poissonianly) distributed over a crystalline matrix [30, 42], $a_0 = e^2/(8\pi \varepsilon I_s)$ is the Bohr orbit radius for a hole, $\varepsilon = \varepsilon_r \varepsilon_0 = 5.7 \varepsilon_0$ is the static permittivity of a diamond crystal due to $p$-band electrons [43], $\varepsilon_0 = 8.85$ pF m$^{-1}$ is the electric constant, $I_s$ is the thermal ionization energy of a solitary acceptor in the ground (non-excited) state in the crystal lattice site; $I_s = 370$ meV for boron atoms in diamond [43]. In numerical calculations of the ionization equilibrium in $p$-Dia:B crystals at $T_J$ in equations (13) and (14) the quantity $\beta_{am}$ determined by equation (15) will be used instead of $\beta_s$.

According to [9, 44], we assume a Gaussian probability density function $\mathcal{G}_a$ for the fluctuations of acceptor energy levels $E_s$ relative to the average value $E_a$ over the crystal

$$\mathcal{G}_a(E_s - E_a) = \frac{1}{\sqrt{2\pi} W_s} \exp \left[ \frac{-(E_s - E_a)^2}{2 W_s^2} \right],$$

(16)

where $W_s$ is the effective width of the acceptor band (figure 1).

Taking into account only Coulomb interaction between the two nearest point charges in the crystal, we find the following expression for the effective width of the acceptor band $W_s$, which is equal to the root-mean-square fluctuation of the electrostatic energy of the ionized acceptor [35, 45]:

$$W_s \approx 2.64 \frac{e^2}{4\pi \varepsilon N_{ch}}^{1/3},$$

(17)

where $N_{ch} = N_{-1} + KN + p = 2(KN + p) = 2N_{-1}$ is the concentration of all point charged particles in the crystal.

The root-mean-square fluctuation of the electrostatic potential energy $U_p$ of a $v$-band hole $W_p$ is smaller than $W_s$ due to smoothing of the potential (with characteristic amplitude $W_s$) by a hole within the scale of its de Broglie wavelength [15, 30]:

$$W_p \approx 0.29 \left( \frac{p}{N_{ch}} \right)^{1/2} W_s,$$

(18)

where $p$ is the concentration of $v$-band holes; $W_s$ is determined by equation (17).

From equations (17) and (18) it is seen that the quantities $W_s$ and $W_p$ depend on the concentration of $v$-band holes $p$, the concentration of ionized acceptors $N_{-1}$, and the compensation ratio $K$.

From formulas (3) and (7) for $v$-band holes and holes in acceptor band we obtain

$$\frac{D_p}{\mu_p} = \frac{p}{e} \frac{dE_p}{dp} = \frac{\varepsilon}{e} \frac{k_B T}{\mu_p} = \frac{\varepsilon M_p}{N_{ch} dE_p} = \xi_p \frac{k_B T}{\mu_p},$$

$$\frac{D_h}{M_h} = \frac{E_p}{e} \frac{dE_p}{dN_{-1}} = \frac{\varepsilon}{e} \frac{k_B T}{\mu_p} = \frac{\varepsilon M_h}{N_{ch} dE_p} = \xi_h \frac{k_B T}{M_h},$$

(19)

where the dimensionless parameters $\xi_p$ and $\xi_h$ characterize the deviation of the ratio of the diffusion coefficient to the drift mobility from the classical value $k_B T/e$. According to [26, 28, 29, 46] these parameters are

$$\xi_p = \frac{e}{k_B T} \frac{D_p}{\mu_p} = \frac{p}{(1/V) \int_{-\infty}^{\infty} \varepsilon f_0 (1 - f_p) dE_p} \geq 1,$$

$$\xi_h = \frac{e}{k_B T} \frac{D_h}{M_h} = \frac{\int_{-\infty}^{\infty} \varepsilon f_0 f_{-1} d(E_s - E_a)}{\int_{-\infty}^{\infty} \varepsilon f_0 f_{-1} d(E_s - E_a)} \geq 1.$$
weakly (compared to the probabilities of filling hole states \( f_0 \) and \( f_0 = 1 - f_{-1} \)) dependent on the Fermi level \( E_F \). The quantities \( \xi_p \geq 1 \) and \( \xi_h \geq 1 \) characterize the difference in the extent to which the diffusion coefficient and the mobility of \( v \)-band and acceptor band holes are affected by fluctuations of the electrostatic potential energy in the crystal. The fluctuations decrease drift mobilities of holes stronger than their diffusion coefficients.

Equations (20) and (21) are supported by experiments [47] measuring the ratio of the diffusion coefficient to the drift mobility of holes \( (\xi_p \geq 1 \) and \( \xi_h \geq 1) \) in amorphous hydrogenated silicon at temperature \( T_{ph} \), where the turbulent (jumping or relay) regime of hole transport probably occurs [15, 48].

For the region of high temperature \( (T \approx T_i) \), at which practically all acceptors are ionized, the concentration of \( v \)-band holes \( p \approx (1 - K)N \). In particular, at \( T \approx T_i \), the fluctuations of the potential energy of holes are small \( (W_p' \approx k_B T) \) and \( |\delta E_v| \ll k_B T \), from equation (20) taking into account equations (8)–(11) we find (see also [49]):

\[
\frac{D_p}{\mu_p} = \frac{k_B T}{e} \xi_p = \frac{k_B T}{e} \frac{F_{1/2}(y_p)}{E_{-1/2}(y_p)},
\]

where \( F_j(y_p) \) is the Fermi–Dirac integral; \( y_p = E_F/k_B T \) is the ratio of the Fermi level \( E_F \) to the thermal energy \( k_B T \);

\[
F_j(y_p) = \frac{1}{\Gamma(j + 1)} \int_0^\infty \frac{q^j dq}{1 + \exp(q - y_p)};
\]

\[
\Gamma(j + 1) = \int_0^\infty t^j \exp(-t) dt; \quad E_{-1/2}(y_p) = \frac{dF_{1/2}(y_p)}{dy_p}.
\]

Two particular cases follow from equation (22): equation (4) for an ideal nondegenerate gas of \( v \)-band holes of \( p \)-type diamond, when \( y_p < 0 \) and \( |y_p| \gg 1 \), and equation (5) for an ideal degenerate gas of \( v \)-band holes, when \( y_p \gg 1 \). (Let us note that in [50] it is unreasonably stated that the relation \( D_p/\mu_p = k_B T/e, \) is also valid for an ideal degenerate gas of holes.)

For the region of low temperature \( (T < T_i) \), when \( p \ll N_A \approx K(1 - K)N \), only a fraction of acceptors, \( N_m/N \approx K \), is ionized, the other acceptors are electrically neutral, \( N_A/N \approx 1 - K \). For the narrow acceptor band \( (W_p' \ll k_B T) \) from equation (21), taking into account equations (13)–(17), we find \( \xi_h \approx 1 \), i.e. for hopping via acceptors holes \( D_h/M_h = k_B T/e \), which coincides with equation (4) for ideal nondegenerate gas of \( v \)-band holes. For the wide acceptor band \( (W_p' \gg k_B T) \), from equation (21) it follows that [29]

\[
\frac{D_h}{M_h} = \frac{k_B T}{e} \xi_h = K(1 - K) W_p' \frac{\sqrt{2\pi}}{e} \exp\left(\frac{-\gamma_h^2}{2}\right),
\]

where \( \gamma_h = (E_F + E_a + k_B T \ln \beta_a)/W_p' \) is found from the condition \( 2K = 1 - \text{erf}(\gamma_h/\sqrt{2}) \), which is followed from equation (13).

Note that \( D_h/M_h \) value according to equations (21) and (23) increases with the amplitude of electrostatic potential energy fluctuations \( W_p \). This means that the hopping mobility \( M_h \) of holes decreases more rapidly compared to their diffusion coefficient \( D_h \). This is explained by the fact that the actual trajectory of a hole diffusing via acceptors, on average, passes through the lower barriers as compared to the barriers that are produced by an external electric field and are responsible for the drift mobility \( M_h \) of this hole. The parameter \( \xi_h \) enters the expression for the coefficient of the differential thermo-emf for hopping migration of holes via acceptors [51].

To calculate \( \xi_p \) and \( \xi_h \) using equations (20) and (21) we need to establish the dependence of the energy of the acceptor band center \( E_a \) on the acceptor concentration \( N_A \), the compensation ratio \( K \), and the temperature \( T \).

According to [13, 30] and figure 1 the center of the acceptor band \( E_a > 0 \) (relative to the top of the \( v \)-band in the ideal crystal \( E_v = 0 \)) is given by the following expression

\[
E_a = I_s + \delta E_v = I_s + E_{\text{cor}} + E_{\text{per}} + E_{\text{exc}},
\]

where \( I_s \) is the energy level of a solitary acceptor in the ideal crystal, \( \delta E_v < 0 \) is the shift of the top of the \( v \)-band into the band gap due to the doping of crystal by impurity atoms, \( E_{\text{cor}} < 0 \) is the energy of the correlative reduction of the affinity of an acceptor in the charge state \(( -1) \) to a \( v \)-band hole due to the screening of the Coulomb field of the ionized acceptor by a cloud of charges surrounding it (with total charge \( +e \)), \( E_{\text{per}} < 0 \) is the percolation threshold for \( v \)-band holes, i.e. the minimum energy needed for \( v \)-band holes to migrate within the entire crystalline sample [13, 52], \( E_{\text{exc}} < 0 \) is the shift of the top of the \( v \)-band into the band gap due to the exchange interaction of holes in the \( v \)-band.

Let us consider three cases for energy quantities that compose \( \delta E_v \) in equation (24): (a) \( E_{\text{cor}} < 0 \) for \( E_{\text{per}} = E_{\text{exc}} = 0 \); (b) \( E_{\text{per}} < 0 \) for \( E_{\text{cor}} = E_{\text{exc}} = 0 \); and (c) \( E_{\text{exc}} < 0 \) for \( E_{\text{cor}} = E_{\text{per}} = 0 \).

(a) Calculation of \( E_{\text{cor}} \) taking into account screening of point charges in the Debye–Hückel approximation. We assume that the screening of the Coulomb field of a point charge in a semiconductor begins from the distance
$d_s \approx 0.554[N + KN + \rho]^{-1/3}$ which is the average distance between nearest neighbor acceptors, donors, and $v$-band holes responsible for the screening and for the maintenance of the electrical neutrality and ionization equilibrium [13, 30]. At the distances $r \geq d_s$ the total electrostatic potential $\Phi$ of an acceptor in the charge state $(-1)$ with a screening cloud of charges is determined by the solution of the linearized Poisson equation [19, 53]:

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\Phi}{dr} \right) = -\frac{\rho(\Phi)}{\varepsilon} = \Lambda_s^{-2} \Phi,$$

(25)

where $\rho(\Phi) = e \left( \rho(\Phi) + KN - N_{\text{ion}}(\Phi) \right)$ is the volume density of the screening electric charge, $\varepsilon = \varepsilon_0 \varepsilon_r$ is the dielectric permittivity of the crystal matrix, $\Lambda_s^{-2} = -(1/\varepsilon)(d\rho(\Phi)/d\Phi)$ at $\Phi \rightarrow 0$. For $r \geq d_s$ the solution of equation (25) with the boundary conditions $d\Phi/dr = e/4\pi\varepsilon_0 r_0^2$ at $r = d_s$ and $\Phi \rightarrow 0$ at $r \rightarrow \infty$ has the form [54]:

$$\Phi = \frac{-e}{4\pi\varepsilon r_0} \exp \left( \frac{d_s - r}{\Lambda_s} \right),$$

(26)

where $\Lambda_0$ is the screening radius of the Coulomb field of the impurity ion (and generally of a point charge) in an electrically neutral crystal.

Calculation [55–57] of the energy of electrostatic interaction of the acceptor ion with the cloud of screening charges with charge density $\rho(\Phi) = -e\Phi/\Lambda_s^2$ gives:

$$E_e = -e^2/4\pi\varepsilon(\Lambda_0 = d_i).$$

The energy of interaction between charges in the cloud is $E_{\text{ss}} = e^2/16\pi\varepsilon(\Lambda_s = d_s)$. As a result, the total electrostatic correlation energy $E_{\text{cor}}$ in the system ‘acceptor in the charge state $(-1)$ plus cloud of charges screening it’ is [35, 52, 57]:

$$E_{\text{cor}} = E_{\text{is}} + E_{\text{ss}} = \frac{-3e^2}{16\pi\varepsilon(\Lambda_0 + d_i)} < 0,$$

(27)

The quantity $E_{\text{cor}}$ can be treated as the local energy of a hole at the top of the $v$-band (with zero kinetic energy) with a cloud of charges screening it, i.e. as the energy of a plasma hole polaron [45, 52].

Note that in the Debye–Hückel approximation [53, 54] the charge density of charges screening an ion is proportional to the total electrostatic potential of the ion (acceptor in the charge state $(-1)$, i.e. having charge $-e < 0$) with the screening cloud of mobile charges ($v$-band holes and holes in the acceptor band); see linearized Poisson equation (25). According to [46, 57] only the linear approximation of the screening charge density [$\rho(\Phi) \propto \Phi$] is appropriate for the description of screening of the ion Coulomb field in the presence of fluctuations of electrostatic potential energy in a sample, i.e. at $W_p > k_B T$ and $W_e > k_B T$.

Taking into account equations (3) and (7), the radius of static screening of the Coulomb field of the impurity ion by $v$-band holes and holes of the acceptor band migrating over the crystal is determined by the following expression [see also [26, 28, 29, 46]]:

$$\Lambda_s^{-2} = \frac{e^2}{\varepsilon} \left( \frac{dp}{dE_F} - \frac{dN_{v-1}}{dE_F} \right) = \frac{e}{\varepsilon} \left( \frac{p \mu_p}{D_p} + \frac{N_h M_h}{D_h} \right) = \frac{e^2}{\varepsilon k_B T} \left( \frac{p}{\xi_p + \xi_h} \right).$$

(28)

where $p = N_{v-1} - KN$ according to equations (1) and (2) is the concentration of $v$-band holes in the vicinity of the screening ion, $N_h = (N - N_{\text{ion}})N_{v-1}/N$ according to equations (1) and (6) is the effective concentration of holes hopping via acceptors in the vicinity of the screening ion; $\xi_p$ and $\xi_h$ are the dimensionless parameters defined by equations (20) and (21).

Let us point out that the screening length $\Lambda_s$ is defined for the state of the thermodynamic equilibrium, i.e. at zero current densities $J_p = J_h = 0$. According to equation (28) at low temperatures ($T < T_J$, when $p/\xi_p \ll N_h/\xi_h$) the quantity $\Lambda_s$ is determined solely by holes hopping via acceptors $\Lambda_s \propto (N_h/\xi_h)^{-1/2}$, where $N_h = N_h N_{v-1}/N = K(1 - K)N$. The problem of the physical meaning of $N_h$ was formulated already in [58, 59] and solved in [16, 17], where it is shown that $N_h$ is the concentration of holes hopping via hydrogen-like acceptors, while $\xi_h \geq 1$ indicates the deviation of the $D_h/M_h$ ratio from the classical value $k_B T/\varepsilon$. By analogy with expression for the dc conductivity of $v$-band holes $\sigma_p = e\mu_p$, the dc hopping conductivity can be written as $\sigma_h = eN_h M_h$, where $M_h$ can be defined as the drift mobility of holes hopping via acceptors (see also equation (6) for the hopping current density $J_h$).

(b) Calculation of the percolation threshold $E_{\text{perc}}$ for $v$-band holes. Following [1, 36, 39] we assume that the critical part of the volume of a bulk semiconductor sample that is unavailable for the diffusive motion of $v$-band holes is equal to 0.17. Thus, taking into account equation (9) the threshold energy $E_{\text{perc}}$, above which the percolation of $v$-band holes sets on, is determined from the relation

$$\int_{-\infty}^{0} G_p dU_p = \frac{1}{\sqrt{2\pi W_p}} \int_{-\infty}^{0} \exp \left( -\frac{U_p^2}{2W_p^2} \right) dU_p = 0.17,$$
that yields

\[ E_{\text{per}} \approx -0.955W_p < 0, \]  

(29)

where \( W_p \) is given by equation (18).

(c) Calculation of the exchange energy \( E_{\text{exc}} \) for \( \nu \)-band holes. As the concentration of \( \nu \)-band holes increases, their exchange interaction becomes significant [52, 57, 60]. As a result, the energy of the top of the \( \nu \)-band \( (E_v = 0) \) for an undoped crystal shifts deeper into the band gap, decreasing the energy level \( E_{\text{per}} \) for hole percolation, equation (29), by the value of the exchange energy \( E_{\text{exc}} \) for a single \( \nu \)-band hole. That is equivalent to the top of the \( \nu \)-band approaching the center of the acceptor band \( E_a \) and is taken into account in equation (24).

The energy of the exchange interaction of \( \nu \)-band holes \( E_{\text{exc}} < 0 \) results from the symmetry of the wave function of holes relative to their transposition. In the effective mass approximation the Bloch wave functions of \( \nu \)-band electrons (and \( \nu \)-band holes) are replaced with the plane waves. In the absence of fluctuations of the potential energy of holes (i.e. when the density of states of \( \nu \)-band holes \( g_p \) in the ideal diamond crystal is determined by equation (11)) the energy of a hole with the absolute value of quasi-wave vector \(|k| = k \) and the effective mass \( m_p \) is equal to \((\hbar k)^2/2m_p + E_{\text{exc}}\). For these conditions the single-particle exchange energy \( E_{\text{exc}} < 0 \) is given by [60]:

\[ E_{\text{exc}} = -\frac{e^2}{2\pi^2 \varepsilon} k_1^2 \frac{H(y_e)}{F_{1/2}(y_e)}, \]  

(30)

where \( k_1 = \sqrt{2m_p k_0^2 \hbar^2 / \hbar} \) is the absolute value of the wave vector of a hole \( (k_1 \) is determined by the equation \((\hbar k_1)^2/2m_p = k_0^2 T)\); \( y_e = E_p / k_0^2 T; \)

\[ H(y_e) = \int_0^\infty qL^2(q) dq, \quad L(q) = \int_0^\infty \cos(qt) \ln[1 + \exp(y_e - t^2)] dt, \]

\[ F_{1/2}(y_e) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{t}}{1 + \exp(q - y_e)} dq. \]

For a nondegenerate gas of \( \nu \)-band holes \( (E_p < 0 \) and \(|E_p| \gg k_0^2 T) \) from equation (30) it follows that [60]:

\[ E_{\text{exc}} = -\frac{e^2}{8\pi^2 \varepsilon} k_p \exp \left( \frac{E_p}{k_0^2 T} \right). \]

For a degenerate gas of \( \nu \)-band holes \( (E_p > 0 \) and \(|E_p| \gg k_0^2 T) \) in the limit of zero temperature \( (T \rightarrow 0) \) equation (30) turns into the Slater formula [60–62]:

\[ E_{\text{exc}} = -\frac{3e^2}{8\pi^2 \varepsilon} k_p = -\frac{3e^2}{8\pi^2 \varepsilon} \sqrt{2m_p E_p}, \]

(31)

where \( \hbar k_p = \hbar (3\pi^2 \varepsilon)^{1/3} \) is the Fermi quasi-momentum of a \( \nu \)-band hole \( (k_p \) is determined by the equation \((\hbar k_p)^2/2m_p = E_p)\).

On the metallic side of the Mott transition, where the Fermi level \( E_p \gg k_0^2 T \) and \( E_p > E_{\text{per}} \) (figure 1), the quantity \( E_{\text{exc}} \) based on equation (31) can be tentatively averaged over the fluctuations of the potential energy \( U_p \) of holes [52]:

\[ \overline{E_{\text{exc}}} = \int_{-\infty}^{E_p} E_{\text{exc}}(U_p) G_p \ dU_p < 0, \]

where \( E_{\text{exc}}(U_p) = -(3e^2/8\pi^2 \varepsilon) \sqrt{2m_p (E_p - U_p)} \) is the exchange energy of a \( \nu \)-band hole with kinetic energy \( E_{\text{kin}} \approx E_p - U_p \); the probability density function \( G_p \) of potential energy \( U_p \) fluctuations relative to \( E_p = 0 \) is given by equation (9).

It should be pointed out that equation (27) for \( E_{\text{cot}} \) was derived at \( E_{\text{per}} = 0 \) and \( E_{\text{exc}} = 0 \); equation (29) for \( E_{\text{per}} \)—at \( E_{\text{cot}} = 0 \) and \( E_{\text{exc}} = 0 \), and equation (30) for \( E_{\text{exc}} \)—at \( E_{\text{cot}} = 0 \) and \( E_{\text{per}} = 0 \).

We based the estimate of the ratio of concentration of \( \nu \)-band holes \( p_{\text{per}} \) that have the energy \( E_p < \delta E_v \) and may migrate only in restricted regions of a bulk crystal sample to the total concentration of holes in the \( \nu \)-band on equation (8) and found

\[ \frac{p_{\text{exc}}}{p} = \frac{\int_{E_p}^{E_\text{exc}} g_p (E_p - \Delta_p) f_p (E_p - \Delta_p) dE_p}{\int_{-\infty}^{E_\text{exc}} g_p (E_p - \Delta_p) f_p (E_p - \Delta_p) dE_p}, \]

(32)

where \( \Delta_p = E_{\text{cot}} + E_{\text{exc}} = \delta E_v - E_{\text{per}} \), taking into account equations (27), (29) and (30). In equation (32) the density of states of holes in the \( \nu \)-band \( g_p (E_p - \Delta_p) \) is given by equation (10) with the energy of the hole \( E_p \) replaced by \( E_p - \Delta_p \); the Fermi–Dirac distribution function for \( \nu \)-band holes \( f_p (E_p - \Delta_p) = [1 + \exp((E_p - \Delta_p - E_p)/k_0^2 T)]^{-1} \) is written taking into account the shift of the reference point for the total energy \( E_p \) of a hole (see inset in figure 1) from \( E_v = 0 \) by \( \Delta_v < 0 \) deep into the band gap.
3. Algorithm of numerical calculations

Let us consider the algorithm for solving the system of equations (1), (8), (13) and (24). For an initial estimate of the target values \( E_b, W_v, W_p, E_{b, e}, N_{-1}, p \) we consider the case of \( p \)-type diamond crystals lightly doped with boron. In such crystals \( W_b \ll \hbar k T, W_v \ll \hbar k T, \delta E_e = 0, \) and \( E_x \approx I_b = 370 \text{ meV} \). Taking into account the excited states of electrically neutral boron atoms the electrical neutrality condition (1) takes the form (see, e.g., [19, 21, 37]):

\[
p(KN + p + p_e) = p_0 (1 - K) N,
\]

where \( p_0 = (p_e / \beta_w) \exp(-I_b / kT); p_e = (2(2\pi m_p kT)^{3/2} / (2\pi \hbar)^3; \) the degeneracy factor \( \beta_w \) is determined from equation (15) where \( E_x = \hbar k \).

The algorithm for solving for the system of equations (1), (8)–(30) numerically consists of four steps (see also [13, 30]):

(i) Initial parameters of a diamond doped with boron atoms are set: \( \varepsilon_t, \beta_w, I_b, m_p, \) the temperature \( T, \) the compensation ratio \( K, \) the range of variation of the doping impurity concentration (boron) \( N, \) and the relative error of calculations \( \varepsilon_{\text{goal}} = 10^{-5}. \)

(ii) Using the initial estimate, from equation (33), the concentration of \( v \)-band holes \( p \) in an ideal \( p \)-Dia:B is calculated. Then, according to equations (17) and (18), where \( N_{bh} = 2(p + KN), \) seed values of the root-mean-square fluctuations \( W_v \) and \( W_p \) are evaluated.

(iii) The nonlinear electrical neutrality equation (1) is solved for the unknown Fermi level \( E_b \) using the values of \( W_v \) and \( W_p \) obtained in the previous step. The quantities \( p \) and \( N_{-1} \) in equation (1) are determined using equations (8) and (13) taking into account equations (9), (10), (14)–(30). The computed value of \( E_b \) allows to refine the values of \( W_v, W_{b, e}, E_{b, e}, N_{-1}, \) and \( p. \)

(iv) The solution of the electrical neutrality equation (1) and refinement of the values of \( W_v, W_{b, e}, E_{b, e}, N_{-1}, \) and \( p \) are iteratively performed until their relative error becomes less than a cutoff value \( \varepsilon_{\text{goal}}. \) The relative error \( \varepsilon(X) \) for the value of a calculated quantity \( X = \{E_b, W_v, W_{b, e}, E_{b, e}, N_{-1}, p \} \) is \( \varepsilon(X) = 2[X_k - X_{k-1}] / [X_k + X_{k-1}], \) where \( X_k \) is the value of a quantity \( X \) at the \( k \)th step of the iterative procedure.

Let us test this algorithm on the experimental results of [63], where a homoepitaxial crystalline film of \( p \)-Dia:B treated in hydrogen plasma in order to obtain a negative electron affinity was studied using photoelectric spectroscopy at \( T = 300 \text{ K}. \) According to [63] at the concentration of boron atoms \( N = (2 - 3) \times 10^{20} \text{ cm}^{-3} \) the Fermi level \( E_b \) is located in the band gap at \( 90 - 120 \text{ meV} \) above the top of the \( v \)-band of the undoped diamond crystal. Calculations using equations (1), (8)–(30) at \( T = 300 \text{ K} \) gives \( E_b \approx 100 \text{ meV} \) for \( N = 2.5 \times 10^{20} \text{ cm}^{-3} \) at \( K \approx 0.27. \) (The relatively high compensation ratio at this boron concentration can be attributed to the compensation of boron atoms by hydrogen; see also [64].)

4. Numerical calculation of the ionization equilibrium in \( p \)-Dia:B crystals at the temperature \( T_j \)

In [4, 13, 30] the characteristic temperature \( T_j \) of the transition from the HC regime to the BC regime of hole migration is determined on the basis of the virial theorem. According to these references, the value of temperature \( T_j, \) where \( \sigma_b = \sigma_h \) (figure 1), is found from the equation

\[
T_j = \frac{0.728}{k_B} \frac{e^2}{4\pi\varepsilon} [N_{-1}(T_j) + p(T_j)]^{1/3},
\]

where \( N_{-1}(T_j) \) and \( p(T_j) \) are determined according to the electroneutrality condition (1).

Note that in [30] for calculation of \( T_j \) by equation (34) the concept of the nearest neighbors (ionized acceptors and mobile \( v \)-band holes) was introduced at their Poisson distribution over a crystal. For instance, the \( v \)-band hole and the acceptor in the charge state \((-1)\) are the nearest neighbors when this acceptor is the nearest to this hole and this hole is the nearest to this ionized acceptor.

In the limit of a low concentration of \( v \)-band holes, \( p(T_j) \ll N_{-1}(T_j) \approx KN, \) from equation (34) it follows that

\[
T_j \approx \frac{0.728}{k_B} \frac{e^2}{4\pi\varepsilon} (KN)^{1/3},
\]

where \( KN \) is the concentration of hydrogen-like donors that compensate the boron atoms (as hydrogen-like acceptors) in the \( p \)-type diamond.

Calculations of the temperature \( T_j \) as a function of the concentration of doping and compensating impurities using equations (34) and (35) agree with experimental data for diamond (\( \varepsilon_t = \varepsilon / \varepsilon_0 = 5.7, \))
germanium ($\varepsilon_1 = 15.4$), silicon ($\varepsilon_2 = 11.47$), and gallium arsenide ($\varepsilon_3 = 12.4$) crystals doped with hydrogen-like impurities \cite{4, 13, 30}.

The algorithm for calculating $W_a$, $W_p$, $E_a$, $N_1$, and $p$ at temperature $T_j$ using equation (34) is similar to that described in section 3 and consists of four steps:

(i) The seed value $T_j$ using equation (35) is initially set.

(ii) Using the described iterative procedure the values $W_a$, $W_p$, $E_a$, $N_1$, and $p$ at the seed temperature $T_j$ are calculated until their relative error becomes less than $\varepsilon_{\text{goal}}$.

(iii) Using equation (34) the value of $T_j$ is refined.

(iv) Steps (ii) and (iii) are performed until the relative error of $T_j$ becomes less than $\varepsilon_{\text{goal}}$.

Figure 2 shows the temperature $T_j$ of the transition from $v$-band to hopping conduction (upper panel; calculation using equation (34)), the Fermi level $E_F < 0$ and the shift of the top of the $v$-band into the band gap $\delta E_v < 0$ at $T = T_j$ (lower panel) on the concentration $N$ of the doping impurity (boron atoms as acceptors) in a $p$-type diamond at compensation ratios of acceptors by donors: $K = 0.03$ (curves 1) and 0.3 (curves 2). The temperature $T_j$ calculated using equation (35) is shown by dashed lines.

Figure 3 shows the parameters $\xi_p = eD_p/\mu_p k_B T$ (for $v$-band holes) and $\xi_v = eD_h/\mu_h k_B T$ (for acceptor band holes) calculated using equations (20) and (21) at the temperature $T = T_j$ obtained from equation (34) on the concentration $N$ of the doping impurity (boron atoms) in a $p$-type diamond for the compensation ratios: $K = 0.03$ (curves 1) and 0.3 (curves 2).
5. Discussion of the calculation results

5.1. Hall effect at temperatures close to \( T_j \)

Numerical calculation using equation (32) gives the ratio \( P_{\text{loc}}/P < 0.1 \) for \( N < 3 \times 10^{20} \text{ cm}^{-3} \) at \( K \geq 0.01 \). This estimate allows to conclude that the concentration of totally free \( \nu \)-band holes \( P_{\text{mob}} = p - P_{\text{loc}} \) is practically equal to the average hole concentration \( p \) given by equation (8). This conclusion is supported by the analytical estimates \([65]\) that identify the measured Hall concentration of holes in strong magnetic field with the average concentration of \( \nu \)-band holes in a bulk \( p \)-type semiconductor.

At the temperature \( T_j \), where \( \sigma_H(T_j) \approx \sigma_H(T_j) \), the experimentally measured Hall coefficient \( R_{11}(T_j) \) is \([20, 21, 37, 66]\):

\[
R_{11} = \frac{R_p \sigma_p^2 + R_s \sigma_h^2}{(\sigma_p + \sigma_h)^2} \approx \frac{R_p}{4} = \frac{r_p}{4eF},
\]

where we assumed that the Hall coefficient \( R_H(T_j) \) of holes hopping via acceptors is much smaller than the Hall coefficient \( R_p(T_j) \) of \( \nu \)-band holes; \( r_p(T_j) \) is the Hall-factor; in classically strong magnetic fields \( r_p \approx 1 \). (Here and below we neglect the effect of the external magnetic field on \( \sigma_p \) and \( \sigma_h \).)

At \( T_j \) the conditions \( eF \mu_p = eN_h M_p \) and \( p \ll N_h \approx K (1 - K) N \) hold. Taking this into account, from equation (36) we find the ratio of the drift mobility \( M_p \) of holes hopping via acceptors to the drift mobility \( \mu_p \) of \( \nu \)-band holes in the form

\[
\frac{M_p(T_j)}{\mu_p} = \frac{r_p}{4eF (1 - K) N},
\]

where the notation \( \mu_p^{(H)} = \mu_p(T_j) \) is introduced.

It follows from equation (37) that by measuring the Hall coefficient \( R_{11} \) and the Hall mobility of \( \nu \)-band holes \( \mu_p^{(H)} = R_{11}(\sigma_p + \sigma_h) = 2R_{11}\sigma_p = r_p \mu_p^{(H)} / 2 \) at \( T_j \) we can assess the value of the drift hopping mobility via acceptors (see also \([13]\)): \( M_p(T_j) = \mu_p^{(H)} / 2eR_{11} K (1 - K) N \). According to \([67]\), at the boron concentration \( N \approx 1.2 \times 10^{19} \text{ cm}^{-3} \) and the temperature \( T_j \approx 364 \text{ K}, \) the Hall coefficient \( R_{11} \approx 349 \text{ cm}^2/\text{C}, \) and \( \mu_p^{(H)} = \sigma_p R_{11} \approx 71 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}. \) For \( K = 0.3 \) we find \( M_p(T_j) \approx 0.25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}. \) Thus, at \( T_j \) the drift hopping mobility \( M_p(T_j) \) of holes via boron atoms is much smaller than the Hall mobility \( \mu_p^{(H)} \) of \( \nu \)-band holes; this result agrees with the approximate equation (36) that reflects the negligible contribution of hopping holes to the Hall effect.

5.2. Hopping electrical conductivity at temperatures close to \( T_j/2 \)

In the vicinity of \( T_j \approx T_j/2 \) (figure 1) the temperature dependence of the dc hopping electrical conductivity via acceptors \( \sigma_h \gg \sigma_p \) is described by the expression \([13, 18, 36]\):

\[
\sigma_h = \sigma_3 \exp \left(-\frac{\varepsilon_3}{k_b T}\right),
\]

where \( \sigma_3 \) is a pre-exponential factor that weakly depends on the temperature (compared to the exponent), \( \varepsilon_3 \) is the thermal activation energy of hopping migration of holes between nearest acceptors in the charge states (0) and (−1).

At the temperature \( T_j \) the concentration of holes hopping via acceptors \( N_h \approx K (1 - K) N \) is much greater than the concentration of \( \nu \)-band holes \( p \) and the electrical neutrality condition (1) takes the form: \( N_{-1} = K N \).

For a wide acceptor band (\( W_a \gg k_b T_j \)) at the temperature \( T_j = T_j/2, \) where \( T_j \) is given by equation (35), we obtain the integral activation energy of hopping migration of holes via acceptors, from equation (38) taking into account equations (13), (17), (21), and (23), in the form \([28, 29]\):

\[
\varepsilon_3 = -k_b T_j \ln(\sigma_h / \sigma_3) = k_b T_j \ln \xi_3,
\]

where

\[
T_j = \frac{0.364}{k_b} \frac{e^2}{4\pi \varepsilon \varepsilon_0} (K N)^{1/3}; \quad \xi_3 = \xi_3(T_j) = K (1 - K) \frac{W_a \sqrt{2\pi}}{k_b T_j} \exp \left(\frac{\gamma_a}{2}\right); \quad W_a \approx 2.64 \frac{e^2}{4\pi \varepsilon \varepsilon_0} (2KN)^{1/3}; \quad 2K = 1 - \text{erf}\left(\frac{\gamma_a}{\sqrt{2}}\right); \quad \frac{W_a}{k_b T_j} \approx 9.14.
\]

Calculations that use equation (39) agree (see figure 4) with the experimental data \([67–72]\) for \( p \)-DiaB with the compensation ratios \( K \) from 0.1 to 0.5 at \( N < 0.3 N_M \), where \( N_M \approx 4 \times 10^{20} \text{ cm}^{-3} \) is the concentration of boron atoms corresponding to the transition of diamond (at temperature \( T \to 0 \)) from the insulating to the
metallic state. One should bear in mind that the compensation ratio \( K \) of the majority impurity (boron atoms as acceptors) by the minority impurity (donors) usually decreases with the boron concentration in synthetic \( p \)-type diamond crystals.

Note that according to [73] equation (39) is applicable when the variance of acceptor energy levels \( W_a \) due to electrostatic fluctuations is larger than the broadening of these levels due to the finiteness of localization time of holes on them.

6. Conclusions

The ionization equilibrium and the migration of holes at temperatures close to the temperature \( T_n \), for which the dc electrical conductivity of the \( \nu \)-band holes is approximately equal to the dc hopping electrical conductivity of holes via boron atoms (hydrogen-like acceptors), are studied for a \( p \)-type diamond crystal. For the first time, the ratios of the diffusion coefficient to the drift mobility are calculated for both \( \nu \)-band holes (hydrogen-like acceptors) and holes hopping via boron atoms (hydrogen-like donors). A quantitative estimate for the shift \( \delta E_v \) of the valence band into the band gap as a function of the boron atom (majority impurity) concentration and the compensation ratio is also given.

The dependence of the thermal activation energy \( \varepsilon_3 \) of the dc hopping electrical conductivity of \( p \)-Dia:B on the concentration of boron atoms at the temperature \( T_n = T_j/2 \) and moderate compensation ratios \((K = 0.1-0.5)\) of acceptors by hydrogen-like donors is calculated. For diamond with boron concentration \( N \) in the range from \( 3 \times 10^{17} \) to \( 3 \times 10^{20} \) cm\(^{-3}\) (i.e. on the insulating side of the Mott transition) we find quantitative agreement of calculation results with the experimental values of \( \varepsilon_3 \) obtained from measurements of the thermal dependence of hopping electrical conductivity.

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References

[1] Sen A K, Bardhan K K and Chakrabarti B K (ed) 2009 Quantum and Semi-Classical Percolation and Breakdown in Disordered Solids (Berlin: Springer)

[2] Rogalski A 2012 Progress in focal plane array technologies Prog. Quant. Electron. 36 342–473
[3] Shlimak I 2015 Is Hopping a Science? Selected Topics of Hopping Conductivity (Singapore: World Scientific)

[4] Poklonski N A, Vyrko S A, Poklonskaya O N and Zabrodskii A G 2011 Transition temperature from band to hopping direct current in crystalline semiconductors with hydrogen-like impurities: heat versus Coulomb attraction J. Appl. Phys. 110 123702

[5] Takahashi K, Yoshikawa A and Sandhu A (ed) 2007 Wide Bandgap Semiconductors: Fundamental Properties and Modern Photonic and Electronic Devices (Berlin: Springer)

[6] Klemencic G M, Mandal S, Werrell J M, Giblin S R and Williams O A 2017 Superconductivity in planarised nanocrystalline diamond films Sci. Technol. Adv. Mater. 18 239–44

[7] Okazaki H, Wakita T, Muro T, Nakamura T, Muraoka Y, Yokota Y, Kurihara S, Kawarada H, Osachi T and Takano Y 2015 Signature of high Tc above 25 K in high quality superconducting diamond Appl. Phys. Lett. 106 052601

[8] Bennet K E et al 2016 A diamond-based electrode for detection of neurochemicals in the human brain Front. Hum. Neurosci. 10 102

[9] Neumark G F 1979 Analysis of the pretransition range of the metal–insulator transition in doped semiconductors Phys. Rev. B 20 1519–26

[10] Mott N 1987 The mobility edge since 1967 J. Phys. C: Solid State Phys. 20 3075–102

[11] Gantmakher V F and Dolgopolov V T 2008 Localized—delocalized electron quantum phase transitions Phys. Usp. 51 3–22

[12] Klein T et al 2007 Metal–insulator transition and superconductivity in boron-doped diamond Phys. Rev. B 75 165313

[13] Poklonski N A, Vyrko S A, Poklonskaya O N, Kovalev A I and Zabrodskii A G 2016 Ionization equilibrium at the transition from valence-band to acceptor-band migration of holes in boron-doped diamond J. Appl. Phys. 119 245701

[14] Wagner C 1931 Zur Theorie der Gleichrichterwirkung (Theory of the rectifier effect) Z. Phys. 32 641–5

[15] Mott N F and Gurney R W 1948 Electronic Processes in Ionic Crystals (Oxford: Clarendon)

[16] Poklonski N A, Stelmakh V F and Tkachev V D 1976 To phenomenological theory of hopping conduction in semiconductors Dokl. Akad. Nauk USSR 20 783–5

[17] Poklonski N A and Stelmakh V F 1983 Screening of electrostatic fields in crystalline semiconductors by electrons hopping over defects Phys. Status Solidi B 117 93–9

[18] Grundmann M 2016 The Physics of Semiconductors. An Introduction Including Nanophysics and Applications (Berlin: Springer)

[19] Seeger K 2004 Semiconductor Physics. An Introduction (Berlin: Springer)

[20] Bonch-Bruevich V L and Kalashnikov S G 1990 Physics of Semiconductors (Moscow: Nauka)

[21] Blakemore J S 2002 Semiconductor Statistics (New York: Dover)

[22] Castner T G 1997 Einstein relations near the metal–insulator transition Phys. Rev. B 55 4003–6

[23] Wagner C 1930 Über den Zusammenhang zwischen Ionenbeweglichkeit und Diffusionsgeschwindigkeit in festen Salzen (The connection between ionic mobility and diffusion velocity in solid salts) Z. Phys. Chem. B 11 139–51

[24] Landeberg P T 1952 On the diffusion theory of rectification Proc. R. Soc. Lond. A 213 226–57

[25] Sondheimer E H 2001 The mean free path of electrons in metals Adv. Phys. 50 499–537

[26] Poklonski N A and Lapatin S Y 2000 A model of hopping and band DC photoconduction in doped crystals Phys. Solid State 42 224–9

[27] Poklonski N A and Lapatin S Y 2000 Fiz. Tverd. Tela 42 218–23

[28] Posnov A V, Jansson, Baranovskii S D, Osterbacka R, Dvurechenskii A V and Gebhard F 2010 Effect of electric field on diffusion in disordered materials: II. Two- and three-dimensional hopping transport Phys. Rev. B 81 115204

[29] Poklonski N A, Vyrko S A and Zabrodskii A G 2010 Quasiclassical description of the nearest-neighbor hopping dc conduction via hydrogen-like donors in intermediate compensated GaAs crystals Semicond. Sci. Technol. 25 085006

[30] Poklonski N A, Vyrko S A and Zabrodskii A G 2009 Model of hopping dc conductivity via nearest neighbor boron atoms in moderately compensated diamond crystals Solid State Commun. 149 1248–53

[31] Poklonski N A, Vyrko S A, Poklonskaya O N and Zabrodskii A G 2016 Role of electrostatic fluctuations in doped semiconductors upon the transition from band to hopping conduction (by the example of p-Ge:Ga) Semiconductors 50 722–34

[32] Poklonski N A, Vyrko S A, Poklonskaya O N and Zabrodskii A G 2016 Fiz. Tekh. Poluprovodn. 50 738–50

[33] Baranovskii S D, Faber T, Hensel F and Thomas P 1998 On the Einstein relation for hopping electrons Phys. Status Solidi b 205 87–90

[34] Ghosh S and Chakravarti A N 1988 Effect of broadening of tail states on the Einstein relation in heavily doped compensated semiconductors Phys. Status Solidi b 147 355–60

[35] Chakravarti A N, Ghatak K P, Ghosh S and Chowdhury A K 1982 Effect of heavy doping on the electronic heat capacity in semiconductors Phys. Status Solidi b 109 705–10

[36] Ghatak K P, Chowdhury A K, Ghosh S and Chakravarti A N 1980 Effect of temperature on the validity of the Einstein relation in heavily doped semiconductors Appl. Phys. 23 241–4

[37] Poklonski N A, Vyrko S A, Poklonskaya O N and Zabrodskii A G 2009 A model of ionization equilibrium and Mott transition in boron doped crystalline diamond Phys. Status Solidi b 246 158–63

[38] Shklovskii B I and Efros A L 1984 Electronic Properties of Doped Semiconductors (Berlin: Springer)

[39] Poklonski N A, Vyrko S A and Podenok S I. L 2005 Statistical Physics of Semiconductors (Moscow: KomKniga)

[40] Kane E O 1985 Band tails in semiconductors Solid State Electron. 28 3–10

[41] Ziman J M 1979 Models of Disorder: The Theoretical Physics of Homogeneously Disordered Systems (Cambridge: Cambridge University Press)

[42] Adachi S 2009 Properties of Semiconductor Alloys: Group-IV, III–V and II–VI Semiconductors (Chippenham: Wiley)

[43] Poklonski N A, Vyrko S A, Kovalev A I and Zabrodskii A G 2016 A quasi-classical model of the Hubbard gap in lightly compensated semiconductors Semiconductors 50 299–308

[44] Poklonski N A, Vyrko S A and Kovalev A I and Zabrodskii A G 2016 Fiz. Tekh. Poluprovodn. 50 302–12

[45] Whittle P 2000 Probability via Expectation (New York: Springer)

[46] Madelung O 2004 Semiconductors: Data Handbook (Berlin: Springer)

[47] Lucovsky G 1965 Gaussian impurity bands in GaAs Solid State Commun. 3 105–8

[48] Poklonski N A, Syaglo A I and Borovik F N 1996 Quasiclassical calculation of narrowing of the band gap in silicon with heavy doping Semiconductors 30 924–7

[49] Poklonski N A, Syaglo A I and Borovik F N 1996 Fiz. Tekh. Poluprovodn. 30 1767–73

[50] Poklonski N A 1984 Screening of the electric field in covalent crystals containing point defects Surf. Phys. 27 945–7

[51] Poklonski N A 1984 Izv. Vyssh. Uchebn. Zaved. Fiz. 27 41–3

[52] Gu Q, Schiff E A, Grebner S, Wang F and Schwarz R 1996 Non–Gaussian transport measurements and the Einstein relation in amorphous silicon Phys. Rev. Lett. 76 3136–9

[53] Datta S 1980 Simple theory for conductivity and Hall mobility in disordered systems Phys. Rev. Lett. 44 828–31
[49] Khan A and Das A 2010 Diffusivity–mobility relationship for heavily doped semiconductors with non-uniform band structures Z. Naturforsch. A 65 882–6
[50] Palenskis V 2014 Transport of electrons in donor-doped silicon at any degree of degeneracy of electron gas World J. Condens. Matter Phys. 4 123–33
[51] Poklonski N A and Lopatin S Y 2001 A lattice model of thermopower in hopping conduction: application to neutron-doped crystalline germanium Phys. Solid State 43 2219–28
Poklonski N A and Lopatin S Y 2001 J. Phys. T.ela 43 2126–34
[52] Poklonski N A and Vyryko S A 2002 Electrostatic model of edge luminescence of heavily doped degenerate semiconductors J. Appl. Spectrosc. 69 434–43
Poklonski N A and Vyryko S A 2002 Zh. Prikl. Spektrosk. 69 375–82
[53] Delvy P and Hückel E 1923 Zur Theorie der Elektrolyte Phys. Zeitschrift 24 185–206
[54] Kubo R, Ichimura H, Usui T and Hashitsume N 2004 Statistical Mechanics. An Advanced Course with Problems and Solutions (Amsterdam: North-Holland)
[55] Lanyon H P D and Tuft R A 1979 Bandgap narrowing in moderately to heavily doped silicon IEEE Trans. Electron Dev. 26 1014–8
[56] Poklonski N A, Syaglo A I and Biskupski G 1999 A model of how the thermal ionization energy of impurities in semiconductors depends on their concentration and compensation Semiconductors 33 402–6
Poklonski N A, Syaglo A I and Biskupski G 1999 Fiz. Tekh. Poluprovodn. 33 415–9
[57] Poklonski N A and Vyryko S A 2002 Nonlinear screening of the field of a dopant ion on the metal side of the Mott phase transition in semiconductors Phys. Solid State 44 1425–40
Poklonski N A and Vyryko S A 2002 Fiz. T.ela 44 1185–9
[58] Brooks H 1955 Theory of the electrical properties of germanium and silicon Advances in Electronics and Electron Physics vol 7 ed L Marton (New York: Academic) pp 85–182
[59] Stern F 1974 Low-temperature limit of screening length in semiconductors Phys. Rev. B 9 4597–8
[60] Konstantinov O V, Obolenskii O I and Tsarenkov B V 1997 Exchange energy of a free electron in a semiconductor Semiconductors 31 484–8
Konstantinov O V, Obolenskii O I and Tsarenkov B V 1997 Fiz. Tekh. Poluprovodn. 31 571–6
[61] Slater J C 1967 Insulators, Semiconductors and Metals (New York: McGraw-Hill)
[62] Ashcroft N W and Mermin N D 1976 Solid State Physics (New York: Harcourt College Publishers)
[63] Takeuchi D, Ogura M, Tokuda N, Okushi H and Yamasaki S 2009 Doping-induced changes in the valence band edge structure of homoepitaxial 6 boron-doped diamond films below Mott’s critical density Phys. Stat. Solidi a 206 1991–5
[64] Kumar A et al 2011 Boron-deuterium complexes in diamond: How inhomogeneity leads to incorrect carrier type identification J. Appl. Phys. 110 033718
[65] Shik A Y 1983 Percolation Hall effect in strong magnetic field Sov. Phys. Semicond. 17 1422
Shik A Y 1983 Fiz. Tekh. Poluprovodn. 17 2220–2
[66] Aono M, Maida O and Ito T 2011 Hall data analysis of heavily boron-doped CVD diamond films using a model considering an impurity band well separated from valence bands Diam. Relat. Mater. 20 1357–62
[67] Borst T H and Weis O 1996 Boron-doped homoepitaxial diamond layers: fabrication, characterization, and electronic applications Phys. Status Solidi a 158 423–44
[68] Malta D M, von Windheim J A, Wynands H A and Fox B A 1995 Comparison of the electrical properties of simultaneously deposited homoepitaxial and polycrystalline diamond films J. Appl. Phys. 77 1536–45
[69] Visser E P, Bauhuis G J, Janssen G, Vollenberg W, van Enckevort W J P and Giling L J 1992 Electrical conduction in homoepitaxial, boron-doped diamond films J. Phys.: Condens. Matter 4 7365–76
[70] Mamin R F and Inushima T 2001 Conductivity in boron-doped diamond Phys. Rev. B 63 033201
[71] Mortet V, Daenen M, Teraji T, Lazee A, Vorlicek V, D’Haen J, Haenen K and D’Olieslaeger M 2008 Characterization of boron doped diamond epilayers grown in a NIRIM type reactor Diam. Relat. Mater. 17 1330–4
[72] Jaggio G, Messina G, Santangeli S, Prestopino G, Ciancaglini I and Marinelli M 2012 Raman scattering in boron-doped single-crystal diamond used to fabricate Schottky diode detectors J. Quant. Spectrosc. Radiat. Transfer 113 2476–81
[73] Poklonski N A, Lopatin S Y and Zabrodskii A G 2000 A lattice model of nearest-neighbor hopping conduction and its application to neutron-doped GeGa Phys. Solid State 42 441–9
Poklonski N A, Lopatin S Y and Zabrodskii A G 2000 Fiz. T.ela 42 432–9