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

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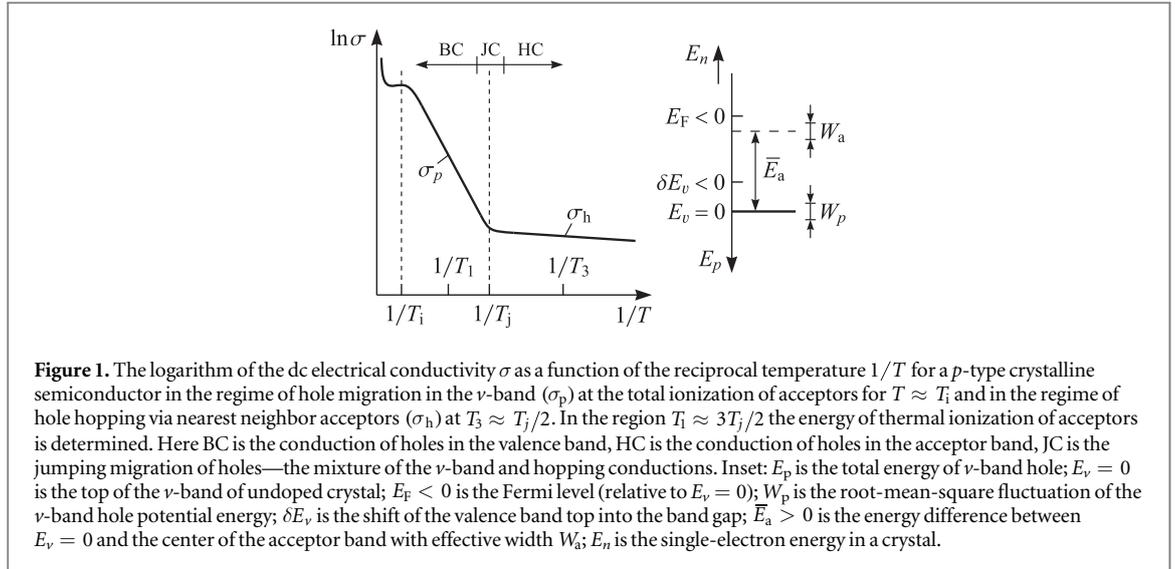
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Abstract

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 $T_3 \approx T_j/2$. 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 3×10^{17} to 3×10^{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)

Figure 1. The logarithm of the dc electrical conductivity σ 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 (σ_p) at the total ionization of acceptors for $T \approx T_i$ and in the regime of hole hopping via nearest neighbor acceptors (σ_h) at $T_3 \approx T_j/2$. In the region $T_i \approx 3T_j/2$ the energy of thermal ionization of acceptors is determined. Here BC is the conduction of holes in the valence band, HC is the conduction of holes in the acceptor band, JC is the jumping migration of holes—the mixture of the v-band and hopping conductions. Inset: E_p is the total energy of v-band hole; $E_v = 0$ is the top of the v-band of undoped crystal; $E_F < 0$ is the Fermi level (relative to $E_v = 0$); W_p is the root-mean-square fluctuation of the v-band hole potential energy; δE_v is the shift of the valence band top into the band gap; $\overline{E}_a > 0$ is the energy difference between $E_v = 0$ and the center of the acceptor band with effective width W_a; E_n is the single-electron energy in a crystal.

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

$$p + KN = N_{-1}, \tag{1}$$

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 $\delta E_v < 0$ (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 σ_p and the stationary Hall effect. We will denote their concentration as p_{mob}. On the other hand, holes in the v-band with energy $E_p < \delta E_v$ 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_{loc} be the concentration of partially free v-band holes. The total concentration of v-band holes is $p = p_{\mathrm{mob}} + p_{\mathrm{loc}}$. We will show that $p_{\mathrm{loc}}/p \ll 1$ on the insulating side of the concentration transition insulator–metal (Mott transition) for $K \leqslant 0.5$ 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 $N = N_{\mathrm{M}} \approx 4 \times 10^{20}$ 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 σ_p and the hopping σ_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]:

$$J_p = ep\mu_p \mathscr{E} - eD_p \frac{dp}{dx} = \sigma_p \mathscr{E} - eD_p \frac{dp}{dx}, \tag{2}$$

where e is the elementary charge, p is the concentration of v-band holes, μ_p is the hole drift mobility, $\mathscr{E} = -d\varphi/dx$ is the value of the external electric field strength directed along x axis; φ is the electric potential, x is the coordinate, D_p is the diffusion coefficient, $\sigma_p = ep\mu_p$ is the dc conductivity of v-band holes.

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 $\mathscr{E} \neq 0$, in the limit $\varphi(x) \to 0$ for all x we get [19–21]:

$$\frac{D_p}{\mu_p} = \frac{p\mathscr{E}}{dp/dx} = -\frac{p}{dp}\frac{d\varphi}{dp} = \frac{p}{e}\frac{d\zeta_F}{dp} = \frac{p}{e}\frac{dE_F}{dp}, \tag{3}$$

where $\zeta_F(x) = E_F - e\varphi(x)$ is the electrochemical potential of holes in the point with the coordinate x; E_F 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 v-band holes $\sigma_p = e^2 D_p\, dp/d\zeta_F = e^2 D_p\, dp/dE_F$, that is used for analyzing the conditions and quantitatively describing the insulator–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 v-band hole W_p is much smaller than the thermal energy $k_B T$, the shift of the v-band top $\delta E_v = 0$, and the Fermi level $E_F < 0$, $|E_F| \gg k_B T$, from equation (3) follows the Nernst–Einstein–Smoluchowski relation [23] (see also [15]):

$$\frac{D_p}{\mu_p} = \frac{k_B T}{e}, \tag{4}$$

where k_B is the Boltzmann constant, T is the absolute temperature; $k_B T$ is the thermal energy.

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

$$\frac{D_p}{\mu_p} = \frac{2E_F}{3e} > \frac{k_B T}{e}. \tag{5}$$

Comparison of equations (4) and (5) shows that for degenerate gas of v-band holes the D_p/μ_p ratio become greater than the one for nondegenerate gas of v-band holes. This is due to the fact that $D_p \propto l_F^2/\tau_F = \tau_F v_F^2$ and $\mu_p \propto \tau_F$, where $l_F = v_F \tau_F$ is the mean free path [25] of hole in a crystal, τ_F is the quasimomentum relaxation time of v-band hole, $v_F \propto \sqrt{E_F}$ 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]:

$$J_h = eN_h\left[M_h\mathscr{E} - D_h\frac{d}{dx}\ln\left(\frac{N_0}{N_{-1}}\right)\right] = \sigma_h\mathscr{E} - eD_h\frac{dN_0}{dx}, \tag{6}$$

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, $\mathscr{E} = -d\varphi/dx$ 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 $\mathscr{E} \neq 0$, 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 $\mathscr{E} = -d\varphi/dx \neq 0$ and that the electrochemical potential $\zeta_F(x) = E_F - e\varphi(x)$ in the limit $\varphi(x) \to 0$ for all x we get

$$\frac{D_h}{M_h} = \frac{\mathscr{E}}{d\ln(N_0/N_{-1})/dx} = -\frac{d\varphi}{d\ln(N_0/N_{-1})} = \frac{N_h}{e}\frac{d\zeta_F}{dN_0} = \frac{N_h}{e}\frac{dE_F}{dN_0}, \tag{7}$$

where $dE_F/dN_0 = -dE_F/dN_{-1}$, 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 ($e\mathscr{E}d \ll k_B T$, 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 $k_B T/e$.

Finally, the values of effective hole or electron concentrations involved in hopping migration via hydrogen-like impurities in crystalline semiconductors are determined in [13, 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 $N_{hp} = N_0 N_{-1}/N_a$. For an n-type semiconductor with the

average concentration of donors $N_d = N_0 + N_{+1}$ in the charge states (0) and (+1) the concentration of electrons hopping via donors is $N_{hn} = N_0 N_{+1}/N_d$. However, derivations of the relation D_h/M_h for holes hopping via acceptors and electrons hopping via donors in [31–34] used particular forms of the expressions for N_{hp} and N_{hn} 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

$$p = \frac{1}{V} \int_{-\infty}^{+\infty} g_p f_p \, dE_p,$$ (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 hole, the sum of its 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, $\overline{E}_a$, δE_v, and U_p are given relative to the top of the *v*-band ($E_v = 0$) 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

$$\mathcal{G}_p(U_p) = \frac{1}{\sqrt{2\pi}\, W_p} \exp\left(-\frac{U_p^2}{2W_p^2}\right),$$ (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 $\mathcal{G}_p$ of potential energy U_p fluctuations given by equation (9), for the energy density of states of holes in the *v*-band we find

$$g_p = \frac{V(2m_p)^{3/2}}{2\pi^2\hbar^3} \int_{-\infty}^{E_p} (E_p - U_p)^{1/2} \, \mathcal{G}_p \, dU_p,$$ (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 $\mathcal{G}_p \to \delta(U_p)$, where $\delta(U_p)$ is the Dirac delta function, equation (10) takes the standard form [18–20]:

$$g_{pi} = \frac{V(2m_p)^{3/2}}{2\pi^2\hbar^3} \sqrt{E_{kin}},$$ (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 $|\mathbf{k}| = k$.

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]:

$$m_p = (m_h^{3/2} + m_l^{3/2} + m_{so}^{3/2})^{2/3} = 0.992 m_0,$$ (12)

where $m_h = 0.78 m_0$ is the heavy hole effective mass, $m_l = 0.14 m_0$ is the light hole effective mass, $m_{so} = 0.394 m_0$ 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 $\overline{E}_a > 0$, can be written as [30]:

$$N_{-1} = N \int_{-\infty}^{+\infty} \mathcal{G}_a f_{-1} \, d(E_a - \overline{E}_a) = N\overline{f_{-1}} = N(1 - \overline{f_0}),$$ (13)

where $\mathcal{G}_a$ is the probability density function for the distribution of energy levels in the diamond band gap, $f_{-1} = 1 - f_0$ is the probability that an arbitrary acceptor with energy level E_a is ionized, $\overline{f_{-1}} = N_{-1}/N$; $\overline{f_0} = N_0/N$.

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

$$f_{-1} = 1 - f_0 = \{1 + \beta_a \exp[(E_a + E_F)/k_B T]\}^{-1},$$ (14)

where $\beta_a = 4 + 2\exp(-\varepsilon_{so}/k_B T)$ is the degeneracy factor of energy level E_a 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 $T_1 \approx 3T_j/2$; figure 1) is substantially larger than ε_{so} then $\beta_a \approx 6$. The reference point for the acceptor energy level $E_a > 0$ and the Fermi level $E_F < 0$ in equation (14) is chosen at $E_v = 0$. For calculation of $\overline{f_{-1}} = 1 - \overline{f_0}$ by equation (13) in the exponent of the function f_{-1} given by equation (14) the quantity E_a should be replaced by $(E_a - \overline{E_a})$ and E_F should be replaced by $(E_F + \overline{E_a})$.

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

$$\beta_{am} \approx \beta_a\left(1 + \int_1^{l_m} l^2 \exp\left[\frac{(1-l^2)E_a}{l^2 k_B T}\right]dl\right),$$ (15)

where $l_m = (d_{im}/2a_H)^{1/2} \approx 0.526(8\pi\varepsilon I_a/e^2)^{1/2}[(1+K)N]^{-1/6} \geqslant 1$ is the largest number of possible excited states of the average acceptor in the charge state (0), $d_{im} \approx 0.554[(1+K)N]^{-1/3}$ is the average distance between the nearest impurity atoms considered as point particles randomly (Poissonianly) distributed over a crystalline matrix [30, 42], $a_H = e^2/8\pi\varepsilon I_a$ 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 v-band electrons [43], $\varepsilon_0 = 8.85$ pF m^{-1} is the electric constant, I_a is the thermal ionization energy of a solitary acceptor in the ground (non-excited) state in the crystal lattice site; $I_a = 370$ 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 β_{am} determined by equation (15) will be used instead of β_a.

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

$$\mathcal{G}_a(E_a - \overline{E_a}) = \frac{1}{\sqrt{2\pi}\,W_a}\exp\left[\frac{-(E_a - \overline{E_a})^2}{2W_a^2}\right],$$ (16)

where W_a 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_a, which is equal to the root-mean-square fluctuation of the electrostatic energy of the ionized acceptor [35, 45]:

$$W_a \approx 2.64\frac{e^2}{4\pi\varepsilon}N_{ch}^{1/3},$$ (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_a due to smoothing of the potential (with characteristic amplitude W_a) by a hole within the scale of its de Broglie wavelength [13, 30]:

$$W_p \approx 0.29\left(\frac{p}{N_{ch}}\right)^{1/2}W_a,$$ (18)

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

From equations (17) and (18) it is seen that the quantities W_a 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

$$\frac{D_p}{\mu_p} = \frac{p}{e}\frac{dE_F}{dp} = \xi_p\frac{k_B T}{e}; \qquad \frac{D_h}{M_h} = \frac{N_h}{e}\frac{dE_F}{dN_0} = \xi_h\frac{k_B T}{e},$$ (19)

where the dimensionless parameters ξ_p and ξ_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

$$\xi_p = \frac{e}{k_B T}\frac{D_p}{\mu_p} = \frac{p}{(1/V)\int_{-\infty}^{+\infty} g_p f_p(1 - f_p)dE_p} \geqslant 1,$$ (20)

$$\xi_h = \frac{e}{k_B T}\frac{D_h}{M_h} = \frac{\overline{f_0}\,\overline{f_{-1}}}{\int_{-\infty}^{+\infty}\mathcal{G}_a f_0 f_{-1}\,d(E_a - \overline{E_a})} \geqslant 1.$$ (21)

Let us note that in writing equations (1)–(21) we assumed that on the insulating side of the Mott transition v-band holes and holes of acceptor band coexist in the crystal matrix separately. Consequently, in the derivation of equations (20) and (21) we assumed that the densities of states in the v-band g_p and in the acceptor band $\mathcal{G}_a$ are

weakly (compared to the probabilities of filling hole states f_p and $f_0 = 1 - f_{-1}$) dependent on the Fermi level E_F. The quantities $\xi_p \geqslant 1$ and $\xi_h \geqslant 1$ 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 ($\xi_p \geqslant 1$ and $\xi_h \geqslant 1$) in amorphous hydrogenated silicon at temperature T_j, where the turbulent (jumping or relay) regime of hole transport probably occurs [13, 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 ($W_p \ll k_B T$) and $|\delta E_v| \ll k_B T$, from equation (20) taking into account equations (8)–(11) we find (see also [49]):

$$\frac{D_p}{\mu_p} = \frac{k_B T}{e} \xi_p = \frac{k_B T}{e} \frac{F_{1/2}(y_F)}{F_{-1/2}(y_F)}, \tag{22}$$

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

$$F_j(y_F) = \frac{1}{\Gamma(j+1)} \int_0^\infty \frac{q^j \, dq}{1 + \exp(q - y_F)};$$

$$\Gamma(j+1) = \int_0^\infty t^j \exp(-t) dt; \quad F_{-1/2}(y_F) = \frac{dF_{1/2}(y_F)}{dy_F}.$$

Two particular cases follow from equation (22): equation (4) for an ideal nondegenerate gas of v-band holes of p-type diamond, when $y_F < 0$ and $|y_F| \gg 1$, and equation (5) for an ideal degenerate gas of v-band holes, when $y_F \gg 1$. (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 ($T < T_j$), when $p \ll N_h \approx K(1 - K)N$, only a fraction of acceptors, $N_{-1}/N \approx K$, is ionized, the other acceptors are electrically neutral, $N_0/N \approx 1 - K$. For the narrow acceptor band ($W_a \ll k_B T$) from equation (21), taking into account equations (13)–(17), we find $\xi_h = 1$, 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 ($W_a \gg k_B T$), from equation (21) it follows that [29]

$$\frac{D_h}{M_h} = \frac{k_B T}{e} \xi_h = K(1 - K) \frac{W_a \sqrt{2\pi}}{e} \exp\left(\frac{\gamma_a^2}{2}\right), \tag{23}$$

where $\gamma_a = (E_F + \overline{E}_a + k_B T \ln \beta_a)/W_a$ is found from the condition $2K = 1 - \mathrm{erf}(\gamma_a/\sqrt{2})$, 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_a. This means that the hopping mobility M_h of holes decreases more rapidly comparing 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 ξ_h enters the expression for the coefficient of the differential thermo-emf for hopping migration of holes via acceptors [51].

To calculate ξ_p and ξ_h using equations (20) and (21) we need to establish the dependence of the energy of the acceptor band center $\overline{E}_a$ on the acceptor concentration N, the compensation ratio K, and the temperature T.

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

$$\overline{E}_a = I_a + \delta E_v = I_a + E_{cor} + E_{per} + E_{exc}, \tag{24}$$

where I_a 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, $E_{cor} < 0$ 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 $+e$), $E_{per} < 0$ 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], $E_{exc} < 0$ 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 δE_v in equation (24): (a) $E_{cor} < 0$ for $E_{per} = E_{exc} = 0$; (b) $E_{per} < 0$ for $E_{cor} = E_{exc} = 0$; and (c) $E_{exc} < 0$ for $E_{cor} = E_{per} = 0$.

(a) *Calculation of E_{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

$d_{\mathrm{s}} \approx 0.554[N + KN + p]^{-1/3}$ 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 $r \geqslant d_{\mathrm{s}}$ the total electrostatic potential Φ_{s} 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]:

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2 \frac{\mathrm{d}\Phi_{\mathrm{s}}}{\mathrm{d}r}\right) = -\frac{\rho(\Phi_{\mathrm{s}})}{\varepsilon} = \Lambda_{\mathrm{s}}^{-2}\Phi_{\mathrm{s}}, \tag{25}$$

where $\rho(\Phi_{\mathrm{s}}) = e[p(\Phi_{\mathrm{s}}) + KN - N_{-1}(\Phi_{\mathrm{s}})]$ is the volume density of the screening electric charge, $\varepsilon = \varepsilon_{\mathrm{r}}\varepsilon_0$ is the dielectric permittivity of the crystal matrix, $\Lambda_{\mathrm{s}}^{-2} = -(1/\varepsilon)(\mathrm{d}\rho(\Phi_{\mathrm{s}})/\mathrm{d}\Phi_{\mathrm{s}})$ at $\Phi_{\mathrm{s}} \to 0$. For $r \geqslant d_{\mathrm{s}}$ the solution of equation (25) with the boundary conditions $\mathrm{d}\Phi_{\mathrm{s}}/\mathrm{d}r = e/4\pi\varepsilon_{\mathrm{r}}\varepsilon_0 d_{\mathrm{s}}^2$ at $r = d_{\mathrm{s}}$ and $\Phi_{\mathrm{s}} \to 0$ at $r \to \infty$ has the form [54]:

$$\Phi_{\mathrm{s}} = \frac{-e}{4\pi\varepsilon r(1 + d_{\mathrm{s}}/\Lambda_{\mathrm{s}})}\exp\left(\frac{d_{\mathrm{s}} - r}{\Lambda_{\mathrm{s}}}\right), \tag{26}$$

where Λ_{s} 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 $\rho(\Phi_{\mathrm{s}}) = -\varepsilon\Phi_{\mathrm{s}}/\Lambda_{\mathrm{s}}^2$ gives $E_{\mathrm{is}} = -e^2/4\pi\varepsilon(\Lambda_{\mathrm{s}} + d_{\mathrm{s}})$. The energy of interaction between charges in the cloud is $E_{\mathrm{ss}} = e^2/16\pi\varepsilon(\Lambda_{\mathrm{s}} + d_{\mathrm{s}})$. As a result, the total electrostatic correlation energy E_{cor} in the system 'acceptor in the charge state (-1) plus cloud of charges screening it' is [35, 52, 57]:

$$E_{\mathrm{cor}} = E_{\mathrm{is}} + E_{\mathrm{ss}} = -\frac{3e^2}{16\pi\varepsilon(\Lambda_{\mathrm{s}} + d_{\mathrm{s}})} < 0. \tag{27}$$

The quantity E_{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 $[\rho(\Phi_{\mathrm{s}}) \propto \Phi_{\mathrm{s}}]$ 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 $W_{\mathrm{p}} \gg k_{\mathrm{B}}T$ and $W_{\mathrm{a}} \gg k_{\mathrm{B}}T$.

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]):

$$\Lambda_{\mathrm{s}}^{-2} = \frac{e^2}{\varepsilon}\left(\frac{\mathrm{d}p}{\mathrm{d}E_{\mathrm{F}}} - \frac{\mathrm{d}N_{-1}}{\mathrm{d}E_{\mathrm{F}}}\right) = \frac{e}{\varepsilon}\left(p\frac{\mu_{\mathrm{p}}}{D_{\mathrm{p}}} + N_{\mathrm{h}}\frac{M_{\mathrm{h}}}{D_{\mathrm{h}}}\right) = \frac{e^2}{\varepsilon k_{\mathrm{B}}T}\left(\frac{p}{\xi_{\mathrm{p}}} + \frac{N_{\mathrm{h}}}{\xi_{\mathrm{h}}}\right), \tag{28}$$

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

Let us point out that the screening length Λ_{s} is defined for the state of the thermodynamic equilibrium, i.e. at zero current densities $J_{\mathrm{p}} = J_{\mathrm{h}} = 0$. According to equation (28) at low temperatures ($T < T_j$, when $p/\xi_{\mathrm{p}} \ll N_{\mathrm{h}}/\xi_{\mathrm{h}}$) the quantity Λ_{s} is determined solely by holes hopping via acceptors $\Lambda_{\mathrm{s}} \propto (N_{\mathrm{h}}/\xi_{\mathrm{h}})^{-1/2}$, where $N_{\mathrm{h}} = N_0 N_{-1}/N = K(1 - K)N$. 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 $\xi_{\mathrm{h}} \geqslant 1$ indicates the deviation of the $D_{\mathrm{h}}/M_{\mathrm{h}}$ ratio from the classical value $k_{\mathrm{B}}T/e$. By analogy with expression for the dc conductivity of v-band holes $\sigma_{\mathrm{p}} = ep\mu_{\mathrm{p}}$ the dc hopping conductivity can be written as $\sigma_{\mathrm{h}} = eN_{\mathrm{h}}M_{\mathrm{h}}$, 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_{per} 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_{per}, above which the percolation of v-band holes sets on, is determined from the relation

$$\int_{-\infty}^{E_{\mathrm{per}}} \mathcal{G}_{\mathrm{p}} \, \mathrm{d}U_{\mathrm{p}} = \frac{1}{\sqrt{2\pi}\,W_{\mathrm{p}}}\int_{-\infty}^{E_{\mathrm{per}}}\exp\left(-\frac{U_{\mathrm{p}}^2}{2W_{\mathrm{p}}^2}\right)\mathrm{d}U_{\mathrm{p}} = 0.17,$$

that yields

$$E_{\mathrm{per}} \approx -0.955 W_{\mathrm{p}} < 0, \qquad (29)$$

where W_{p} is given by equation (18).

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

The energy of the exchange interaction of v-band holes $E_{\mathrm{exc}} < 0$ results from the symmetry of the wave function of holes relative to their transposition. In the effective mass approximation the Bloch wave functions of c-band electrons (and v-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 v-band holes g_{pi} in the ideal diamond crystal is determined by equation (11)) the energy of a hole with the absolute value of quasi-wave vector $|\boldsymbol{k}| = k$ and the effective mass m_{p} is equal to $(\hbar k)^2 / 2m_{\mathrm{p}} + E_{\mathrm{exc}}$. For these conditions the single-particle exchange energy $E_{\mathrm{exc}} < 0$ is given by [60]:

$$E_{\mathrm{exc}} = -\frac{e^2}{2\pi^{5/2}\varepsilon} k_{\mathrm{t}} \frac{H(y_{\mathrm{F}})}{F_{1/2}(y_{\mathrm{F}})}, \qquad (30)$$

where $k_{\mathrm{t}} = \sqrt{2m_{\mathrm{p}}k_{\mathrm{B}}T}\,/\,\hbar$ is the absolute value of the wave vector of a hole (k_{t} is determined by the equation $(\hbar k_{\mathrm{t}})^2 / 2m_{\mathrm{p}} = k_{\mathrm{B}}T$); $y_{\mathrm{F}} = E_{\mathrm{F}}/k_{\mathrm{B}}T$;

$$H(y_{\mathrm{F}}) = \int_0^\infty q L^2(q)\,\mathrm{d}q, \quad L(q) = \int_0^\infty \cos(qt)\ln[1 + \exp(y_{\mathrm{F}} - t^2)]\,\mathrm{d}t,$$

$$F_{1/2}(y_{\mathrm{F}}) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{q}\,\mathrm{d}q}{1 + \exp(q - y_{\mathrm{F}})}.$$

For a nondegenerate gas of v-band holes (at $E_{\mathrm{F}} < 0$ and $|E_{\mathrm{F}}| \gg k_{\mathrm{B}}T$) from equation (30) it follows that [60]:

$$E_{\mathrm{exc}} = -\frac{e^2 k_{\mathrm{t}}}{8\pi^{3/2}\varepsilon} \exp\left(\frac{E_{\mathrm{F}}}{k_{\mathrm{B}}T}\right).$$

For a degenerate gas of v-band holes (at $E_{\mathrm{F}} > 0$ and $E_{\mathrm{F}} \gg k_{\mathrm{B}}T$) in the limit of zero temperature ($T \to 0$) equation (30) turns into the Slater formula [60–62]:

$$E_{\mathrm{exc}} = -\frac{3e^2}{8\pi^2\varepsilon} k_{\mathrm{F}} = -\frac{3e^2}{8\pi^2\hbar\varepsilon} \sqrt{2m_{\mathrm{p}}E_{\mathrm{F}}}, \qquad (31)$$

where $\hbar k_{\mathrm{F}} = \hbar\,(3\pi^2 p)^{1/3}$ is the Fermi quasi-momentum of a v-band hole (k_{F} is determined by the equation $(\hbar k_{\mathrm{F}})^2 / 2m_{\mathrm{p}} = E_{\mathrm{F}}$).

On the metallic side of the Mott transition, where the Fermi level $E_{\mathrm{F}} \gg k_{\mathrm{B}}T$ and $E_{\mathrm{F}} > E_{\mathrm{per}}$ (figure 1), the quantity E_{exc} based on equation (31) can be tentatively averaged over the fluctuations of the potential energy U_{p} of holes [52]:

$$\overline{E_{\mathrm{exc}}} = \int_{-\infty}^{E_{\mathrm{F}}} E_{\mathrm{exc}}(U_{\mathrm{p}}) \mathcal{G}_{\mathrm{p}}\,\mathrm{d}U_{\mathrm{p}} < 0,$$

where $E_{\mathrm{exc}}(U_{\mathrm{p}}) = -(3e^2/8\pi^2\hbar\varepsilon)\sqrt{2m_{\mathrm{p}}(E_{\mathrm{F}} - U_{\mathrm{p}})}$ is the exchange energy of a v-band hole with kinetic energy $E_{\mathrm{kin}} \approx E_{\mathrm{F}} - U_{\mathrm{p}}$; the probability density function $\mathcal{G}_{\mathrm{p}}$ of potential energy U_{p} fluctuations relative to $E_v = 0$ is given by equation (9).

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

We based the estimate of the ratio of concentration of v-band holes p_{loc} that have the energy $E_{\mathrm{p}} < \delta E_v$ and may migrate only in restricted regions of a bulk crystal sample to the total concentration of holes in the v-band on equation (8) and found

$$\frac{p_{\mathrm{loc}}}{p} = \frac{\int_{-\infty}^{\delta E_v} g_{\mathrm{p}}(E_{\mathrm{p}} - \Delta_v) f_{\mathrm{p}}(E_{\mathrm{p}} - \Delta_v)\,\mathrm{d}E_{\mathrm{p}}}{\int_{-\infty}^{+\infty} g_{\mathrm{p}}(E_{\mathrm{p}} - \Delta_v) f_{\mathrm{p}}(E_{\mathrm{p}} - \Delta_v)\,\mathrm{d}E_{\mathrm{p}}}, \qquad (32)$$

where $\Delta_v = E_{\mathrm{cor}} + E_{\mathrm{exc}} = \delta E_v - E_{\mathrm{per}}$, taking into account equations (27), (29) and (30). In equation (32) the density of states of holes in the v-band $g_{\mathrm{p}}(E_{\mathrm{p}} - \Delta_v)$ is given by equation (10) with the energy of the hole E_{p} replaced by $E_{\mathrm{p}} - \Delta_v$; the Fermi–Dirac distribution function for v-band holes $f_{\mathrm{p}}(E_{\mathrm{p}} - \Delta_v) = \{1 + \exp[(E_{\mathrm{p}} - \Delta_v - E_{\mathrm{F}})/k_{\mathrm{B}}T]\}^{-1}$ 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_F, W_a, W_p, $\overline{E}_a$, N_{-1}, p we consider the case of p-type diamond crystals lightly doped with boron. In such crystals $W_a \ll k_B T$, $W_p \ll k_B T$, $\delta E_v = 0$, and $\overline{E}_a \approx I_a = 370$ 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]):

$$p(KN + p + p_a) = p_a(1 - K)N, \qquad (33)$$

where $p_a = (p_v/\beta_{ai})\exp(-I_a/k_B T)$; $p_v = 2(2\pi m_p k_B T)^{3/2}/(2\pi\hbar)^3$; the degeneracy factor β_{ai} is determined from equation (15) where E_a is replaced by I_a.

The algorithm for solving of 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: ε_r, β_a, I_a, 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 $\varepsilon_{goal} = 10^{-5}$.

(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 $N_{ch} = 2(p + KN)$, seed values of the root-mean-square fluctuations W_a and W_p are evaluated.

(iii) The nonlinear electrical neutrality equation (1) is solved for the unknown Fermi level E_F using the values of W_a 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_F allows to refine the values of W_a, W_p, $\overline{E}_a$, N_{-1}, and p.

(iv) The solution of the electrical neutrality equation (1) and refinement of the values of W_a, W_p, $\overline{E}_a$, N_{-1}, and p are iteratively performed until their relative error becomes less than a cutoff value ε_{goal}. The relative error $\varepsilon(X)$ for the value of a calculated quantity $X = \{E_F, W_a, W_p, \overline{E}_a, N_{-1}, p\}$ 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 kth 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 $T = 300$ K. According to [63] at the concentration of boron atoms $N = (2-3) \times 10^{20}$ cm^{-3} the Fermi level E_F is located in the band gap at 90–120 meV above the top of the v-band of the undoped diamond crystal. Calculations using equations (1), (8)–(30) at $T = 300$ K gives $E_F \approx 100$ meV for $N = 2.5 \times 10^{20}$ 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 $\sigma_p = \sigma_h$ (figure 1), is found from the equation

$$T_j = \frac{0.728}{k_B} \frac{e^2}{4\pi\varepsilon} [N_{-1}(T_j) + p(T_j)]^{1/3}, \qquad (34)$$

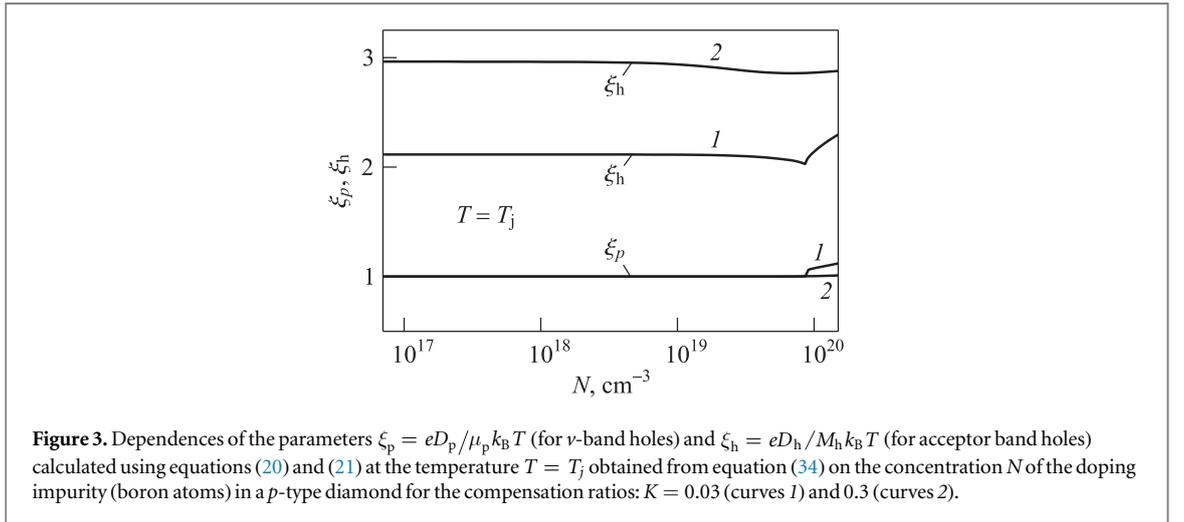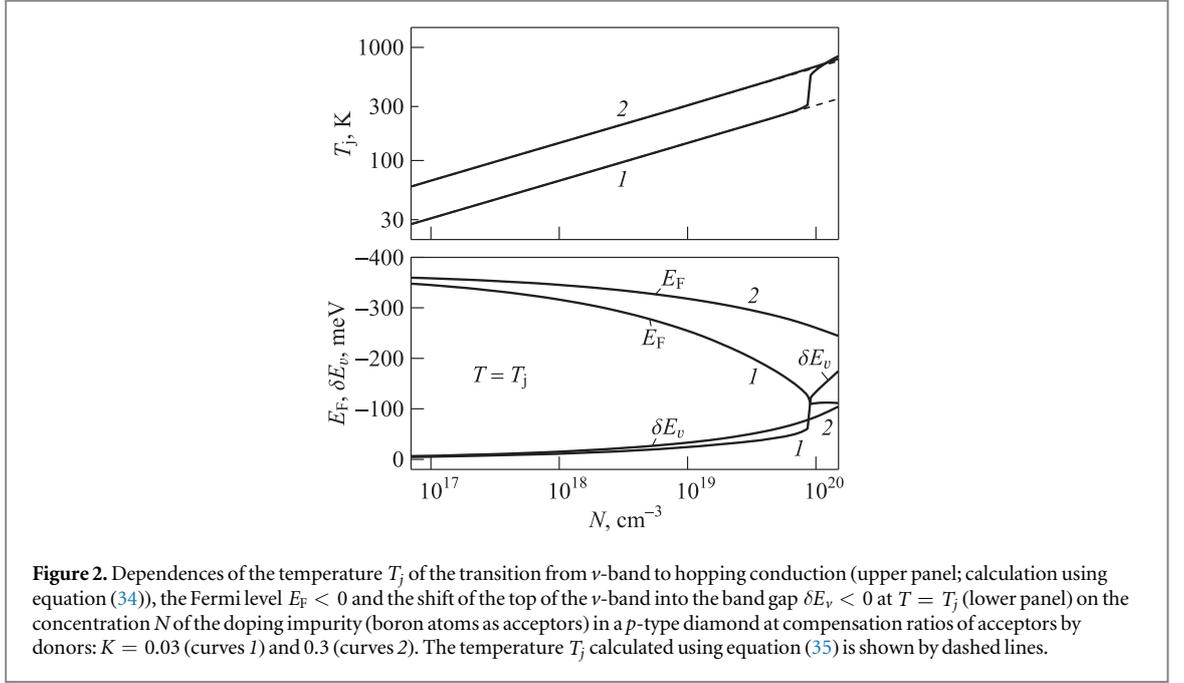where $N_{-1}(T_j)$ and $p(T_j)$ are determined according to the electroneutrality condition (1).

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

$$T_j \approx \frac{0.728}{k_B} \frac{e^2}{4\pi\varepsilon} (KN)^{1/3}, \qquad (35)$$

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 ($\varepsilon_r = \varepsilon/\varepsilon_0 = 5.7$),

Figure 2. Dependences of 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. Dependences of the parameters $\xi_p = eD_p/\mu_p k_B T$ (for v-band holes) and $\xi_h = eD_h/M_h k_B T$ (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*).

germanium ($\varepsilon_r = 15.4$), silicon ($\varepsilon_r = 11.47$), and gallium arsenide ($\varepsilon_r = 12.4$) crystals doped with hydrogen-like impurities [4, 13, 30].

The algorithm for calculating W_a, W_p, $\overline{E}_a$, 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, $\overline{E}_a$, N_{-1}, and p at the seed temperature T_j are calculated until their relative error becomes less than ε_{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 ε_{goal}.

Figure 2 shows the temperature T_j calculated using equation (34), the Fermi level $E_F < 0$ obtained using the electrical neutrality condition (1) and the shift of the top of the v-band into the crystal band gap $\delta E_v = E_{cor} + E_{per} + E_{exc} < 0$ found using equations (27), (29), and (30) as functions of the boron atom concentration N in a diamond crystal for low ($K = 0.03$) and intermediate ($K = 0.3$) compensation ratios.

Figure 3 shows the parameters $\xi_p = eD_p/\mu_p k_B T$ and $\xi_h = eD_h/M_h k_B T$ calculated using equations (20) and (21) at the temperature $T = T_j$ obtained from equation (34) as functions of the concentration N of the doping impurity (boron atoms as acceptors in a p-type diamond crystal; $I_a = 370$ meV). It is evident that $\xi_h > \xi_p$, since according to the equation (18), other things being equal, the root-mean-square fluctuation W_a of the acceptor energy levels E_a relative to the average value $\overline{E}_a$ is larger than the root-mean-square fluctuation of the v-band hole potential energy W_p.

5. Discussion of the calculation results

5.1. Hall effect at temperatures close to T_j

Numerical calculation using equation (32) gives the ratio $p_{loc}/p < 0.1$ for $N < 3 \times 10^{20}$ cm^{-3} at $K \geqslant 0.01$. This estimate allows to conclude that the concentration of totally free v-band holes $p_{mob} = p - p_{loc}$ 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 v-band holes in a bulk p-type semiconductor.

At the temperature T_j, where $\sigma_p(T_j) \approx \sigma_h(T_j)$, the experimentally measured Hall coefficient $R_H(T_j)$ is [20, 21, 37, 66]:

$$R_H = \frac{R_p \sigma_p^2 + R_h \sigma_h^2}{(\sigma_p + \sigma_h)^2} \approx \frac{R_p}{4} = \frac{r_p}{4ep}, \tag{36}$$

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 v-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 σ_p and σ_h.)

At T_j the conditions $ep\mu_p = eN_h M_h$ 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_h of holes hopping via acceptors to the drift mobility μ_p of v-band holes in the form

$$\frac{M_h(T_j)}{\mu_{pj}} = \frac{r_p}{4eR_H K(1 - K)N}, \tag{37}$$

where the notation $\mu_{pj} = \mu_p(T_j)$ is introduced.

It follows from equation (37) that by measuring the Hall coefficient R_H and the Hall mobility of v-band holes $\mu_{pj}^{(H)} = R_H(\sigma_p + \sigma_h) = 2R_H\sigma_p = r_p\mu_{pj}/2$ at $T = T_j$ we can assess the value of the drift hopping mobility via acceptors (see also [13]): $M_h(T_j) = \mu_{pj}^{(H)}/[2eR_H K(1 - K)N]$. According to [67], at the boron concentration $N \approx 1.2 \times 10^{19}$ cm^{-3} and the temperature $T_j \approx 364$ K, the Hall coefficient $R_H \approx 349$ cm^3/C, and $\mu_{pj}^{(H)} = \sigma_p R_H \approx 71$ cm^2 V^{-1} s^{-1}. For $K = 0.3$ we find $M_h(T_j) \approx 0.25$ cm^2 V^{-1} s^{-1}. Thus, at T_j the drift hopping mobility $M_h(T_j)$ of holes via boron atoms is much smaller than the Hall mobility $\mu_{pj}^{(H)}$ of v-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 $T_3 \approx T_j/2$ (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]:

$$\sigma_h = \sigma_3 \exp\left(-\frac{\varepsilon_3}{k_B T}\right), \tag{38}$$

where σ_3 is a pre-exponential factor that weakly depends on the temperature (compared to the exponent), ε_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_3 the concentration of holes hopping via acceptors $N_h \approx K(1 - K)N$ is much greater than the concentration of v-band holes p and the electrical neutrality condition (1) takes the form: $N_{-1} = KN$. For a wide acceptor band ($W_a \gg k_B T_3$), at the temperature $T_3 = T_j/2$, 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]:
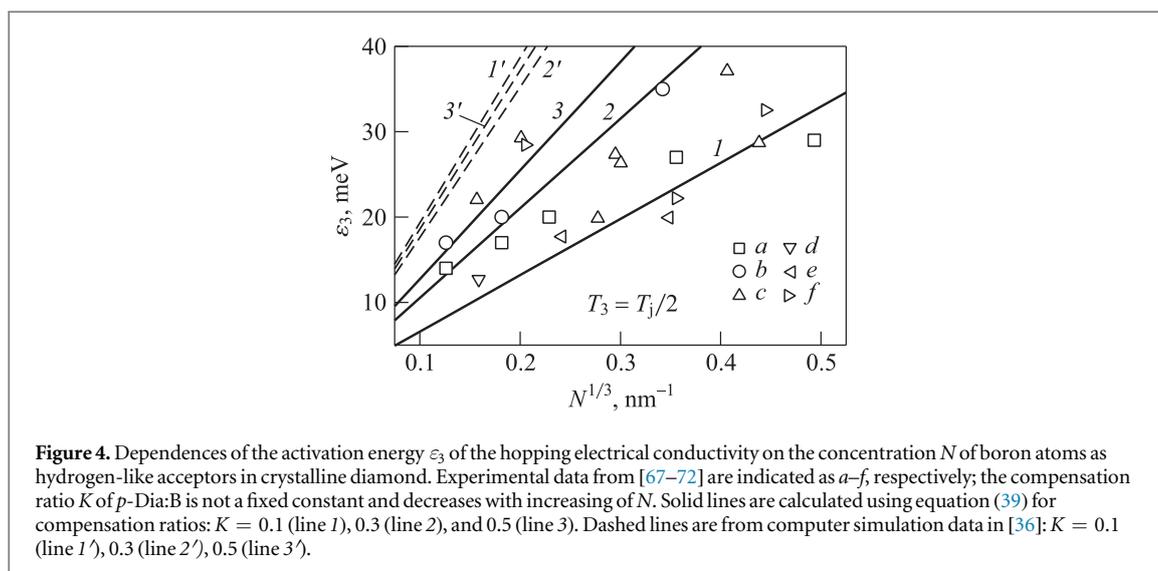
$$\varepsilon_3 = -k_B T_3 \ln(\sigma_h/\sigma_3) = k_B T_3 \ln \xi_{h3}, \tag{39}$$

where

$$T_3 = \frac{0.364}{k_B} \frac{e^2}{4\pi\varepsilon_r\varepsilon_0}(KN)^{1/3}; \quad \xi_{h3} = \xi_h(T_3) = K(1 - K)\frac{W_a\sqrt{2\pi}}{k_B T_3}\exp\left(\frac{\gamma_a^2}{2}\right);$$

$$W_a \approx 2.64\frac{e^2}{4\pi\varepsilon_r\varepsilon_0}(2KN)^{1/3}; \quad 2K = 1 - \mathrm{erf}\left(\frac{\gamma_a}{\sqrt{2}}\right); \quad \frac{W_a}{k_B T_3} \approx 9.14.$$

Calculations that use equation (39) agree (see figure 4) with the experimental data [67–72] for p-Dia:B with the compensation ratios K from 0.1 to 0.5 at $N < 0.3N_M$, where $N_M \approx 4 \times 10^{20}$ cm^{-3} is the concentration of boron atoms corresponding to the transition of diamond (at temperature $T \to 0$) from the insulating to the

Figure 4. Dependences of the activation energy ε_3 of the hopping electrical conductivity on the concentration N of boron atoms as hydrogen-like acceptors in crystalline diamond. Experimental data from [67–72] are indicated as *a–f*, respectively; the compensation ratio K of *p*-Dia:B is not a fixed constant and decreases with increasing of N. Solid lines are calculated using equation (39) for compensation ratios: $K = 0.1$ (line *1*), 0.3 (line *2*), and 0.5 (line *3*). Dashed lines are from computer simulation data in [36]: $K = 0.1$ (line *1'*), 0.3 (line *2'*), 0.5 (line *3'*).

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_j, for which the dc electrical conductivity of the v-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 v-band holes ($\xi_p = eD_p/\mu_p k_B T_j$) and holes hopping via boron atoms ($\xi_h = eD_h/M_h k_B T_j$). A quantitative estimate for the shift δE_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 ε_3 of the dc hopping electrical conductivity of *p*-Dia:B on the concentration of boron atoms at the temperature $T_3 = T_j/2$ 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 3×10^{17} to 3×10^{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 ε_3 obtained from measurements of the thermal dependence of hopping electrical conductivity.

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