Release of carriers from traps enhanced by hopping

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Trapping of electrons in localized states strongly affects optoelectronic phenomena in disordered semiconductors. In this paper, it is shown by numerical simulations and by analytical calculations that the release of the trapped electrons into the conduction band can be substantially enhanced by hopping of electrons between the traps. The effect strongly depends on several factors, such as the energy depth of the given trap, the concentration of the assisting traps, and the magnitude of the applied electric field. Recipes are given for theoretical studies of the effect by analytical equations and by kinetic Monte Carlo simulations.

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I. INTRODUCTION

The processes of trapping and detrapping of charge carriers govern numerous optoelectronic phenomena in disordered semiconductors with localized states in the mobility gap [1–4]. For instance, charge transport, photoinduced light absorption, and thermostimulated luminescence belong to such effects. The appropriate theoretical description of trapping and detrapping processes is therefore of vital importance for the theoretical interpretation of various optoelectronic phenomena in disordered semiconductors.

In order to illustrate the importance of trapping and detrapping processes, we consider in Fig. 1 the so-called multiple-trapping (MT) mechanism of charge transport, which is inherent in disordered inorganic semiconductors [1–4] and which is often considered to be valid also in organic disordered semiconductors [5–8]. In the MT process, a charge carrier moves only via delocalized states with energies above the mobility edge ϵ_c. This motion is interrupted by trapping of carriers into localized states with a subsequent activation of carriers into conducting states above the mobility edge. The time which a carrier spends in the system, i.e., the time which determines the carrier mobility, is controlled by the rates of the carrier release from the traps into conducting states above ϵ_c.

The standard approach to describe the trapping and detrapping processes is as follows. Without the electric field, the escape rate from a trap into the conduction band is assumed to be equal to

$$\nu_{\rm esc}(\varepsilon) = \nu_0 \exp\left(-\frac{\varepsilon}{kT}\right), \tag{1}$$

where ε is the energy of the trap counted positively downwards from the mobility edge and ν_0 is the preexponential factor determined by the interaction mechanism responsible for the transition. If transitions are caused by interaction with phonons, ν_0 is usually assumed to be of the order of the phonon frequency. Focusing on the effect of the electric field F on the exponential factor, we will not consider the effect of F on ν_0.

The effect of the electric field on $\nu_{\rm esc}(\varepsilon)$ was first studied theoretically by Keldysh [9], who showed that the applied electric field can diminish the activation barrier for the electron escape from a trap, as illustrated schematically in Fig. 2, where the process of thermally assisted tunneling due to the electron-phonon coupling is depicted. This is a thermal equivalent of the well-known Franz-Keldysh effect. In this scheme, the escape event consists of two processes: activation with the energy deficit $\Delta\varepsilon$, as compared to the trap depth ε, and tunneling over the distance $\Delta x = \Delta\varepsilon/(eF)$ under the triangle energy barrier. Ascribing to the preexponential factor a universal value ν_0 and introducing the variable $z \equiv (\Delta\varepsilon)/kT$, one can represent the result of Keldysh in the form

$$\nu_{\rm esc}(\varepsilon) = \nu_0 \exp\left\{-\frac{\varepsilon}{kT}\right\} \times \left[1 + \int_0^{\varepsilon/kT} \exp\left\{z - \frac{4\sqrt{2m}(zkT)^{3/2}}{3e\hbar F}\right\} {\rm d}z\right], \tag{2}$$

where m is the effective mass.

Localized states in organic disordered semiconductors and traps in the band tails of inorganic disordered materials are considered electrically neutral in the absence of carriers and charged if carriers are present on the traps [1–4]. The release of carriers from the traps in our study is therefore in contrast to the ionization of traps considered, for instance, by Frenkel [10], who treated traps as neutral when occupied by electrons and ionized (positively charged) when electrons were released from the traps.

It was recently shown [11] that the combined effects of an electric field F and temperature T on the release rate given by Eq. (2) can be described by a single parameter, the so-called

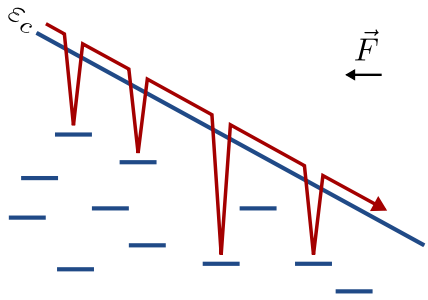

FIG. 1. Sketch of the multiple-trapping process.

effective temperature $T_{eff}(T, F)$. In the following calculations, we use Eq. (2), which accounts for the effect of the electric field on the escape probability from an individual trap. The major, exponential effect of the electric field on the escape rate from a single trap is captured by Eq. (2). Besides this major effect, the presence of the electric field can change the conduction band wave functions and concomitantly change the transition rate matrix elements, so that the factor ν_0 in Eq. (2) can also be field dependent. In the current study, we will not address the field dependence of ν_0 in Eq. (2) because it should be only a weak correction to the main, exponential field dependence that occurs due to the interplay between the Boltzmann exponent and the tunneling exponent accounted for by Eq. (2). Interested readers can find a thorough study of the field dependence of the escape rate from a single trap in the paper by Karpus and Perel [12]. That paper takes into account all the effects of the electric field on the release rate from a single trap. Not the straight release of a carrier from a single trap to the conduction band is the topic of the current paper. Therefore, we will avoid the elaborate mathematics of Karpus and Perel [12] that is only necessary to treat the minor effects of the electric filed on the escape probability for a single trap. We instead adopt in the current study the more transparent approach of Keldysh [9] and Vincent *et al.* [13], keeping ν_0 in Eq. (2) field independent.

In Eqs. (1) and (2), it is assumed that the rate of carrier release from a given trap is not affected by the presence of other traps. We verify this assumption in the current paper and prove by analytical calculations and by numerical simulations that hopping transitions between the traps can significantly enhance the exchange of electrons between the traps and the conducting states above the mobility edge. In Sec. II, we consider a single additional trap and analytically derive the expression for the release rate of a carrier from a given trap if hopping between the traps is taken into account. In Sec. III, equations are derived for the case when electron transitions between a given trap and several other traps can contribute to the release rate. Results of the straightforward Monte Carlo simulations, which take into account transitions between several traps, are presented in Sec. IV. Concluding remarks are gathered in Sec. V.

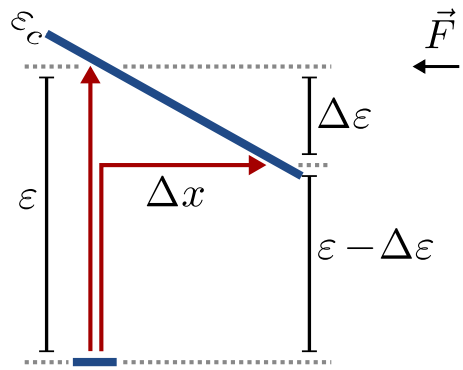

FIG. 2. Schematic picture of the field-enhanced escape from a single trap.

II. DETRAPPING ENHANCED BY A SINGLE EXTRA TRAP: ANALYTICALLY SOLVABLE PROBLEM

Let us consider the simplest model illustrated in Fig. 3(a), in which the hopping-assisted detrapping can take place. It includes one electron, two localized states (trap 1 and trap 2), and the conduction band, which is tilted due to the external electric field. An electron initially resides on trap 1. Possible electron transitions from trap 1 are the escape to the conduction band and the hop to trap 2, with rates Γ_1 and Γ_{12}, respectively. Similarly, if the electron resides on trap 2, the possible processes are the escape to the conduction band (with rate Γ_2) and a hop to trap 1 (with rate Γ_{21}). We are interested in the mean time t between the moment when an electron arrives in trap 1 and the moment when it escapes to the conduction band. The question is, can the value of t be considerably smaller than the corresponding time $1/\Gamma_1$ in the absence of trap 2? In other words, can the presence of the additional trap significantly enhance the process of the electron escape from a trap to the conduction band?

In order to calculate the mean time t exactly, it is convenient to analyze a steady state with a continuous supply of electrons into trap 1 with a constant rate γ_0 that is infinitely small compared to the rates of other processes. When an electron reaches the conduction band, it disappears from our consideration. In this setting, the mean escape time t is expressed as

$$t = \frac{p_1 + p_2}{\gamma_0}, \tag{3}$$

where p_1 and p_2 are the probabilities of finding the electron in the steady state on trap 1 and on trap 2, respectively. These probabilities can be calculated from a system of balance equations for the two traps,

$$\begin{aligned} (\Gamma_1 + \Gamma_{12})\, p_1 &= \Gamma_{21}\, p_2 + \gamma_0, \\ (\Gamma_2 + \Gamma_{21})\, p_2 &= \Gamma_{12}\, p_1. \end{aligned} \tag{4}$$

Equations (3) and (4) provide the solution in the form

$$t = \frac{\Gamma_2 + \Gamma_{12} + \Gamma_{21}}{\Gamma_1\Gamma_2 + \Gamma_{12}\Gamma_2 + \Gamma_{21}\Gamma_1}. \tag{5}$$

Let us consider a particular case of traps with equal energies. Let the direction from trap 1 to trap 2 be against the electric field, so that trap 2 is shallower than trap 1, as depicted in Fig. 3(b). Since the traps are isoenergetic, the principle of detailed balance implies that $\Gamma_{12} = \Gamma_{21}$. The dependence of the hopping rates on the distance d between the traps is

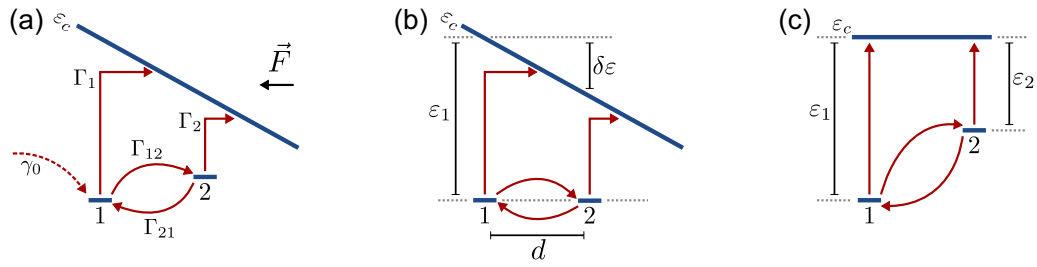

FIG. 3. Two localized states under electric field **F**: (a) space-energy diagram for the general case, (b) specific case of isoenergetic traps, and (c) specific case of $F = 0$.

governed by the localization length a for electron states on single traps,

$$\Gamma_{12} = \Gamma_{21} = \nu_h \exp\left(-\frac{2d}{a}\right). \tag{6}$$

In a more general case of nonisoenergetic localized states i and j, the rate Γ_{ij} obeys the Miller-Abrahams expression [14]:

$$\Gamma_{ij} = \nu_h \exp\left(-\frac{2d_{ij}}{a}\right)\begin{cases}1 & \text{if } \Delta_{ij} < 0,\\ \exp(-\Delta_{ij}/kT) & \text{if } \Delta_{ij} > 0,\end{cases}$$

where Δ_{ij} is the difference between the energies of states j and i. The expression for the preexponential factor ν_h in the case of one-phonon transitions caused by deformation potential can be found in the monograph by Shklovskii and Efros [15]. One can deduce from their Eqs. (4.2.6) and (4.2.18) that

$$\nu_h = \frac{E_1^2|\Delta_{ij}|}{\pi\rho s^5\hbar^4} I_0^2\left[1 + \left(\frac{\Delta_{ij}a}{2\hbar s}\right)^2\right]^{-4},$$

where E_1 is a deformation potential constant, ρ is the mass density, s is the sound velocity, and I_0 is the preexponent in the dependence of the energy overlap integral I_{ij} on the distance d_{ij}: $I_{ij} = I_0 \exp(-d_{ij}/a)$. For hydrogenlike impurities, the expression for I_{ij} is given by Eq. (4.2.6) of Shklovskii and Efros [15].

The ratio of the escape rates Γ_2/Γ_1 is defined mainly by the difference $\delta\varepsilon$ between their depths with respect to the mobility edge,

$$\frac{\Gamma_2}{\Gamma_1} \simeq \exp\left(\frac{\delta\varepsilon}{kT}\right) = \exp\left(\frac{eFd}{kT}\right). \tag{7}$$

Substituting $\Gamma_{21} = \Gamma_{12}$ into Eq. (5) and taking into account that $\Gamma_1 \ll \Gamma_2$, one obtains

$$t \approx \frac{1}{\Gamma_2}\,\frac{\Gamma_2 + 2\Gamma_{12}}{\Gamma_1 + \Gamma_{12}}. \tag{8}$$

In Fig. 4, we schematically plot the dependence $t(d)$ for a given depth of trap 1. When the distance d is sufficiently small, Γ_{12} is much larger than the other rates in Eq. (8). Neglecting Γ_1 and Γ_2 compared to Γ_{12}, one can conclude that

$$t(d) \approx \frac{2}{\Gamma_2(d)} \simeq \frac{2}{\Gamma_1}\exp\left(-\frac{eFd}{kT}\right), \tag{9}$$

where we have expressed Γ_2 via Γ_1 using Eq. (7). In this regime [a decreasing part of the dependence $t(d)$ in Fig. 4], an electron typically hops back and forth between the traps many times, and only afterwards does it escape from the shallow trap 2. Hence, the process of electron escape is controlled in this regime by the rate Γ_2.

With increasing distance d, the hopping rate Γ_{12} *decreases* according to Eq. (6), and the escape rate Γ_2 *increases* because trap 2 becomes shallower with increasing d. At some "optimal" distance $d_{\rm opt}$ the two rates become equal to each other:

$$\Gamma_{12}(d_{\rm opt}) = \Gamma_2(d_{\rm opt}). \tag{10}$$

Neglecting Γ_1 in Eq. (8), one obtains the corresponding optimal mean escape time $t_{\rm opt} = t(d_{\rm opt})$,

$$t_{\rm opt} \approx \frac{3}{\Gamma_2(d_{\rm opt})}. \tag{11}$$

At larger distances d, the hopping rate Γ_{12} is small compared to Γ_2, although still large compared to Γ_1. According to Eqs. (8) and (6), this yields

$$t(d) \approx \frac{1}{\Gamma_{12}(d)} = \nu_h^{-1}\exp\left(\frac{2d}{a}\right). \tag{12}$$

The corresponding regime is depicted by the increasing part of the dependence $t(d)$ in Fig. 4. In this regime, an electron typically resides on trap 1 until it hops to trap 2, which is followed by a fast escape from trap 2 into the conduction band. The dynamics of this process is mainly governed by the hopping rate Γ_{12}.

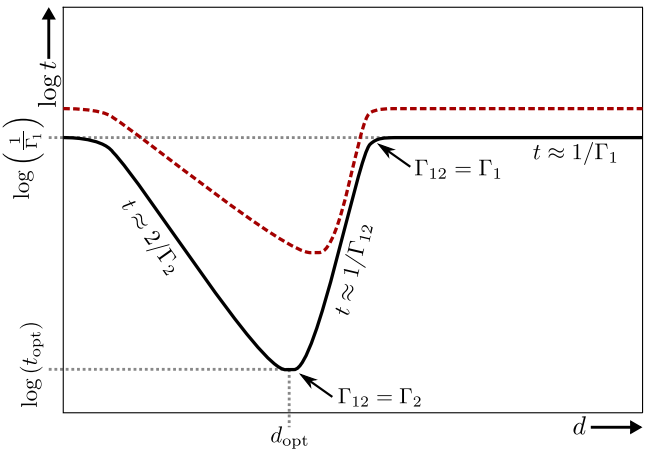

FIG. 4. Escape time t versus the distance d between the traps in the model of the two isoenergy traps depicted in Fig. 3(b). The red dashed line corresponds to an electric field two times smaller than the field for the solid black line.

Finally, at sufficiently large distances d, the hopping rate Γ_{12} becomes smaller than both Γ_1 and Γ_2, and it therefore can be neglected in Eq. (8). In this regime, the escape time does not depend on d anymore:

$$t(d) \approx \frac{1}{\Gamma_1} \tag{13}$$

[the horizontal section of the dependence $t(d)$ in Fig. 4]. Indeed, if $\Gamma_{12} \ll \Gamma_1$, the most probable scenario is that the electron escapes to the conduction band directly from trap 1, instead of visiting the additional trap 2 because trap 2 becomes too remote from trap 1 to be involved in the escape process.

The overall dependence $t(d)$ (solid line in Fig. 4) consists, therefore, of three regions corresponding to Eqs. (9), (12), and (13). If the strength of the electric field is halved, the dependence $t(d)$ is represented in Fig. 4 by the dashed line. One can see that the additional trap enhances the process of the electron release most efficiently when such a trap is located at a distance $d_{\rm opt}$, which can be found via Eqs. (6), (7), and (10),

$$d_{\rm opt} = \left(\frac{2}{a} + \frac{eF}{kT}\right)^{-1} \ln\frac{\nu_h}{\Gamma_1}. \tag{14}$$

According to Eqs. (7), (11), and (14), the corresponding mean escape time $t_{\rm opt}$ is equal to

$$t_{\rm opt} \approx \frac{3}{\Gamma_1}\left(\frac{\Gamma_1}{\nu_h}\right)^{1/(1+2kT/eFa)}. \tag{15}$$

At a moderate electric field, when $eFa \ll kT$, one can simplify this expression by replacing the exponent $1/(1 + 2kT/eFa)$ with $eFa/2kT$ and neglecting all contributions to the ratio Γ_1/ν_h except the Boltzmann factor,

$$\frac{\Gamma_1}{\nu_h} \simeq \exp\left(-\frac{\varepsilon_1}{kT}\right), \tag{16}$$

with ε_1 being the depth of the trap 1. Herewith one obtains the following estimate:

$$t_{\rm opt} \simeq \Gamma_1^{-1} \exp\left[-\frac{\varepsilon_1 eFa}{2(kT)^2}\right]. \tag{17}$$

Aiming to reveal how efficiently the additional trap may enhance the release of an electron into the conduction band, it is convenient to consider the *enhancement factor* $\mathcal{F}$, defined as the ratio between the mean escape time from a single trap Γ_1^{-1} and the escape time $t_{\rm opt}$ in the presence of an additional trap at the optimal position,

$$\mathcal{F} = \frac{\Gamma_1^{-1}}{t_{\rm opt}}. \tag{18}$$

With $t_{\rm opt}$ estimated in Eq. (17), the enhancement factor is

$$\mathcal{F} \simeq \exp\left[\frac{\varepsilon_1 eFa}{2(kT)^2}\right]. \tag{19}$$

The factor $\mathcal{F}$ increases with an applied electric field, and it reaches exponentially large values if the trap is sufficiently deep ($\varepsilon_1 \gg kT$).

One can see in Eq. (19) that the carrier release process is also enhanced with lowering the temperature T and with increasing the depth ε_1 of the trap for a given electric field strength. The role of the trap depth will be clearer in Sec. IV B, which gives a comparison between the simulation results for trap depth $\varepsilon_1 = 0.3$ eV and those for depth $\varepsilon_1 = 0.5$ eV. In order to understand the role of temperature, one can note that the field F and the trap depth ε_1 may appear in the dimensionless enhancement factor $\mathcal{F}$ only as the dimensionless combinations $F^* = eFa/kT$ and $\varepsilon_1^* = \varepsilon_1/kT$. Therefore, the lowering of temperature results in the increase of both F^* and ε_1^*, which affects the enhancement factor in exactly the same way as a simultaneous increase of the electric field and the trap depth.

The increase of the enhancement factor with decreasing temperature can also be seen directly from Eq. (5). Consider for simplicity the case of the isoenergetic traps depicted in Fig. 3(b). Substituting Eq. (5) into the enhancement factor $\mathcal{F} = \Gamma_1^{-1}/t$ and taking into account that $\Gamma_{12} = \Gamma_{21}$, one obtains that

$$\mathcal{F} = \Gamma_{12}\frac{\Gamma_2/\Gamma_1 - 1}{\Gamma_2 + 2\Gamma_{12}} + 1.$$

When the temperature decreases, the numerator $\Gamma_2/\Gamma_1 - 1$ increases because $\Gamma_2/\Gamma_1 = \exp(eFd/kT)$ according to Eq. (7). At the same time, the denominator $\Gamma_2 + 2\Gamma_{12}$ decreases since $\Gamma_2 \propto \exp(-\varepsilon_2/kT)$, while the hopping rate Γ_{12} between the isoenergetic sites remains the same (up to the preexponential factor). As a consequence, the enhancement factor increases with decreasing temperature *at any distance d between the traps*. This increase is especially strong at the optimal distance $d_{\rm opt}$ where, according to Eqs. (11), (7), and (18), $\mathcal{F} \simeq \Gamma_2(d_{\rm opt})/\Gamma_1 = \exp(eFd_{\rm opt}/kT)$. One can briefly formulate the effect of temperature on the enhancement factor as follows. The lower the temperature is, the faster the way of escaping via site 2 is, compared to the direct escape from site 1.

The obtained strong dependence of the enhancement factor on the electric field is illustrated in Fig. 4, where we schematically plot the two dependences $t(d)$ for the two different values of the electric field F. The decreasing part of the dependence demonstrates a smaller slope at smaller F (red dashed line) because $\ln(\Gamma_2/\Gamma_1)$ is proportional to F due to Eq. (7). Therefore, the logarithm of the enhancement factor is also approximately proportional to the field, in agreement with Eq. (19). Furthermore, the transition rate $\Gamma_1 \equiv \nu_{\rm esc}(\varepsilon_1)$ depends on the electric field F: a smaller field efficiently causes trap 1 to be at a larger energy depth relative to the conduction band, thereby decreasing Γ_1. This effect is described by Eq. (2) and is also schematically depicted in Fig. 4, where the red dashed line (corresponding to smaller F) in the limits of small and large distances d demonstrates a larger value of the escape time $t \approx 1/\Gamma_1$.

The enhancement of the detrapping efficiency has been derived so far for the specific case of the additional trap having the same energy as the first trap. In a more general case, the enhancement can be even more pronounced. It is worth emphasizing that the effect appears in the presence of an external electric field. In contrast, the increase in the release rate due to the presence of an additional trap *without electric field* cannot exceed a factor of 2. In the case of $F = 0$ depicted in Fig. 3(c), the ratio Γ_{21}/Γ_{12} and the ratio Γ_2/Γ_1 are defined

by the same Boltzmann factor $\exp[(\varepsilon_1 - \varepsilon_2)/kT]$,

$$\Gamma_{21} = \Gamma_{12} \exp\left(\frac{\varepsilon_1 - \varepsilon_2}{kT}\right) \tag{20}$$

and

$$\Gamma_2 = \Gamma_1 \exp\left(\frac{\varepsilon_1 - \varepsilon_2}{kT}\right). \tag{21}$$

Substituting Eqs. (20) and (21) into Eq. (5), one can express the enhancement factor $\mathcal{F}$ in the absence of an electric field as

$$\mathcal{F} = \frac{\Gamma_1^{-1}}{t} = \frac{\Gamma_1 + 2\Gamma_{12}}{\Gamma_1 + [1 + e^{-(\varepsilon_1 - \varepsilon_2)/kT}]\Gamma_{12}}. \tag{22}$$

Apparently, $\mathcal{F}$ cannot exceed 2 because, in any case, the numerator on the right-hand side is smaller than twice the denominator. The largest possible value of $\mathcal{F} \approx 2$ can be reached if $\exp[-(\varepsilon_1 - \varepsilon_2)/kT] \ll 1$ (i.e., the additional trap 2 is higher in energy than trap 1 by at least several kT) and, simultaneously, $\Gamma_{12} \gg \Gamma_1$, which can be fulfilled if the traps are sufficiently close to each other. In such a case, the additional trap just provides another channel for the electron escape, which is as fast as the direct escape from the first trap. At the same time, the additional trap provides a channel for the electron *capture* from the conduction band to trap 1. The capture efficiency and the release efficiency are enhanced in the same ratio, as prescribed by the detailed balance in the absence of an electric field.

Therefore, it is shown using the simplest model that the electron release from a trap to the conduction band can be substantially enhanced by the presence of an additional, shallower trap. In the absence of the external electric field, the factor of enhancement $\mathcal{F}$ is not larger than 2. In the presence of the external electric field F, the factor of enhancement depends on F exponentially, in agreement with Eq. (19). Thus, the release rate can be enhanced by several orders of magnitude.

III. DETRAPPING ENHANCED BY SEVERAL EXTRA TRAPS: NUMERICALLY SOLVABLE PROBLEM

Let us generalize the model considered in Sec. II, taking into account several additional traps. An electron is placed initially on trap 1, and the dynamics is governed by the rates Γ_{mn} of electron hopping between the traps and by the rates Γ_n of electron escape from trap n to the conduction band, as illustrated in Fig. 5. In this model with several traps, Eq. (4) turns into the following system of balance equations (one equation per a trap):

$$\begin{aligned}
\left(\Gamma_1 + \sum_{n\neq 1}\Gamma_{1n}\right) p_1 &= \sum_{n\neq 1}\Gamma_{n1}\, p_n + \gamma_0,\\
\left(\Gamma_2 + \sum_{n\neq 2}\Gamma_{2n}\right) p_2 &= \sum_{n\neq 2}\Gamma_{n2}\, p_n,\\
&\cdots\\
\left(\Gamma_m + \sum_{n\neq m}\Gamma_{mn}\right) p_m &= \sum_{n\neq m}\Gamma_{nm}\, p_n,\\
&\cdots,
\end{aligned} \tag{23}$$

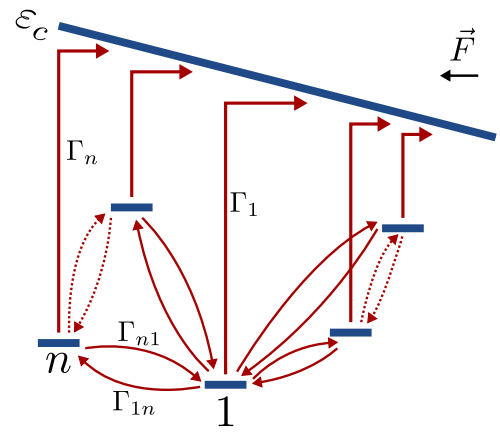

FIG. 5. A model with several traps. Dashed arrows show hopping transitions that are present in the complete model [Eqs. (23) and (24)] but absent in the reduced "bush" model [Eqs. (25)–(29)].

where $p_1, p_2, \ldots$ are the probabilities of finding an electron on the corresponding traps. The mean time t which an electron spends in the system of traps before escaping into the conduction band is equal to

$$t = \frac{\sum_n p_n}{\gamma_0}, \tag{24}$$

which is a direct generalization of Eq. (3).

Equations (23) and (24) permit us to calculate the escape time t by methods of linear algebra, provided the set of hopping rates $\{\Gamma_{mn}\}$ and the set of escape rates $\{\Gamma_n\}$ are given.

The solution for t can be considerably simplified and represented in a closed form if one neglects the hops between traps other than the hops from/to trap 1. In such a reduced "bush" model, the rates for transitions illustrated by the dashed arrows in Fig. 5 are "switched off," and the hopping rate Γ_{mn} is nonzero only if $m = 1$ or $n = 1$. In such a simplified model, the balance equations (23) are reduced to

$$\begin{aligned}
\left(\Gamma_1 + \sum_{n\neq 1}\Gamma_{1n}\right) p_1 &= \sum_{n\neq 1}\Gamma_{n1}\, p_n + \gamma_0,\\
(\Gamma_2 + \Gamma_{21}) p_2 &= \Gamma_{12}\, p_1,\\
&\cdots\\
(\Gamma_m + \Gamma_{m1}) p_m &= \Gamma_{1m}\, p_1,\\
&\cdots.
\end{aligned} \tag{25}$$

This system of equations can be solved by the elimination of p_2 (p_3, etc.) using the second (third, etc.) equation. As a result, the expression for the mean escape time t acquires the closed form

$$t = \frac{1 + \sum_{n\neq 1} \frac{\Gamma_{1n}}{\Gamma_n + \Gamma_{n1}}}{\Gamma_1 + \sum_{n\neq 1} \frac{\Gamma_{1n}\Gamma_n}{\Gamma_n + \Gamma_{n1}}}. \tag{26}$$

In the case of a single assisting trap, Eq. (26) takes on the form of Eq. (5) obtained in Sec. II.

The escape time t should be averaged over the possible random realizations of the distribution of traps around the given trap 1. It is possible, however, to obtain a reasonable estimate

for the averaged t (order of magnitude) without dealing with the random realizations. For that purpose, one can just average the numerator and the denominator in Eq. (26) separately (the angle brackets denote the averaging over realizations):

$$\langle t \rangle \simeq \frac{\left\langle 1 + \sum_{n\neq 1} \frac{\Gamma_{1n}}{\Gamma_n + \Gamma_{n1}} \right\rangle}{\left\langle \Gamma_1 + \sum_{n\neq 1} \frac{\Gamma_{1n}\Gamma_n}{\Gamma_n + \Gamma_{n1}} \right\rangle}. \tag{27}$$

This procedure is justified for estimating the average $\langle t \rangle$ if the denominator does not vary in an exponentially broad range. Summations in the averaging can be replaced by integrations

$$\sum_n \quad \rightarrow \quad \int d\mathbf{r}_n \int d\varepsilon_n \; g(\varepsilon_n), \tag{28}$$

where $g(\varepsilon)$ is the density of states of the traps. This yields an analytical estimate for the average escape time in the form

$$\langle t \rangle \simeq \frac{1 + \int d\mathbf{r}_n \int d\varepsilon_n \; g(\varepsilon_n) \, \frac{\Gamma_{1n}(\mathbf{r}_n, \varepsilon_n)}{\Gamma_n(\varepsilon_n) + \Gamma_{n1}(\mathbf{r}_n, \varepsilon_n)}}{\Gamma_1 + \int d\mathbf{r}_n \int d\varepsilon_n \; g(\varepsilon_n) \, \frac{\Gamma_{1n}(\mathbf{r}_n, \varepsilon_n) \, \Gamma_n(\varepsilon_n)}{\Gamma_n(\varepsilon_n) + \Gamma_{n1}(\mathbf{r}_n, \varepsilon_n)}}. \tag{29}$$

All the rates contributing to Eq. (29) should be found while taking the external electric field into account. The range of the integration over $d\varepsilon_n$ starts at the energy of the given trap 1 and extends towards the conduction band edge.

Hence, there are three methods of calculating the mean escape time from a given trap: (i) by solving the system of equations (23) and (24); (ii) by Eq. (26) in the bush model, which neglects the hopping transitions if the given trap 1 is not involved; and (iii) by the approximate analytical formula (29). The first and second methods assume the averaging over realizations of the traps around the given trap 1, while in the third method, this averaging is incorporated by the integration.

Alternatively to solving the system of balance equations, one can use a kinetic Monte Carlo (KMC) method to simulate the carrier escape from a given trap due to hopping transitions to the surrounding traps accompanied by electron activation from those traps into the conduction band. If the number of involved traps is large, the KMC approach can be favored as a less elaborate one than the solution of the balance equations. In Sec. IV, we provide the KMC algorithm for studying the role of the hopping transitions in the detrapping process and highlight the results of simulations.

IV. MONTE CARLO SIMULATIONS OF THE ELECTRON ESCAPE ASSISTED BY SEVERAL TRAPS

In this section, we present the results of the numerical study of the hopping-assisted detrapping using the KMC approach. In Sec. IV A, the algorithm is described in detail, while in Sec. IV B, the obtained results are discussed.

A. Simulation details

The simulation algorithm consists of the following steps.

(1) First, a set of N_0 traps, also called sites, is generated. The sites are distributed exponentially in energy with a characteristic energy E_0. The sites are distributed randomly in space with concentration N determined by a given value of the dimensionless parameter Na^3, where a is the localization length of a single trap.

(2) A trap with energy E_i is placed at the origin of the coordinate system (0,0,0), and the escape of a charge carrier from this trap is simulated. Since the detrapping from the localized states with energies in the vicinity of the Fermi level dominates all the transport phenomena, we assume that E_i corresponds to the Fermi level. The traps with energies below E_i are therefore assumed to be occupied by carriers, while sites with energies above E_i are assumed to be empty.

(3) The rates of all possible events are calculated. The rate of the straight release of a charge carrier from a trap into the conduction band is described by Eq. (2). The hopping rates are assumed to be described by the Miller-Abrahams expression [14]. For each pair of sites (i, j), the transition rate ν_{ij} is determined by the separation between sites, $\mathbf{r}_{ij} \equiv \mathbf{r}_j - \mathbf{r}_i$, and the energy difference $\varepsilon_j - \varepsilon_i$,

$$\nu_{ij} = \nu_0 \exp\left(-\frac{2|\mathbf{r}_{ij}|}{a}\right) \gamma(\varepsilon_j - \varepsilon_i + e\mathbf{F}\cdot\mathbf{r}_{ij}), \tag{30}$$

with

$$\gamma(\Delta\varepsilon) = \begin{cases} \exp(-\Delta\varepsilon/kT) & \text{if } \Delta\varepsilon > 0, \\ 1 & \text{otherwise.} \end{cases} \tag{31}$$

(4) The cumulative event rate $\Gamma_i = \nu_{\text{esc}} + \sum_{i\neq j} \nu_{ij}$ is calculated, and the time until the next event is determined as $\Delta\tau_i = \Gamma_i^{-1} R_i$, where $R_i = -\ln(x_i)$ includes the random number x_i uniformly distributed in the range [0,1].

(5) In order to determine the particular event that happens with the charge carrier, the rates of all possible events were normalized via the cumulative event rate Γ_i, and another random number $p \in [0, 1]$ was used in order to choose the event in agreement with its rate.

(6) If the chosen event is a release of the carrier to the conduction band, the simulation with the given charge carrier was finished by updating the cumulative time. If the chosen event is a hopping transition, the carrier is moved, the cumulative time which the carrier spends in the localized states $\tau = \tau + \Delta\tau_i$ is updated, and the algorithm returns to step 3.

The results were averaged over a large number of realizations between 10^4 and 10^5. The number of traps in the simulations was $N_0 = 10^3$. The characteristic energy of the exponential DOS was set to $E_0 = 5 \times 10^{-2}$ eV. The values of the parameter Na^3 were varied from 10^{-3} to 10^{-1}, and the strength of the electric field F was varied from 0 to 1 MV/cm. Simulations were carried out at room temperature $T = 300$ K.

B. Simulation results

Using the algorithm described above, the hopping-assisted release of charge carriers from deep traps with energies 0.3 and 0.5 eV was simulated for different values of the parameter Na^3 that determines the efficiency of the hopping exchange of carriers between the traps. In Figs. 6 and 7 the simulation results are given for a trap with an energy depth of 0.3 eV, while the results for a trap with an energy depth of 0.5 eV are presented in Figs. 8 and 9.

The red dotted lines in Figs. 6 and 8 correspond to the case of a single trap. These results were obtained in agreement with Eq. (2). The value of the effective mass in these calculations was taken to be equal to the free-electron mass m_0. The green dotted lines in Fig. 6 and the blue dotted lines in

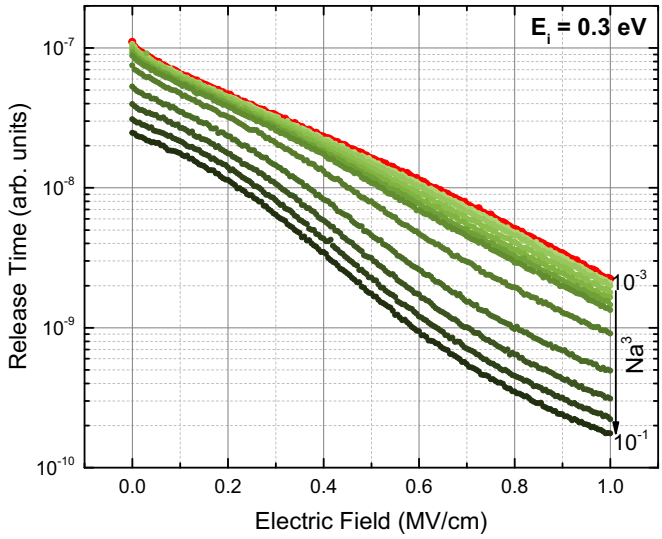

FIG. 6. Release time versus field F for the trap with energy $E_i = 0.3\,\mathrm{eV}$. The red dotted line corresponds to the straight release from the trap into the conduction band given by Eq. (2); green dotted lines correspond to the release assisted by hopping for different values of Na^3.

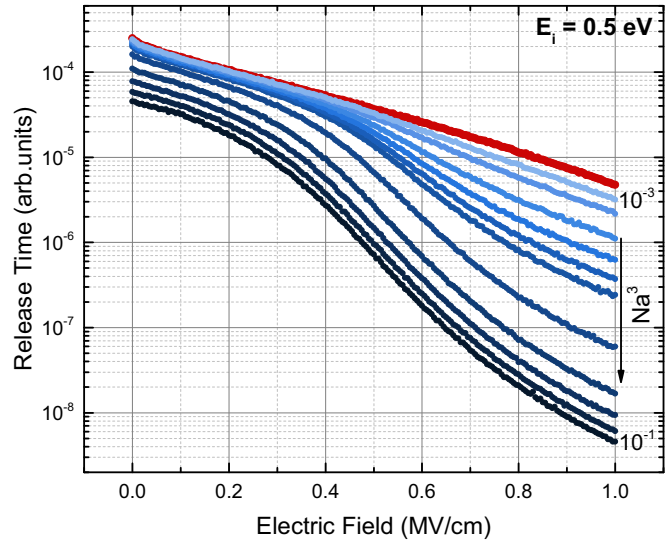

FIG. 8. Release time versus field F for the trap with energy $E_i = 0.5\,\mathrm{eV}$. The red dotted line corresponds to the straight release from the trap into the conduction band given by Eq. (2); blue dotted lines correspond to the release assisted by hopping for different values of Na^3.

Fig. 8 correspond to the hopping-assisted release for different concentrations of traps in the range between $Na^3 = 10^{-3}$ and 10^{-1}. It is apparent that the release time (rate) from the given trap significantly decreases (increases) due to the hopping exchange of carriers between the traps. The effect depends on the value of the parameter Na^3. At high fields, the effect for $Na^3 = 10^{-1}$ achieves several orders of magnitude. In order to illustrate the effect of the release enhancement due to the hopping exchange between the traps, we plot in Figs. 7 and 9 the ratio between the release time in the case of the hopping exchange and the release time given by Eq. (2). The release enhancement for the trap with a depth of 0.5 eV achieves three orders of magnitude at $Na^3 = 10^{-1}$, $F = 1\,\mathrm{MV/cm}$. At a low concentration of traps $Na^3 = 10^{-3}$, the effect is less significant.

It is seen in Figs. 6, 7, 8, and 9 that the release rate $\nu_{\mathrm{esc}}(\varepsilon) = t^{-1}(\varepsilon)$ from a given trap is enhanced in the presence of other traps compared to the case of a single trap already at $F = 0$ V/cm. This effect is accompanied by the equal enhancement of the trapping rate $\nu_{\mathrm{trap}}(\varepsilon)$ in a given trap due to the assistance of the surrounding traps. The dependence of such an enhancement on Na^3 is shown in Fig. 10. This enhancement of $\nu_{\mathrm{esc}}(\varepsilon)$ does not, however, affect the equilibrium concentration of carriers in the conducting states above the mobility edge because of the validity of the detailed

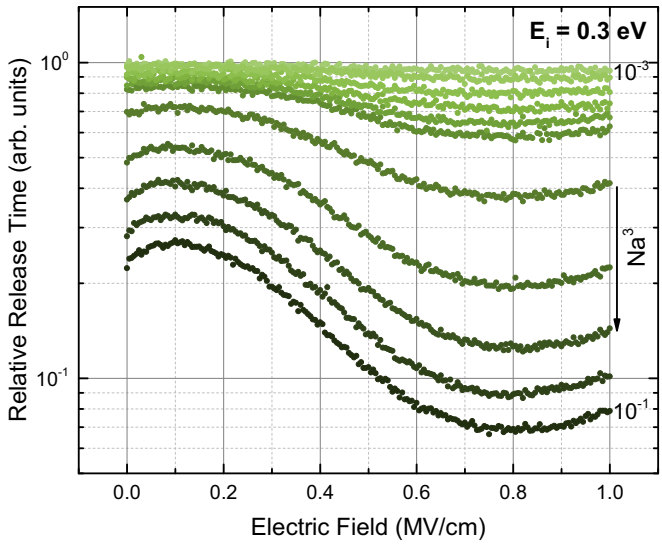

FIG. 7. Release time normalized by the value given by Eq. (2) versus field F for the trap with energy $E_i = 0.3\,\mathrm{eV}$.

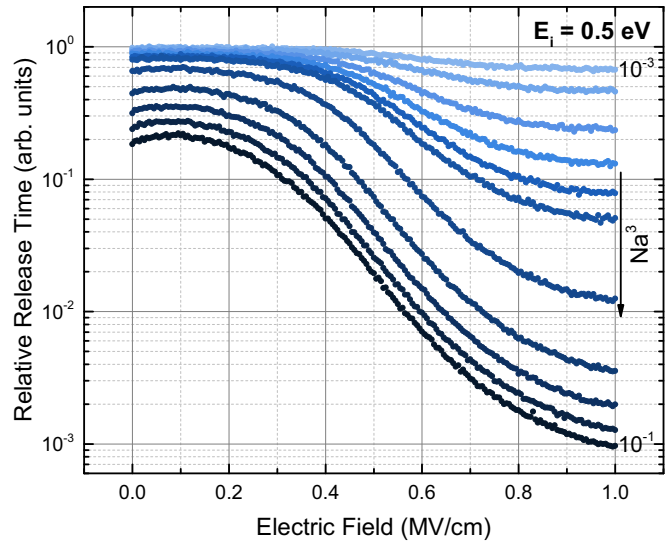

FIG. 9. Release time normalized by the value given by Eq. (2) versus field F for the trap with energy $E_i = 0.5\,\mathrm{eV}$.

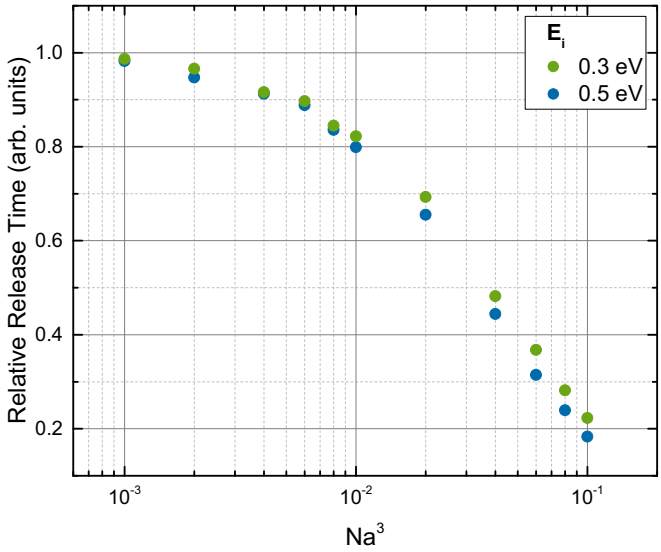

FIG. 10. Relative release times versus Na^3 for traps with energies of 0.3 and 0.5 eV.

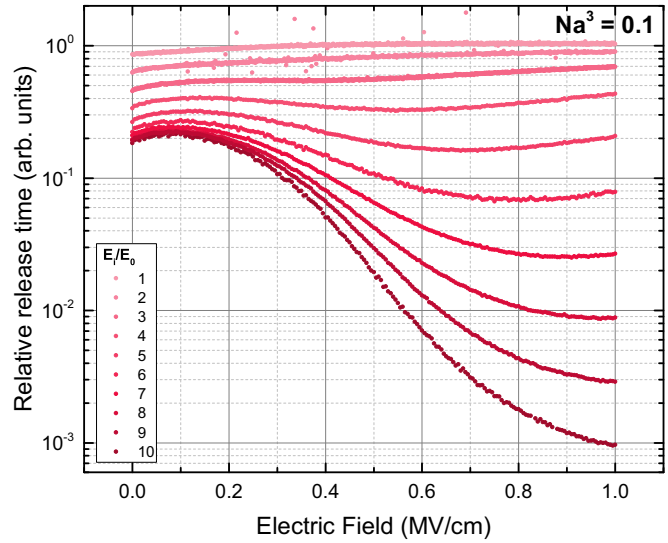

FIG. 11. Dependence of the electron relative release time on the relation between the trap depth E_i and the scale of the DOS E_0 for $Na^3 = 0.1$.

balance,

$$\nu_{\rm esc}(\varepsilon)/\nu_{\rm trap}(\varepsilon) = \exp(-\varepsilon/kT). \tag{32}$$

Not the escape rate itself, but the ratio between the trapping and the escape rates governs the equilibrium concentration of carriers. Because of the detailed balance at $F = 0$, this ratio depends only on the energy of a given trap, and it is not influenced by the presence of other traps. The enhancement of the release rate at $F = 0$ can, however, affect phenomena which are determined solely by the escape rate $\nu_{\rm esc}(\varepsilon)$, such as the thermally stimulated luminescence. In contrast to the thermally stimulated conductivity, which is governed by the interplay between the trapping and detrapping processes [16], the thermally stimulated luminescence is often claimed to be determined solely by a single event of the carrier release from a trap into the conduction band [17,18].

On the contrary, in the presence of an electric field, hopping processes affect the release rate more efficiently than the capture rate. This enhances the concentration of carriers in the conduction band in the presence of an applied electric field F.

The results of the simulations presented in Figs. 6, 7, 8, 9, and 10 were obtained for the case of an exponential density of states (DOS) with the characteristic energy scale $E_0 = 5 \times 10^{-2}$ eV. This estimate for the energy scale E_0 of the DOS was reported in the literature for organic [8] and inorganic [2] disordered materials. The choice of E_0 is, however, significant for the phenomenon of the hopping-assisted release from the traps studied in this paper. In order to reveal the effect of E_0 on the hopping-assisted release, we have simulated the release processes at different ratios E_i/E_0 between the depth of the trap E_i and E_0. In Fig. 11, the simulated data for the release time in the hopping-assisted process normalized by the release time given by Eq. (2) are plotted for different values of the ratio E_i/E_0. The simulations were carried out for $E_i = 0.5$ eV at a fixed value of $Na^3 = 0.1$, at which the effect of the hopping-enhanced release is most pronounced.

It is seen that a pronounced enhancement for the hopping-assisted release is observed only in the case of the relatively small E_0 at $E_i/E_0 > 4$. Such an effect is to be expected. At small values of E_0/E_i, there are many localized states with energies above the energy of the given trap, which can help in the release of carriers from the given trap. On the contrary, at large E_0, the energies of the traps, which are spatially close to the given trap, are remote from the band edge. The carrier hopping to such traps can even suppress the efficiency of the release from a given trap, as seen in Fig. 11 for small values of $E_i/E_0 < 2$.

In Fig. 12 we show a comparison between the results of the Monte Carlo simulations and the results obtained with Eq. (26) and with Eq. (29). In order to solve the problem numerically in agreement with Eq. (26), the positions and

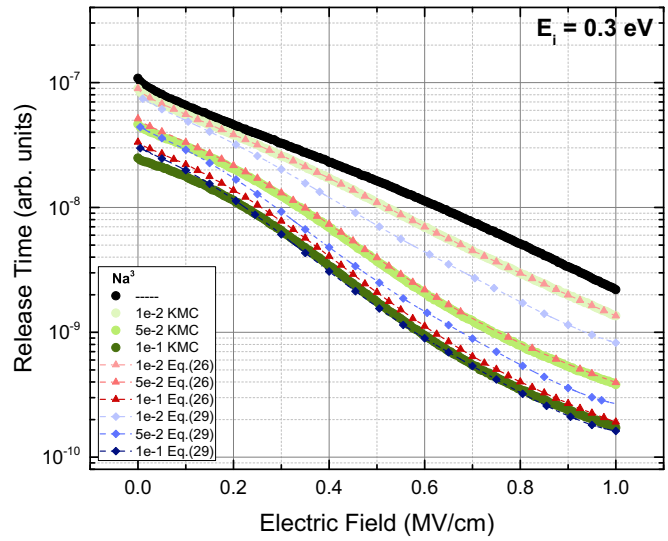

FIG. 12. Comparison between the results of the Monte Carlo simulations with those of Eqs. (26) and (29).

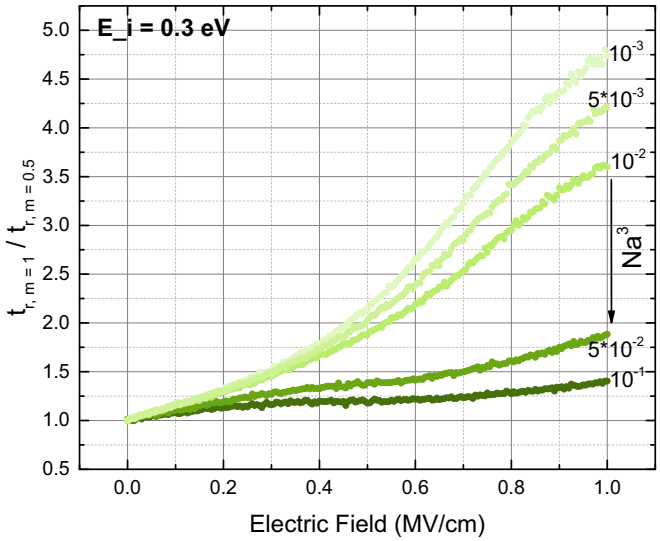

FIG. 13. The ratio of the release times for the hopping-assisted process at two different values of the effective mass, $m = m_0$ and $m = m_0/2$.

energies of traps were generated via the procedure described in Sec. IV A with averaging the result over 10^5 realizations. One can see that the results of Eq. (26) are in good agreement with those of the Monte Carlo simulations. Equation (29), in contrast to Eq. (26), does not imply any averaging over different realizations, being a purely analytical formula which can easily be solved by the routine algorithms of numerical integration. The data in Fig. 12 show that Eq. (29) can be used for the description of the hopping-assisted release from the traps only at high values of the parameter $Na^3 > 0.05$, i.e., at high concentrations of localized states.

The rate of a straight release of a charge carrier from a trap into the conduction band described by Eq. (2) depends on the value of the effective mass m. In the calculations described above, the value of the free-electron mass $m = m_0$ was used to be definite. The effective mass governs the tunneling probability of the carrier under the triangle barrier illustrated in Fig. 2. The smaller m is, the easier the tunneling is, and the larger the rate of the straightforward release of carriers from the traps is. In Fig. 13, the ratio of the release times for the hopping-assisted process at two different values of the effective mass, $m = m_0$ and $m = m_0/2$, is plotted as a function of the parameter Na^3. The larger the parameter Na^3 is, i.e., the larger the concentration of localized states N is, the less important the effect of the effective mass on the release of carriers from the traps assisted by hopping processes is.

V. CONCLUSIONS

Analytical calculations and Monte Carlo simulations evidence that hopping transitions of charge carriers between localized states in the band tails can substantially enhance the process of the field-induced carrier release from the traps into the conducting states above the band edges. The strength of the effect depends on the concentration of the localized states, on their energy distribution, on the localization length of carriers in the localized states, on the carrier effective mass, on the depth of the given trap at which a carrier is initially placed, on temperature, and on the strength of the applied electric field. At the values of material parameters used for numerical studies in this paper, the effect can achieve several orders of magnitude.

A simulation algorithm to study the hopping-assisted release of charge carriers from the traps was formulated and applied for several sets of material parameters. Furthermore, a recipe was suggested for studying the effect numerically without straightforward simulations. The recipe is based on the solution of a set of algebraic equations. Moreover, a closed-form analytical expression was derived which was shown by the numerical solution of the algebraic equations and by the straightforward Monte Carlo simulations to be sufficiently accurate at high concentrations of the localized band tail states.

ACKNOWLEDGMENTS

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