JOURNAL OF APPLIED PHYSICS **119**, 245701 (2016)

Ionization equilibrium at the transition from valence-band to acceptor-band migration of holes in boron-doped diamond

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(Received 30 April 2016; accepted 7 June 2016; published online 22 June 2016)

A quasi-classical model of ionization equilibrium in the p-type diamond between hydrogen-like acceptors (boron atoms which substitute carbon atoms in the crystal lattice) and holes in the valence band (v-band) is proposed. The model is applicable on the insulator side of the insulator–metal concentration phase transition (Mott transition) in p-Dia:B crystals. The densities of the spatial distributions of impurity atoms (acceptors and donors) and of holes in the crystal are considered to be Poissonian, and the fluctuations of their electrostatic potential energy are considered to be Gaussian. The model accounts for the decrease in thermal ionization energy of boron atoms with increasing concentration, as well as for electrostatic fluctuations due to the Coulomb interaction limited to two nearest point charges (impurity ions and holes). The mobility edge of holes in the v-band is assumed to be equal to the sum of the threshold energy for diffusion percolation and the exchange energy of the holes. On the basis of the virial theorem, the temperature T_j is determined, in the vicinity of which the dc band-like conductivity of holes in the v-band is approximately equal to the hopping conductivity of holes via the boron atoms. For compensation ratio (hydrogen-like donor to acceptor concentration ratio) $K \approx 0.15$ and temperature T_j, the concentration of "free" holes in the v-band and their jumping (turbulent) drift mobility are calculated. Dependence of the differential energy of thermal ionization of boron atoms (at the temperature $3T_j/2$) as a function of their concentration N is calculated. The estimates of the extrapolated into the temperature region close to T_j hopping drift mobility of holes hopping from the boron atoms in the charge states (0) to the boron atoms in the charge states (-1) are given. Calculations based on the model show good agreement with electrical conductivity and Hall effect measurements for p-type diamond with boron atom concentrations in the range from 3×10^{17} to $3 \times 10^{20}\,\text{cm}^{-3}$, i.e., up to the Mott transition. The model uses no fitting parameters. *Published by AIP Publishing.*

[http://dx.doi.org/10.1063/1.4954281]

I. INTRODUCTION

Boron-doped p-type diamonds (p-Dia:B) are attractive for use as electrodes in electrochemistry,[1] as well as in power semiconductor electronics.[2] Experimental studies of p-Dia:B superconductivity at liquid helium temperatures are a topic of current interest (see, e.g., Ref. 3). The effect of compensation of acceptors by donors in semiconductor oxide ceramic of p-type on its transition from a superconducting to an insulating state is discussed in Ref. 4. Studies of electrical properties of diamond become especially relevant due to the development of effective technologies for the synthesis of perfect crystalline films and massive (bulk) diamond samples,[5–7] and to the broader application of such materials.

Currently, there is not enough information about the ionization equilibrium and the migration of holes in the temperature range where band-like and hopping dc conductivities in p-Dia:B crystals are comparable. This information is important, for example, in designing diamond based bolometers (see, e.g., Ref. 8), when it is necessary to predict the temperature of the transition from band-like to hopping conduction to block the migration of holes between acceptors. Generally speaking, this line of research of electrical properties of diamond crystals is not developed in the desirable limits. Indeed, in Ref. 9, the model of transition of p-Dia:B from the insulating to the metallic state (Mott transition[10]) under the increase in boron concentration is proposed in the presence of electrical conduction of v-band holes. The critical concentration of boron atoms ($N_M \approx 4 \times 10^{20}\,\text{cm}^{-3}$) at which the Mott transition occurs is found experimentally in Ref. 11. The calculation of dc hopping conductivity of p-type diamond by means of hole hopping via the (0) and (-1) charge states of boron atoms is performed in Ref. 12. However, no quantitative comparison of calculations of the concentration and the mobility of holes with experimental data specifically at the temperature of mass transition from "free" migration of holes in the v-band to hopping migration of holes via acceptors has been performed to date.

The purpose of this work is to develop a quasi-classical model of ionization equilibrium and of hole migration in boron-doped p-type diamond crystals in the temperature range of the transition from band-like to hopping dc electrical conduction.

The temperature dependence of the logarithm of the electrical resistivity ρ on the reciprocal temperature $1/T$ for crystalline semiconductors doped and compensated by

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0021-8979/2016/119(24)/245701/10/$30.00

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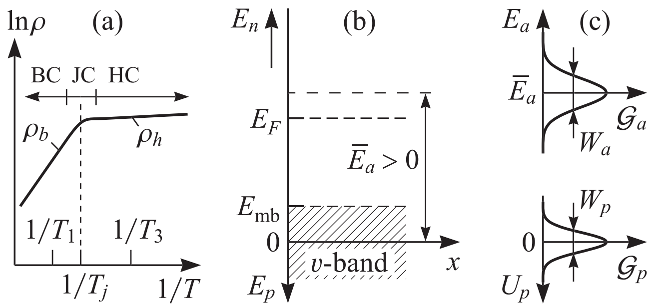

FIG. 1. (a) Diagram showing the dependence of the logarithm of the dc electrical resistance ρ on the reciprocal temperature $1/T$ for a p-type crystalline semiconductor in the regimes of hole migration in the v-band (ρ_b) and hopping via acceptors (ρ_h). (b) Energy band diagram of the crystal: states of the v-band filled with electrons are hatched; the top of the v-band of the undoped crystal is set as the origin of the hole energy E_p; x is an axis of the Cartesian coordinate system; $E_F < 0$ is the Fermi level, $E_{\rm mb} < 0$ is the mobility edge for v-band holes; E_n is the single-electron energy. (c) The probability density functions of fluctuations of potential energy of v-band holes ($\mathcal{G}_p$) and of energy levels of acceptors in the acceptor band ($\mathcal{G}_a$).

hydrogen-like impurity atoms is schematically shown in Fig. 1(a). Note that at the temperature T_j the values of resistivities ρ_b and ρ_h are approximately equal. Band-like conduction (the BC regime) is realized at temperatures $T > T_j$, where an average hole in the v-band mostly moves "freely" through the crystal matrix between successive acts of scattering on phonons and impurity ions. Note that usually the energy of thermal ionization of the major (doping) impurity is measured in the temperature range close to $T_1 \approx 3T_j/2$. In the hopping conduction regime (the HC regime) at $T < T_j$, the hole is localized near a single acceptor most of the time. Holes tunnel through the crystal lattice between acceptors in the charge states (0) and (-1) due to the "assistance" of phonons, so the electrical conductivity $\sigma = 1/\rho$ decreases exponentially with $1/T$ as temperature decreases in the range close to $T_3 \approx T_j/3$. It should be noted that in the vicinity of the temperature T_j the average lifetime of a hole at an acceptor is approximately equal to the "flight" or jump time of hole from an acceptor in the charge state (0) to an acceptor in the charge state (-1). The jump of hole includes a thermally activated transition of hole from an electrically neutral acceptor to the mobility edge $E_{\rm mb}$, a flight with thermal velocity in crystal matrix to the ionized acceptor and capture on it. This migration regime of the holes can be tentatively called "relay,"[13] "turbulent,"[14] or "jumping"[15] (the JC regime). In the JC regime, mass capture of holes from the v-band by acceptors in the charge state (-1) occurs. This results in increased mobility of the remaining holes in the v-band due to the decrease in the concentration of scattering ions.[16]

A stationary current density of "free" v-band holes J_p along the x axis is given by (see, e.g., Refs. 17–19)

$$J_p = ep_{\rm mb}\mu_p\mathscr{E} - eD_p\frac{dp_{\rm mb}}{dx} = \sigma_p\mathscr{E} - eD_p\frac{dp_{\rm mb}}{dx}, \tag{1}$$

where e is the elementary charge, $p_{\rm mb}$ is the concentration of holes with energies greater than the mobility edge $E_{\rm mb}$ that unrestrictedly migrate via the v-band states within the entire crystal sample, μ_p is the drift mobility of holes, $\mathscr{E}$ is the strength of an external electric field along the x axis, D_p is the diffusion coefficient, x is the coordinate, and $\sigma_p = ep_{\rm mb}\mu_p = 1/\rho_b$ is the electrical conductivity of the holes in the v-band. The ratio $D_p/\mu_p = \xi_p k_B T/e$ is higher than the classical value $k_B T/e$, where k_B is the Boltzmann constant, and T is the absolute temperature; parameter $\xi_p \geq 1$ increases with increasing hole concentration.[20,21]

A stationary hopping current density J_h of holes migrating via hydrogen-like acceptors in charge states (0) and (-1) is given by[12,22,23]

$$J_h = eN_h\left[M_h\mathscr{E} - D_h\frac{d}{dx}\ln\left(\frac{N_0}{N_{-1}}\right)\right] = \sigma_h\mathscr{E} - eD_h\frac{dN_0}{dx}, \tag{2}$$

where $N_h = N_0N_{-1}/(N_0 + N_{-1}) \equiv N_0N_{-1}/N$ is the effective concentration of hopping holes, N_0/N is the fraction of the electrically neutral acceptors, N_{-1}/N is the fraction of the ionized acceptors, $\mathscr{E}$ is the strength of an external electric field, M_h is the hopping mobility of holes, D_h is the diffusion coefficient of holes hopping along the x axis, $\sigma_h = eN_hM_h = 1/\rho_h$ is the electrical conductivity of holes of the acceptor band. The ratio $D_h/M_h = \xi_h k_B T/e$ exceeds the classical value $k_B T/e$; the parameter $\xi_h \geq 1$ increases with the broadening of the acceptor band.[23]

It is clear that Eqs. (1) and (2) are applicable in the drift-diffusion approximation. It means that the strength of an external electric field $\mathscr{E}(x)$, as well as the concentrations $p_{\rm mb}(x)$ and $N_0(x) = N - N_{-1}(x)$ significantly change along the x axis only for distances much greater than the mean free path of the hole and the mean hop distance of a hole between the acceptors.

II. STATISTICS OF HOLES AND CHARGE STATES OF HYDROGEN-LIKE ACCEPTORS IN *p*-TYPE DIAMOND CRYSTALS

We assume that the impurity atoms are randomly distributed over the sites of the diamond crystal lattice. Let p be the average over the crystal volume V concentration of holes in the v-band, $N = N_0 + N_{-1}$ be the sum of the average concentrations of acceptors (boron atoms) in the charge states (0) and (-1), and KN be the concentration of donors, all in the charge state $(+1)$, where $0 < K < 1$ is the compensation ratio of acceptors by donors. Then, the electrical neutrality condition has the form (see, e.g., Refs. 18 and 19)

$$p = N_{-1} - KN, \tag{3}$$

where p and N_{-1} are temperature dependent.

The average over the crystal volume V concentration of all holes in the v-band[9,24,25]

$$p = \frac{1}{V}\int_{-\infty}^{+\infty} g_p f_p \, dE_p, \tag{4}$$

where g_p is the energy density of states of holes, $f_p = \{1 + \exp[(E_p - E_F)/k_BT]\}^{-1}$ is the Fermi–Dirac function, $E_p = E_{\rm kin} + U_p$ is the total energy of the hole (the sum of kinetic $E_{\rm kin}$ and potential U_p energies), E_F is the Fermi level

($E_F < 0$ in the band gap), and k_BT is the thermal energy. The top of the v-band ($E_p = 0$) of an undoped crystal is set as the reference point for E_F [Fig. 1(b)]. Holes in the v-band with an energy E_p above the mobility edge E_{mb} ($E_p > E_{\mathrm{mb}}$) are delocalized in a crystal.[26]

According to Refs. 27 and 28, the probability density function of potential energy U_p fluctuations of a hole in the v-band of a bulk crystal is normal (Gaussian)

$$\mathcal{G}_p = \frac{1}{\sqrt{2\pi}\,W_p}\exp\left(-\frac{U_p^2}{2W_p^2}\right), \tag{5}$$

where W_p is the root-mean-square fluctuation of the hole energy [see Fig. 1(c)].

Taking into account Eq. (5) in the quasi-classical approximation[27–29] for the energy density of states of the holes in the v-band, we find[24,25]

$$g_p = \frac{V(2m_p)^{3/2}}{2\pi^2\hbar^3}\int_{-\infty}^{E_p}(E_p - U_p)^{1/2}\mathcal{G}_p\,dU_p, \tag{6}$$

where m_p is the density-of-states effective mass of holes in the v-band of undoped diamond, and $\hbar = h/2\pi$ is the reduced Planck's constant.

Taking into account three subbands of the diamond valence band (v-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 equal[30]

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

where $m_h = 0.78m_0$ is the heavy hole effective mass, $m_l = 0.14m_0$ is the light hole effective mass, $m_{\mathrm{so}} = 0.394m_0$ 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.

The average concentration of mobile v-band holes (characterizes the dc electrical conductivity σ_p and the stationary Hall effect) is determined as

$$p_{\mathrm{mb}} = \frac{1}{V}\int_{E_{\mathrm{mb}}}^{+\infty} g_p f_p\,dE_p, \tag{7}$$

where V is the volume of the diamond sample and E_{mb} is the mobility edge of holes [see Fig. 1(b)].

The average concentration of the acceptors in charge state (-1), taking into account deviations of their energy levels E_a from the average value $\bar{E}_a$, can be written as[31,32]

$$N_{-1} = N\int_{-\infty}^{+\infty} f_{-1}\mathcal{G}_a\,d(E_a - \bar{E}_a) = N\bar{f}_{-1} = N(1 - \bar{f}_0), \tag{8}$$

where $f_{-1} = 1 - f_0$ is the probability that an arbitrary acceptor with energy level $E_a > 0$ higher than the top of the v-band is ionized, $\mathcal{G}_a$ is the probability density function for the distribution of energy levels E_a relative to $\bar{E}_a$ in the diamond band gap [Fig. 1(c)].

Excluding the excited states of all the acceptors for f_{-1}, we find[18,19]

$$f_{-1} = 1 - f_0 = \{1 + \beta_a\exp[(E_a + E_F)/k_BT]\}^{-1}, \tag{9}$$

where $\beta_a = 4 + 2\exp(-\varepsilon_{\mathrm{so}}/k_BT)$ is the degeneracy factor of level E_a considering all three hole subbands in the diamond v-band, $\varepsilon_{\mathrm{so}} = 6\,\mathrm{meV}$ is the value of so-subband split-off (due to spin–orbital interaction) from the degenerate heavy and light hole subbands. If the thermal energy k_BT [e.g., at $T = T_1$; Fig. 1(a)] is substantially larger than $\varepsilon_{\mathrm{so}}$, then $\beta_a \approx 6$.

Taking into account only the excited states of electrically neutral acceptors, the quantity β_a in Eq. (9) should be replaced by[18,32]

$$\beta_{am} = \beta_a\sum_{l=1}^{l_m} l^2\exp\left[\frac{(1 - l^2)E_a}{l^2k_BT}\right], \tag{10}$$

where $l_m \geq 1$ is the largest number of possible excited states of the average acceptor in the charge state (0). The number l_m is determined by the equality of the hole orbit radius $l_m^2a_H$ in the excited state l_m to half the average distance between impurity atoms $d_{\mathrm{im}}/2$. This quantity is taken to be continuous, i.e., $l_m^2a_H = d_{\mathrm{im}}/2$, where $d_{\mathrm{im}} \approx 0.554[(1 + K)N]^{-1/3}$. The Bohr orbit radius a_H for a hole is determined by the thermal ionization energy $I_a = e^2/8\pi\varepsilon a_H$ of a solitary acceptor in the ground (non-excited) state $l = 1$ in the lightly doped diamond crystal. Here, $\varepsilon = \varepsilon_r\varepsilon_0$ is the static permittivity, $\varepsilon_r = 5.7$ is the relative permittivity of the diamond due to v-band electrons,[33] and ε_0 is the electric constant. To this end, the quantity l_m can be viewed as $l_m = (d_{\mathrm{im}}/2a_H)^{1/2}$, where $a_H = e^2/8\pi\varepsilon I_a$. In Eq. (10), the summation over l taking into account $l_m \geq 1$ can be approximately replaced by integration[34]

$$\frac{\beta_{am}}{\beta_a} \approx 1 + \int_1^{l_m} l^2\exp\left[\frac{(1 - l^2)E_a}{l^2k_BT}\right]dl, \tag{11}$$

where $l_m \approx 0.526(8\pi\varepsilon_r\varepsilon_0I_a/e^2)^{1/2}[(1 + K)N]^{-1/6}$. In numerical calculations of the ionization equilibrium in p-Dia:B crystals at T_j in Eqs. (8) and (9) instead of β_a, the quantity β_{am} determined by Eq. (11) will be used. Note that the condition $l_m = 1$ for $I_a = 370\,\mathrm{meV}$ and compensation ratio $K \approx 0.05$ corresponds to the boron concentration $N \approx 5\times10^{20}\,\mathrm{cm}^{-3}$ that is close to the experimental Mott transition concentration $N_M \approx 4\times10^{20}\,\mathrm{cm}^{-3}$ after Ref. 11.

According to Refs. 35 and 36, we assume a Gaussian probability density function $\mathcal{G}_a$ for the acceptor energy level distribution E_a over the crystal (cf. representation of $\mathcal{G}_a$ in Ref. 37)

$$\mathcal{G}_a = \frac{1}{\sqrt{2\pi}\,W_a}\exp\left[\frac{-(E_a - \bar{E}_a)^2}{2W_a^2}\right], \tag{12}$$

where W_a is the effective width of the acceptor band [see Fig. 1(c)].

Let us find according to Refs. 31 and 32, and Fig. 1(b) the position of the "center" of the acceptor band $\bar{E}_a$ (relative to the top of the v-band in the undoped crystal $E_p = 0$). The quantity $\bar{E}_a$ is the energy needed for dissociation of the bound state of hole on a statistically average acceptor due to the thermal fluctuations. Specifically, $\bar{E}_a$ is equal to the energy of ionized acceptor with screening "cloud" of charges $\bar{E}_{-1} = I_{-1} + E_{\mathrm{cor}}$ plus the energy of hole passed into the v-band on its mobility edge $E_{\rm mb}$ and minus the energy of neutral acceptor $\bar{E}_0 \approx I_0$. Thus, we yield

$$\bar{E}_a = \bar{E}_{-1} + E_{\rm mb} - \bar{E}_0 = I_a + E_{\rm cor} + E_{\rm mb}, \qquad (13)$$

where $I_a = I_{-1} - I_0$ is the energy level (thermal ionization potential) of a solitary acceptor (for $E_{\rm cor} = E_{\rm mb} = E_p = 0$), $I_a = 370\,\text{meV}$ for a boron atom as a substitutional impurity in the diamond crystal lattice,[38] $E_{\rm cor} < 0$ is the energy of the correlative reduction of thermal ionization energy of the acceptor in the charge state (0) due to the screening of the acceptor in the charge state (-1) by a "cloud" of charges (with the total charge $+e$), $E_{\rm mb} = E_{\rm per} + E_{\rm exc} < 0$ is the mobility edge of holes in the v-band,[39] $E_{\rm per}$ is the percolation threshold for the diffusion of holes in the v-band, and $E_{\rm exc} < 0$ is the shift of the top of the v-band into the band gap due to the exchange interaction of holes of the v-band.

Note that when the tail of the density of states of holes in the v-band can be neglected ($W_p \ll W_a$), the mobility edge coincides with the top of the v-band: $E_{\rm mb} = E_p = 0$ (see, e.g., Refs. 9, 31, and 32). If the energy of the hole E_p is less than the mobility edge $E_{\rm mb}$, then the hole can only move within a limited volume in the crystalline sample.

Let us specify in Eq. (13), the energy quantities $E_{\rm cor} < 0$, $E_{\rm per} < 0$, $E_{\rm exc} < 0$, and $E_{\rm mb} = E_{\rm per} + E_{\rm exc} < 0$.

According to Refs. 9, 31, 39, and 40, the total electrostatic correlation energy $E_{\rm cor}$ of the system "acceptor impurity ion + cloud of screening point charges" is equal to[41]

$$E_{\rm cor} = -\frac{3e^2}{16\pi\varepsilon(\Lambda_s + d_s)} < 0, \qquad (14)$$

where Λ_s is the screening radius of the Coulomb field of the impurity ion in the Debye–Hückel approximation, $d_s \approx 0.554[N + KN + p]^{-1/3}$ is the average distance between nearest acceptors, donors, and v-band holes (point particles randomly distributed over the crystal; see, e.g., Refs. 42 and 43). When deriving Eq. (14) in accordance with numerical estimates,[9] it was assumed that an average acceptor in the charge state (-1) has the time to gather around it a cloud of screening charges before capturing a hole from the v-band, i.e., prior to electrical neutralization of the ionized acceptor.[31]

The screening radius of the impurity ion Coulomb field, taking into account holes in the v-band, is defined by the expression[12,21,22,44]

$$\Lambda_s^{-2} = \frac{e^2}{\varepsilon k_B T}\left(\frac{p}{\xi_p} + \frac{N_h}{\xi_h}\right), \qquad (15)$$

where $p = N_{-1} - KN$ is the total concentration of holes in the v-band and $N_h = N_0 N_{-1}/N \equiv \bar{f}_0 \bar{f}_{-1} N$ is the effective concentration of holes that hop between acceptors in charge states (0) and (-1); $\xi_p \geq 1$ and $\xi_h \geq 1$ are dimensionless parameters

$$\begin{aligned} \xi_p &= \frac{p}{\dfrac{1}{V}\displaystyle\int_{-\infty}^{+\infty} g_p f_p (1 - f_p)\, dE_p}, \\ \xi_h &= \frac{\bar{f}_0 \bar{f}_{-1}}{\displaystyle\int_{-\infty}^{+\infty} \mathcal{G}_a f_0 f_{-1}\, d(E_a - \bar{E}_a)}. \end{aligned} \qquad (16)$$

Note that for $W_p \ll k_B T$ and $W_a \ll k_B T$, according to Eq. (16), the parameters are $\xi_p = \xi_h = 1$. Analytical approximations and numerical calculations of ξ_p and ξ_h for $W_p \gg k_B T$ and $W_a \gg k_B T$ are given in Refs. 12, 23, and 44–46.

Assuming[24,28,47] that a critical part of the volume of a three-dimensional semiconductor sample that is available for the diffusive motion of holes in the v-band and that corresponds to the energy level of their diffusion percolation $E_{\rm per}$ is

$$\int_{-\infty}^{E_{\rm per}} \mathcal{G}_p\, dU_p = \frac{1}{\sqrt{2\pi}\, W_p}\int_{-\infty}^{E_{\rm per}} \exp\left(-\frac{U_p^2}{2W_p^2}\right) dU_p = 0.17,$$

we obtain[48]

$$E_{\rm per} \approx -0.955 W_p < 0. \qquad (17)$$

As the concentration of v-band holes increases, their exchange interaction becomes significant.[39,40,49] Consequently, the energy position of the top of the v-band ($E_p = 0$ for an undoped crystal) shifts deeper into the band gap, decreasing the energy level of diffusion percolation $E_{\rm per}$ [see Eq. (17)] by

$$E_{\rm exc} = \int_{-\infty}^{E_F} E_{\rm exc}(U_p)\,\mathcal{G}_p(U_p)\, dU_p < 0, \qquad (18)$$

where $E_{\rm exc}(U_p)$ is the exchange energy for a v-band hole, $\mathcal{G}_p(U_p)$ is given by Eq. (5). (According to Refs. 39 and 40, in Eq. (18) averaging over fluctuations of potential energy U_p of v-band holes was performed.) For an isotropic dispersion law of a highly degenerate gas of all holes in the v-band, the exchange energy for a hole $E_{\rm exc}(U_p)$ after Slater[50,51] in accordance with Refs. 39 and 40 takes the form (for $E_F > U_p$)

$$E_{\rm exc}(U_p) = -\frac{3e^2}{8\pi^2\varepsilon\hbar}\,[2m_p(E_F - U_p)]^{1/2}. \qquad (19)$$

In the limit $W_p \to 0$, when $\mathcal{G}_p(U_p)$ takes the form of the Dirac delta function $\delta(U_p)$, Eq. (18) turns into the Slater formula,[49–52] i.e., into Eq. (19) at $U_p = 0$ and $E_F \gg k_B T$.

Thus, taking into account Eq. (19), Eqs. (17) and (18) give the mobility edge of v-band holes [see Eq. (7)]

$$E_{\rm mb} = E_{\rm per} + E_{\rm exc} < 0. \qquad (20)$$

To calculate using Eq. (20), the dependence of $E_{\rm mb}$ on the concentration of impurity atoms and v-band holes, and on the temperature we need to establish in Eqs. (17) and (18) the dependence of W_a and W_p on the same quantities.

Following Refs. 9 and 53, we assume that an insulator–-metal concentration phase transition in the limit of zero temperature ($T \to 0$) takes place when the Fermi level E_F crosses the mobility edge $E_{\rm mb}$ of v-band holes (which is equal to the sum of the percolation threshold $E_{\rm per}$ and the exchange energy $E_{\rm exc}$), i.e., when $E_F = E_{\rm mb}$.

III. ELECTROSTATIC FLUCTUATIONS OF ENERGY OF A HOLE IN THE ACCEPTOR AND VALENCE BANDS

The concentration of all point charged particles $N_{\rm ch}$ that satisfies the condition of electrical neutrality (3) is $N_{\rm ch} = N_{-1} + KN + p = 2(KN + p)$.

Taking into account only Coulomb interaction between the two nearest "point" charges in the crystal, for the effective width of the acceptor band W_a, which is equal to the root-mean-square fluctuation of the energy of the ionized acceptor, we find[31,32,54]

$$W_a = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0}\left[\int_0^\infty \frac{1}{r^2}\sum_{i=1}^{3}\mathcal{P}_i(r)\,dr\right]^{1/2} \approx 2.64\,\frac{e^2}{4\pi\varepsilon}N_{\text{ch}}^{1/3}, \quad (21)$$

where $\sum_{i=1}^{3}\mathcal{P}_i(r)\,dr = 4\pi r^2 N_{\text{ch}}\exp(-4\pi r^3 N_{\text{ch}}/3)\,dr$ is the Poisson probability[55] that the charged particle nearest to a given charged point particle (charged acceptor (-1), charged donor $(+1)$ or v-band hole) is located at a distance from r to $r+dr$, and that there are no other charged particles in the volume $4\pi r^3/3$ of a ball centered on the given charge.

The average distance between the nearest point charged particles in the crystal matrix, taking into account the probability density $\mathcal{P}_i(r)$ from Eq. (21) takes the form[42,43]

$$d_{\text{ch}} = \int_0^\infty r\sum_{i=1}^{3}\mathcal{P}_i(r)\,dr \approx 0.554N_{\text{ch}}^{-1/3}, \quad (22)$$

where $N_{\text{ch}} = 2N_{-1}$.

Let us now find an expression for the mean fluctuation W_p of the v-band hole potential energy. Note that Eq. (21) for the root-mean-square fluctuation W_a of the potential energy of an acceptor in the charge state (-1) is written for "frozen" point particles with charge $\pm e$ randomly distributed (after Poisson) over the volume of a crystal.[56] As noted in Ref. 28, an average hole in the v-band with energy above E_{mb} does not notice potential energy fluctuations on a spatial scale smaller than or comparable to its mean wavelength λ_p (after de Broglie). However, no explicit analytical expression for the root-mean-square fluctuation of the electrostatic potential energy of v-band hole (or c-band electron) is given in Ref. 28 (see also Refs. 47 and 57).

Let us randomly select a region in the crystal with volume $\lambda_p^3 \approx 2/p$. Here, the factor 2 takes into account that, according to the Pauli principle, two v-band holes with opposite spins can simultaneously occupy the same volume $\approx \lambda_p^3$. The corresponding wavelength of an average hole[58,59] is $\lambda_p \approx (p/2)^{-1/3}$. There are $q = \lambda_p^3/d_{\text{ch}}^3$ charged particles located within this volume. Each particle is localized in a region with linear dimensions $d_{\text{ch}} \approx 0.554N_{\text{ch}}^{-1/3}$, where $N_{\text{ch}} = p + KN + N_{-1}$. We assume that the potential energy U_s of each sth charged particle has the same distribution law, thus the average potential energy of the considered v-band hole $U_p = (1/q)\sum_s U_s$. Using the relation for variance of the arithmetic mean of mutually independent identically distributed random variables[60–62]

$$\text{Var}(U_p) = \frac{1}{q}\text{Var}(U_s), \quad (23)$$

where the corresponding variances are $\text{Var}(U_p) = W_p^2$ and $\text{Var}(U_s) = W_a^2$, we get[63]

$$W_p = \frac{1}{q^{1/2}}W_a = \left(\frac{d_{\text{ch}}}{\lambda_p}\right)^{3/2}W_a \approx 0.29\left(\frac{p}{N_{\text{ch}}}\right)^{1/2}W_a, \quad (24)$$

where W_a is determined by Eq. (21). Since for a p-type semiconductor $p < N_{\text{ch}}$, it follows from Eq. (24) that $W_p < W_a$.

We note that, according to Eqs. (17), (20), and (24), as well as condition (3), the energy value E_{mb} of the mobility edge of v-band holes depends on their concentration p, which does not agree with the arguments presented in Ref. 64.

Let us rewrite the condition of electrical neutrality (3) for weakly doped with boron ($N \ll N_M$) p-type diamond crystals taking into account Eqs. (4)–(20). For an "ideal" diamond of p-type, when $W_a \ll k_BT$, $W_p \ll k_BT$, and $\bar{E}_a = I_a = 370\,\text{meV}$, taking into account excited states of the electrically neutral boron atoms from Eq. (3), we yield (see, e.g., Refs. 18, 19, and 25)

$$p(KN + p + p_a) = p_a(1-K)N, \quad (25)$$

where $p_a = (p_v/\beta_{ai})\exp(-I_a/k_BT)$; $p_v = 2(2\pi m_p k_BT)^{3/2}/(2\pi\hbar)^3$; the degeneracy factor β_{ai} is determined by Eq. (11) for E_a substituted by I_a.

For the low temperatures, when $KN \gg p + p_a$, from Eq. (25) we get standard expression relating the concentration p of delocalized holes in the v-band to the thermal ionization energy I_a of a solitary boron atom

$$p = \frac{1-K}{K}p_a = \frac{(1-K)p_v}{K\beta_{ai}}\exp\left(-\frac{I_a}{k_BT}\right). \quad (26)$$

Note that the condition $KN \gg p + p_a$ combined with Eq. (26) gives the restriction on hole concentration $p \ll K(1-K)N$.

For the high temperatures, when $p_a \gg KN + p$, from Eq. (25), we get $p = (1-K)N$ and $p_a \gg N$.

In short, we suggest the following algorithm of the numerical calculations using Eqs. (3)–(24):

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

(ii) By using Eq. (25) the concentration of v-band holes p in an "ideal" p-Dia:B is calculated. Then, according to Eqs. (21) and (24), where $N_{\text{ch}} = 2(p + KN)$, seed values of the root-mean-square fluctuations W_a and W_p can be evaluated.

(iii) By using numerical methods the nonlinear electrical neutrality equation (3) is solved for the unknown Fermi level E_F taking into account obtained seed values of the root-mean-square fluctuations W_a and W_p. The quantities p and N_{-1}, which enter into Eq. (3), are determined on the basis of Eqs. (4) and (8) by involving Eqs. (5), (6), (9), and (11)–(20). The computed value E_F allows to refine the values of W_a, W_p, N_{-1}, and p.

(iv) The solution of the electrical neutrality equation (3) and refinement of the values of W_a, W_p, N_{-1}, and p are iteratively performed until their relative error becomes less than the desired one $\varepsilon_{\text{goal}}$. The relative error $\varepsilon(X)$ of the value of a calculated quantity $X = \{E_F, W_a, W_p, N_{-1}, p\}$ is calculated as: $\varepsilon(X) = 2|X_k - X_{k-1}|/|X_k + X_{k-1}|$, where X_k is the value of a quantity X at the kth step of the iterative procedure.

Let us test this algorithm and the developed quasi-classical theory on the experimental results of Ref. 65. In this work using photoelectric spectroscopy at $T = 300\,\mathrm{K}$, a crystalline film of p-Dia:B was studied. The film was grown by CVD method and then was annealed in microwave hydrogen plasma at temperature $800\,^\circ\mathrm{C}$ during 5 min. According to Ref. 65, the Fermi level E_F at the boron concentration $N = (2\text{–}3) \times 10^{20}\,\mathrm{cm}^{-3}$ is located in the band gap at 90–120 meV above the top of the v-band of the undoped diamond. Calculation using Eqs. (3)–(24) at temperature $T = 300\,\mathrm{K}$ gives $E_F \approx 100\,\mathrm{meV}$ for $N = 2.5 \times 10^{20}\,\mathrm{cm}^{-3}$ at $K \approx 0.28$. Such a compensation ratio can be attributed to the compensation of boron atoms by hydrogen, or, more specific, due to the formation of electrically neutral associates of boron with hydrogen.

IV. CALCULATION OF THE IONIZATION EQUILIBRIUM PARAMETERS IN *p*-Dia:B UNDER TRANSITION FROM BAND-LIKE TO HOPPING CONDUCTION

In Refs. 63 and 66, on the basis of the virial theorem, the characteristic temperature T_j of the transition from the hopping migration of holes via boron atoms (the HC regime) to the band-like migration of holes via states of the v-band (the BC regime) is determined. According to these works, the value of T_j temperature, for which $\sigma_p \approx \sigma_h$ [see Fig. 1(a)], is found from the equation

$$T_j \approx \frac{0.728}{k_B}\frac{e^2}{4\pi\varepsilon_r\varepsilon_0}\left[N_{-1}(T_j) + p(T_j)\right]^{1/3}, \qquad (27)$$

where $N_{-1}(T_j)$ and $p(T_j) = N_{-1}(T_j) - KN$ depends on T_j and the compensation ratio K, according to the electroneutrality condition (3).

In the limit of low concentration of holes in the v-band $p(T_j) \ll N_{-1}(T_j) \approx KN$ from Eq. (27), we yield

$$T_j \approx \frac{0.728}{k_B}\frac{e^2}{4\pi\varepsilon_r\varepsilon_0}(KN)^{1/3}, \qquad (28)$$

where KN is the concentration of hydrogen-like donors which compensate the boron atoms.

An algorithm of calculation of the values W_a, W_p, N_{-1}, and p at temperature T_j according to Eq. (27) is analogous to that given in the end of the Section III. At the beginning, a seed value of T_j using Eq. (28) is calculated. The described iterative procedure for calculation of the values W_a, W_p, N_{-1}, and p at the seed temperature is performed. Using Eq. (27) the value of T_j is refined. The iterative procedure for determination of W_a, W_p, N_{-1}, and p and refinement of T_j are performed until the relative error of T_j becomes less than $\varepsilon_{\mathrm{goal}}$.

Fig. 2 shows the results of calculations of temperature $T_j(N, K)$, determined from Eq. (27), applied to boron-doped p-type diamonds for compensation ratios $K = 0.15$ and $K = 0.5$ as a function of boron atom concentration N. The values of T_j obtained from experimental data[67–75] are also presented. We should note that the compensation ratio of the diamond samples with boron concentration $N \approx 3 \times 10^{17}\,\mathrm{cm}^{-3}$ studied in Refs. 67–75 can reach $K \approx 0.5$, and for $N \approx 3 \times 10^{20}\,\mathrm{cm}^{-3}$, it can reach $K \approx 0.05$. The value of K affects the position of the Fermi level E_F relative to the edges of the allowed energies.[76] It leads to the change in the relation between concentrations of ionized and electrically neutral impurities.[18,19] Note that in Ref. 77, the temperature dependence of electric conduction of n-type homoepitaxial diamond films doped with donor atoms of phosphorus (thermal ionization energy of a solitary atom $\approx 0.6\,\mathrm{eV}$) was measured. The transition from conduction-band to donor-band migration of electrons for donor concentration $N \approx 4 \times 10^{19}\,\mathrm{cm}^{-3}$ occurs at the temperature $T_j \approx 400\,\mathrm{K}$. The calculation using Eq. (28) for the compensation ratio $K \approx 0.15$ gives $T_j \approx 390\,\mathrm{K}$.

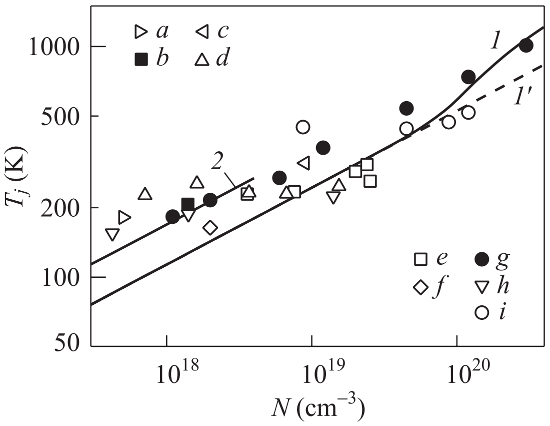

FIG. 2. Dependence of the temperature T_j (at which $\sigma_p \approx \sigma_h$) on the concentration N of boron atoms in a p-type diamond crystal at compensation ratios $K = 0.15$ (curves *1* and *1′*) and $K = 0.5$ (curve *2*). Values of T_j obtained from experimental data are indicated by markers: *a*—Ref. 67, *b*—Ref. 68, *c*—Ref. 69, *d*—Ref. 70, *e*—Ref. 71, *f*—Ref. 72, *g*—Ref. 73, *h*—Ref. 74, and *i*—Ref. 75. Results of calculations using Eq. (27) are shown by solid lines, results of calculations using Eq. (28)—by dashed line.

Fig. 3 shows the concentration p_{mb} of delocalized v-band holes [with energy E_p higher than the mobility edge $E_{\mathrm{mb}}(T_j) = E_{\mathrm{per}} + E_{\mathrm{exc}}$ according to Eq. (20)] as a function of the dopant concentration N at $K = 0.15$, calculated using Eq. (7). Fig. 3 also shows a comparison of these calculations with measurements of the dc electrical conductivity $\sigma = \sigma_p + \sigma_h = 1/\rho$

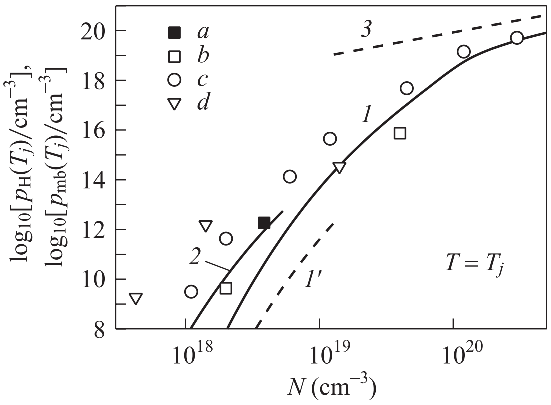

FIG. 3. Concentration of mobile holes $p_{\mathrm{mb}}(T_j)$ as a function of the concentration N of boron atoms in a p-type diamond crystal at the compensation ratios $K = 0.15$ (curves *1*, *1′*, and *3*) and $K = 0.5$ (curve *2*) at temperature $T_j(N, K)$ given by Eq. (27). Experimental values of p_H [see Eq. (30)] at $T = T_j$ from the following references are shown by markers: *a*—Ref. 71, *b*—Ref. 72, *c*—Ref. 73, and *d*—Ref. 74. Lines show calculated results using Eq. (7): *1* and *2*—at $W_a > W_p > 0$; *1′*—at $W_a = 0$, $W_p = 0$ [Eq. (26)]; *3* is the limit of the total thermal ionization of acceptors $p_{\mathrm{mb}} = (1 - K)N$.

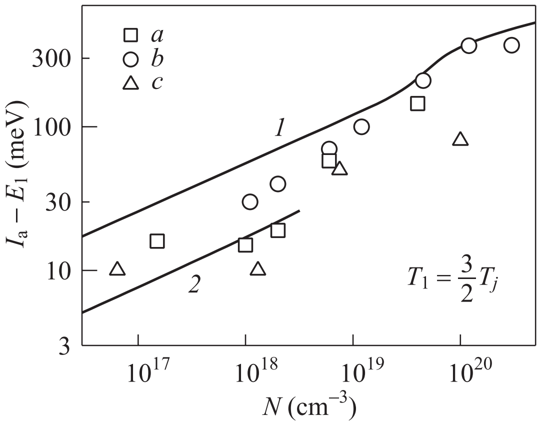

FIG. 4. Thermal ionization energy of boron atoms $E_1 < I_a = 370$ meV at the temperature $T_1 = 3T_j/2$ as a function of their concentration N in a p-type diamond. Calculations of E_1 using Eq. (31) are shown by curves: *1* for $K = 0.15$ and *2* for $K = 0.5$; experimental data are shown by markers: *a*—Ref. 72, *b*—Ref. 73, and *c*—Ref. 80.

and of the stationary Hall effect in homoepitaxial diamond films and p-type diamond crystals.[71–74] For the analysis of the experimental data, we used the relation that takes into account the contribution of both band-like (σ_p) and hopping (σ_h) conductivities to the experimental value of the Hall coefficient[78,79]

$$R_H = \frac{R_p\sigma_p^2 + R_h\sigma_h^2}{(\sigma_p + \sigma_h)^2} \approx \frac{R_p\sigma_p^2}{(\sigma_p + \sigma_h)^2} = \frac{1}{ep_H}\frac{\sigma_p^2}{(\sigma_p + \sigma_h)^2}, \tag{29}$$

where $R_p = 1/ep_H$ is the Hall coefficient due to v-band holes (when the Hall factor equals to unity in a sufficiently strong magnetic field), $R_p\sigma_p$ is the Hall mobility of v-band holes, R_h is the Hall coefficient due to holes hopping between acceptors ($R_h \ll R_p$), and $R_h\sigma_h$ is the hopping Hall mobility of holes in the acceptor band. Then, according to Eq. (29), the experimental value of hole concentration $p_H(T_j)$ determined from Hall effect measurements and electric conductivities at temperature $T = T_j(N, K)$, for which $\sigma_p \approx \sigma_h$, takes the form[18]

$$p_H(T_j) = \frac{\sigma_p^2}{(\sigma_p + \sigma_h)^2}\frac{1}{eR_H} \approx \frac{1}{4eR_H}. \tag{30}$$

We should note that, according to calculations using Eqs. (4) and (7), in the range of boron concentrations indicated in Fig. 3, the concentration of mobile v-band holes p_{mb} hardly differs from the total concentration of holes p (deviation $(p - p_{\mathrm{mb}})/p < 4\%$).

The calculation of $p_{\mathrm{mb}} = p$ using Eq. (26) for $K = 0.15$ is represented in Fig. 3 by the curve *1′*. The calculation of $p \approx p_{\mathrm{mb}} = (1 - K)N$ for $K = 0.15$ is shown in Fig. 3 by the curve *3*.

By analogy with Eq. (26) the differential energy of thermal ionization E_1 of boron atoms in the vicinity of the temperature $T_1 = 3T_j/2$, when $p_{\mathrm{mb}} \ll K(1 - K)N$, is determined as (see, e.g., Refs. 31 and 32)

$$E_1 = -k_B\frac{d\left[\ln\left(p_{\mathrm{mb}}T^{-3/2}\right)\right]}{d(1/T)}, \tag{31}$$

where the concentration p_{mb} of delocalized holes in the v-band (with energy E_p higher than the mobility edge E_{mb} within the volume of crystalline diamond sample) is given by Eq. (7).

The values of E_1 calculated using Eq. (31) for temperature $T_1 = 3T_j/2$ are compared in Fig. 4 to the experimental data of Refs. 72, 73, and 80. Experimental values E_1 were determined in the vicinity of the temperature $T_1 = 3T_j/2$ using linear approximation of the concentration of holes p_H [obtained from the temperature dependences of the Hall coefficient R_H according to Eq. (29)] plotted in the Arrhenius scale: $\ln(p_H T^{-3/2})$ against $1/T$.

V. DRIFT MOBILITY OF v-BAND HOLES IN THE REGIME OF THEIR JUMPING (TURBULENT, RELAY) MIGRATION VIA ACCEPTORS

For the temperature $T \approx T_j(N, K)$, the band-like electrical conductivity σ_p equals to the hopping conductivity σ_h. Then, according to Eqs. (29) and (30), the experimentally determined Hall mobility $\mu_H(T_j)$ of v-band holes is related with the theoretically determined drift mobility $\mu_p(T_j) = \sigma_p/ep_{\mathrm{mb}}$ of v-band holes in the following way:[63]

$$\mu_H(T_j) = R_H\sigma = 2R_H\sigma_p = \frac{\sigma_p}{2ep_H} = \frac{p_{\mathrm{mb}}\mu_p(T_j)}{2p_H} \approx \frac{\mu_p(T_j)}{2}, \tag{32}$$

where $R_H = R_p$ is the Hall coefficient of v-band holes, $\sigma(T_j) = \sigma_p + \sigma_h = 2\sigma_p$ is the total conductivity of v-band holes and of holes hopping between boron atoms, $p_H(T_j) \approx p_{\mathrm{mb}}(T_j)$ is the Hall concentration of v-band holes; $\mu_p(T_j)$ is the drift mobility of v-band holes at temperature T_j.

We assume that in the vicinity of the temperature T_j, the average time of "free" motion t_j of a hole in the crystal matrix with thermal velocity $v_t = (3k_BT_j/m_{p\sigma})^{1/2}$, where $m_{p\sigma}$ is the conductivity effective mass, is approximately equal to the average time of hole localization on an acceptor. Thus, for turbulent transfer of holes (JC regime), the time of flight of a v-band hole on the mobility edge E_{mb} between acceptors is roughly equal to the time of "settled life" of hole at an average acceptor (see also Ref. 81). Therefore, at $T \approx T_j$, the drift mobility $\mu_p(T_j)$ of v-band holes is approximately equal to the jumping drift mobility μ_j of holes via acceptors. Using the Drude model (see, e.g., Refs. 17, 79, and 82), we can estimate the value of μ_j as follows: $\mu_j = et_j/m_{p\sigma}$, where $t_j = L_j/v_t$ is the average time of free "flight" in the form of a jump of hole with the speed v_t between two acceptors in the charge states (0) and (−1), and L_j is the projection of the hole jump distance between acceptors on the direction of the strength of the constant external electric field in the crystal. Taking into account the distribution[42,61] of angles between a half-line with fixed direction and a half-line for which all the directions are equally probable, we get $L_j = S_a/2$, where $S_a = 1.28[(1 + K)N]^{-1/3}$ is the average distance between the closest acceptors in the crystal matrix (determined in Ref. 43 by the Voronoi–Dirichlet polyhedra method).[83] Finally, for the drift mobility of v-band holes $\mu_p(T_j)$ at $T \approx T_j(N, K)$ in the JC regime, we find

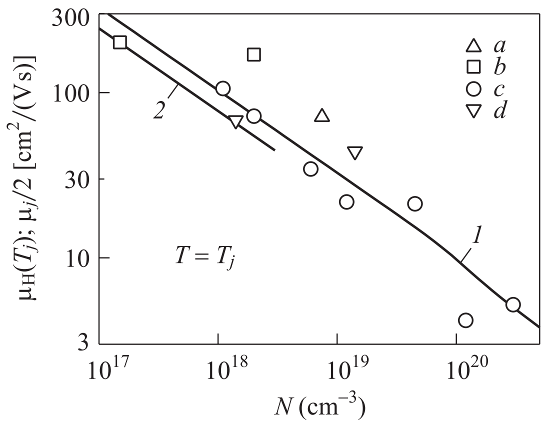

FIG. 5. Jumping (turbulent) mobility of v-band holes $\mu_j/2$ in a p-type diamond crystal as a function of doping impurity (boron atoms) concentration N at the temperature $T = T_j$. Points *a*–*d* are the experimental data on Hall mobility $\mu_H(T_j)$: *a*—Ref. 69, *b*—Ref. 72, *c*—Ref. 73, and *d*—Ref. 74. Lines are calculations of drift mobility $\mu_j/2$ using Eq. (33) taking into account Eqs. (27) and (32) for $K = 0.15$ (curve *1*) and $K = 0.5$ (curve *2*).

$$\mu_p(T_j) \approx \mu_j = \frac{eS_a}{2v_t m_{p\sigma}} \approx \frac{0.37e}{(m_{p\sigma}k_B T_j)^{1/2}[(1+K)N]^{1/3}}, \qquad (33)$$

where $m_{p\sigma}$ is the conductivity effective mass of v-band holes in a diamond crystal[19,25,30,79]

$$m_{p\sigma} = \frac{m_h^{3/2} + m_l^{3/2} + m_{\text{so}}^{3/2}}{m_h^{1/2} + m_l^{1/2} + m_{\text{so}}^{1/2}} = 0.524 m_0.$$

Let us use Eq. (33) taking into account Eq. (32) to calculate the jumping mobility of holes μ_j in p-type diamond at the temperature $T = T_j(N, K)$, found according to Eq. (27). The comparison of calculation results to experimental data[69,72–74] on Hall mobility is shown in Fig. 5. The measured values $\mu_H(T_j)$ agree well with calculations of jumping mobility of holes $\mu_j \approx \mu_p(T_j) = 2\mu_H(T_j)$ up to the boron concentration $N_M \approx 4 \times 10^{20}\,\text{cm}^{-3}$. This boron concentration corresponds after Ref. 11 to the insulator–metal transition (Mott transition) in p-Dia:B. Theoretical estimates of the concentration of boron atoms for the Mott transition (approaching to it from the insulator and from the metal side) according to Ref. 53 for $K = 0.15$ give: 6.1×10^{20} and $4.9 \times 10^{19}\,\text{cm}^{-3}$, respectively.

We should note that we also calculated T_j and μ_j for the experimental data[84] on a ZnO crystal, containing process-related donors with the concentration $N \approx 6.6 \times 10^{18}\,\text{cm}^{-3}$, compensation ratio $K \approx 0.2$, and thermal ionization energy $I_d \approx 18.3$ meV. According to the experiment: $\mu_H(T_j) = 73\,\text{cm}^2/(\text{V s})$ at $T_j = 95$ K. The calculation using Eq. (27) gives the temperature $T_j \approx 270$ K, and the calculation using Eq. (33) gives the jumping (turbulent, relay) drift mobility of electrons via donors $\mu_j/2 \approx 53\,\text{cm}^2/(\text{V s})$. In the calculations, the following parameters of the ZnO crystal were used:[30] $\varepsilon_r = \varepsilon/\varepsilon_0 = 8.28$ and $m_n = m_{n\sigma} = 0.234 m_0$. The difference between the calculated $\mu_j/2$ and experimental $\mu_H(T_j)$ values is related to the fact that the samples of n-ZnO in Ref. 84 are located on the metal side of the Mott transition. Indeed, the calculations according to Ref. 53 give the donor concentration in ZnO for the Mott transition from the insulator and from the metal side: 1.8×10^{17} and $2.4 \times 10^{17}\,\text{cm}^{-3}$, respectively.

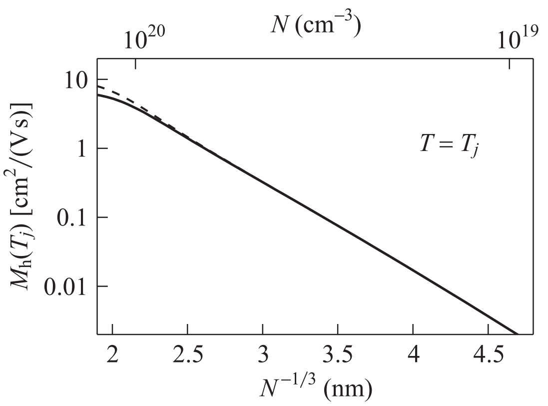

FIG. 6. Hopping drift mobility $M_h(T_j)$ of holes via boron atoms in the charge states (0) and (−1) in a diamond crystal of p-type calculated using Eq. (34) as a function of boron concentration N at the temperature $T = T_j$ for $K = 0.15$. Dashed line is the calculation of $M_h(T_j)$ for $N_h = (1-K)KN$.

Finally, let us estimate the value of drift hopping mobility of holes M_h between boron atoms in diamond at the temperature $T = T_j(N, K)$. From the equality of the electrical conductivities σ_p and $\sigma_h = eN_h M_h$ at $T = T_j$, the expression for the hopping drift mobility of holes via acceptors follows:

$$M_h(T_j) = \frac{\sigma_p(T_j)}{eN_h(T_j)}.$$

Whence taking into account that $\sigma_p(T_j) = ep_{\text{mb}}(T_j)\mu_p(T_j) \approx ep_{\text{mb}}\mu_j$ and $N_h(T_j) = N_0(T_j)N_{-1}(T_j)/N$, we get

$$M_h(T_j) \approx \mu_j \frac{p_{\text{mb}}}{N_0 N_{-1}/N}, \qquad (34)$$

where all the values in Eq. (34) are determined at T_j found from Eq. (27).

In Eq. (34) at T_j the turbulent (jumping, relay) hole mobility μ_j is found using Eq. (33), the concentration of delocalized v-band holes p_{mb} is found using Eq. (7), and the concentration of holes hopping between acceptors $N_h = N_0 N_{-1}/N$ is found using Eq. (8) and taking into account Eq. (3). If $p \ll N_{-1}$ then from Eq. (3) it follows that $N_h = (1-K)KN$.

The hopping drift mobility of holes calculated using Eq. (34) is shown in Fig. 6 as a function of a dopant (boron atoms) concentration. One can see that the quantity $M_h(T_j)$ on the insulator side of the Mott transition is small even at $T = T_j$ and is decreased exponentially at the increase in the average distance $\approx [(1+K)N]^{-1/3}$ between boron atoms. According to Refs. 12 and 44, in the temperature range close to $T_3 \approx T_j/3$, the dc hopping conductivity dominates ($\sigma_h > \sigma_p$). The effective concentration of hopping holes $N_h = (1-K)KN$ does not depend on temperature,[85] and the mobility $M_h(T_3)$ is proportional to $\exp(-\varepsilon_3/k_B T_3)$, where ε_3 is the thermal activation energy for migration of holes via acceptors (boron atoms) in the charge states (0) and (−1). Note that at temperature T_3 [see Fig. 1(a)], the hopping mobility is smaller than at temperature T_j. In fact, the ratio of hopping mobilities of holes $M_h(T_3)/M_h(T_j) \approx \exp[-\varepsilon_3(T_3)/k_B T_3 + \varepsilon_3(T_j)/k_B T_j] < 1$, because $\varepsilon_3(T_3)/k_B T_3 > \varepsilon_3(T_j)/k_B T_j$. This conclusion is also confirmed by theoretical estimates[77] of hopping drift mobility of electrons via donor atoms of phosphorus in the diamond of n-type.

From the comparison of Figs. 5 and 6, it is seen that at the temperature $T = T_j(N, K)$ the calculated jumping (turbulent, relay) drift mobility of v-band holes $\mu_j = \mu_p(T_j)$ is comparable in value with the calculated hopping drift mobility via boron atoms $M_h(T_j)$ for the boron concentration $N > 10^{20}\,\mathrm{cm}^{-3}$ and the compensation ratio $K = 0.15$.

The above estimates may explain the fact that the Hall mobility $R_h\sigma_h$ of holes hopping between acceptors is not registered yet up to the acceptor concentration corresponding to the Mott transition. For example, even for such perfect semiconductor crystals as neutron transmutation doped p-Ge:Ga with compensation ratio $K \approx 0.35$ and the concentration of hopping holes via gallium atoms $N_h = (1 - K)KN \approx 0.23N$, mobility $M_h(T_3)$ cannot be determined from measurements of Hall effect (see Refs. 86–88).

VI. CONCLUSION

We developed a quasi-classical theory for calculating the concentration of holes in the v-band, as well as their drift mobility in boron-doped p-type diamond crystals in the temperature range when the dc band-like conductivity of v-band holes σ_p is roughly equal to the hopping conductivity via boron atoms σ_h. The disorder in crystals is caused by a random spatial distribution of impurity ions and mobile v-band holes. Comparison with the experiment and numerical calculations (without the use of any adjustable parameters) were carried out for the example of p-type diamond crystals doped with boron atoms with concentration $N \approx 3 \times 10^{17}$–$3 \times 10^{20}\,\mathrm{cm}^{-3}$ with an approximately constant ratio of their compensation by donors $K \approx 0.15$. We assumed that boron atoms can be in the charge states (0) and (−1), and donors that compensate them can be only in the charge state (+1) on the background of an electroneutral diamond matrix. Within the frame of the proposed model, a theoretical description of the dependence of the differential energy of thermal ionization of boron atoms as a function of their concentration N in the vicinity of the temperature $T_1 = 3T_j/2$ is given. The calculation of the concentration of mobile v-band holes p_{mb} and their jumping (turbulent, relay) drift mobility μ_j were performed for the temperature T_j. At this temperature, determined on the basis of the virial theorem, the mass capture of holes from the v-band by negatively charged boron atoms ends, and $\sigma_p \approx \sigma_h$. The comparison of the calculation results for p_{mb} and μ_j with experimental data for the temperature T_j shows quantitative agreement for concentrations of boron atoms up to the concentration corresponding to the insulator–metal concentration phase transition (Mott transition), from the insulator side. Estimates of hopping mobility of holes via boron atoms extrapolated from the low temperature region (close to $T_3 \approx T_j/3$) into the high temperature region (close to T_j) are carried out.

ACKNOWLEDGMENTS

This work was supported by the Belarusian National Research Program "MatTekh," by the EU Framework Programme for Research and Innovation Horizon 2020 (Grant No. H2020-MSCA-RISE-2015-691010 HUNTER), and by the Ministry of Education and Science of the Russian Federation (Grant No. NTs-347.2014.2).

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