Effect of backward carrier jumps on variable-range hopping in disordered materials

V. I. Arkhipov
IMEC, Kapeldreef 75, B-3001 Heverlee-Leuven, Belgium

E. V. Emelianova and G. J. Adriaenssens
Semiconductor Physics Laboratory, University of Leuven, Celestijnenlaan 200D, B-3001 Heverlee-Leuven, Belgium

(Received 1 August 2001; revised manuscript received 12 December 2001; published 5 April 2002)

A variable-range hopping model is described that accounts for the effect of back-and-forth carrier jumps between occasionally close hopping sites isolated from the rest of the hopping network. It is shown that accounting for this effect for constant density of states (DOS) does not change the Mott $T^{-1/4}$ law but yields a modified coefficient that can be considered as a percolation threshold for dc conductivity in a positionally and energetically disordered hopping system. In a system with an exponential DOS distribution, the backward jumps significantly reduce dc conductivity but only slightly affect its functional dependence upon temperature.

DOI: 10.1103/PhysRevB.65.165110 PACS number(s): 72.20.Ee, 72.80.Le, 72.80.Ng

I. INTRODUCTION

In a positionally and energetically disordered hopping system, both the distance r and the energy difference ΔE between hopping sites are subject to a considerable variation. Since the carrier hopping rate exponentially decreases with increasing r and ΔE, carrier jumps to nearest hopping neighbors, i.e., to sites with minimum possible values of r and ΔE, should represent the major transport mode. However, groups of two, three, or more sites, that are occasionally close to each other, can form an ''exclusive circle.'' A carrier, localized in one of such sites, must make several jumps back and forth within such an isolated group of sites before it will jump to a site that does not belong to this group. The occurrence of such exclusive circles is well known from Monte Carlo simulations of charge-carrier hopping transport in disordered materials.[1,2]

Analytic approaches to the variable-range hopping (VRH) in disordered systems are based on averaging carrier jump rates.[3,4] The averaging often accounts for all possible carrier jumps including those within exclusive circles. This leads to an overestimate of the average hopping rate and, further, to an overestimated dc hopping conductivity. The reason for that is obvious. The dc conductivity can occur only if charge carriers travel across the whole sample, i.e., only via an infinitely large percolation cluster of connected hopping sites. However, if two sites happen to be very close to each other a carrier would most probably jump back and forth between these sites many times before the less probable jump into a more distant site would occur.

In the present work we formulate an analytic VRH model that eliminates back-and-forth carrier jumps within isolated pairs of hopping sites. It will be shown that the occurrence of such jumps does not affect the functional temperature dependence of the conductivity that still obeys the Mott $T^{-1/4}$ law. This implies applicability of the percolation approach to the VRH problem based on the concept of the minimum number of bonds, p_c, required for the infinite hopping cluster.[4] The value of p_c can then be calculated within the framework of the VRH model. Carrier ''multiple hopping'' between occasionally close hopping neighbors in a positionally and energetically disordered hopping system was recently considered within the framework of a single-particle approximation.[5] This approximation is relevant to the carrier mobility as determined from time-of-flight measurements. However, filling of localized states is disregarded in that case and, therefore, it does not describe the dark dc conductivity that is controlled by carrier hopping around the Fermi level.

II. PERCOLATION APPROACH TO HOPPING IN A POSITIONALLY RANDOM SYSTEM

Charge-carrier transport in positionally random systems of hopping sites is traditionally considered in terms of the percolation theory.[6] Owing to an exponentially strong dependence of the hopping rate upon the jump distance, jumps to nearest hopping neighbors are the dominant mode of charge transport. In a disordered system, hopping distances are subject to strong variation and, therefore, a longest distance between hopping sites, r_c, can be identified in the infinite hopping cluster that is required for dc conductivity. The value of r_c must be proportional to the average distance between sites that is determined by the concentration of hopping sites, N: $r_c = cN^{-1/3}$, where c is a universal numeric coefficient. Various Monte Carlo simulations yielded[7,8] the value of c ranging from 0.86 to 0.89. Carrier jumps between sites, separated by the longest distance, are assumed to be the rate-limiting steps that determine the carrier mobility μ. Concomitantly, the concentration dependence of the mobility takes the form

$$\mu = \mu_0 \exp(-2c\gamma N^{-1/3}), \tag{1}$$

where γ is the inverse carrier localization radius and the prefactor μ_0 contains a weak dependence upon the concentration of hopping sites due to the concentration dependence of the hopping distance.

A conceptually different approach to positional disorder is based on consideration of an ordered (for instance, cubic) lattice of hopping sites in which some bonds are randomly broken or some sites are randomly blocked. The question is: what is the minimum number of survived bonds, or unblocked sites p_c sufficient to form an infinite percolation cluster? The answer to this question depends upon the lattice

configuration and for a cubic lattice $p_c \cong 6 \times 0.32 \cong 1.9$ for sites and $p_c \cong 6 \times 0.25 \cong 1.5$ for bonds was found.[6] It is worth noting that number of unblocked sites should be higher because a broken bond between two unblocked sites does not exclude a finite probability to get from one site to the other. Phenomenologically, one can extend this approach by introducing a minimum effective number of bonds required for an infinite percolation cluster in a positionally disordered system. In such a system, hopping sites may have neighbors over short distances. Jumps to such neighbors are very fast but these jumps could hardly contribute to dc conductivity since the return jump will be equally easy. The effect of such backward jumps can be eliminated if one requires that always at least one hopping neighbor must be found within the sphere of average jump distance $\langle r \rangle$. The distance $\langle r \rangle$ should then be found from the condition that the number of hopping neighbors within this sphere must be equal to $p_c > 1$. In the limit this gives

$$\frac{4\pi}{3} \langle r \rangle^3 N = p_c, \tag{2}$$

and solving Eq. (2) then leads to the following expression for the mobility:

$$\mu = \mu_0 \exp\left[-2\gamma \left(\frac{3p_c}{4\pi} \right)^{1/3} N^{-1/3} \right], \tag{3}$$

which is completely equivalent to Eq. (1) with parameters c and p_c being related to each other as

$$p_c = \frac{4\pi}{3} c^3. \tag{4}$$

Consequently, p_c ranges from 2.7 to 3.0 (Refs. 7–9) for a positionally random hopping system. It is worth noting that these percolation parameters were calculated disregarding the energy disorder. In the following section we suggest a model that accounts for backward carrier jumps and yields the percolation parameters in a hopping system, which is disordered both positionally and energetically.

III. VRH INCLUDING BACKWARD CARRIER JUMPS

Charge-carrier transport in a positionally *and* energetically random system of localized states is described in terms of the VRH theory.[3,4] The rate of carrier jumps, $\nu(r, E_{\rm st}, E_t)$, over the distance r between a starting site of energy $E_{\rm st}$ and a target site of energy E_t is described by the Miller-Abrahams formula as

$$\nu(r, E_{\rm st}, E_t) = \nu_0 \exp[-u(r, E_{\rm st}, E_t)],$$

$$u(r, E_{\rm st}, E_t) = 2\gamma r + \frac{E_t - E_{\rm st}}{kT} \eta(E_t - E_{\rm st}), \tag{5}$$

where u is the hopping parameter, η the unity step function, T the temperature, and k the Boltzmann's constant.

Low-temperature dark equilibrium conductivity in amorphous semiconductors is due to carrier jumps via localized states around the Fermi level. The rate-limiting step is then thermally activated carrier jumps from occupied localized states at the Fermi level and the starting energy for such jumps must be just the Fermi energy E_F. Every neighbor of a given starting site can be characterized by its hopping parameter. For a site of the energy E_F, the average number of neighbors, $n(u)$, whose hopping parameters are not larger than u, can be calculated as

$$n(u) = 4\pi \int_0^{u/2\gamma} dr\, r^2 \int_{E_F}^{E_F + kT(u - 2\gamma r)} g(E_t)\, dE_t, \tag{6}$$

where $g(E)$ is density of states (DOS) distribution function.

The dc conductivity σ will be governed by carrier jumps to the sites with the most probable values of the hopping parameter. The most probable jump from a starting state to a target site can be characterized by the average hopping parameter $\langle u \rangle$. This parameter can be calculated by averaging u over the Poisson probability distribution of finding a nearest hopping neighbor of the hopping parameter u. The result reads

$$\langle u \rangle = \int_0^\infty du\, u \exp[-n(u)] \frac{dn(u)}{du} = \int_0^\infty du \exp[-n(u)]. \tag{7}$$

In the classical Mott version of the VRH, which disregards the backward jumps of carriers, the dc conductivity is calculated for a DOS distribution that remains constant on the energy scale relevant to the low-temperature hopping: $g(E) = g_0$. The use of a constant DOS distribution in Eqs. (6) and (7) leads to the following expression for $\langle u \rangle_M$:

$$\langle u \rangle_M = \int_0^\infty du \exp\left[-\left(\frac{u}{u_0} \right)^4 \right] = u_0 \int_0^\infty d\nu \exp(-\nu^4)$$

$$= \frac{u_0}{4} \Gamma\left(\tfrac{1}{4}\right) \approx 0.906 u_0, \tag{8}$$

where Γ is the gamma-function and u_0 is the dimensionless parameter defined as

$$u_0 = \left[\frac{3(2\gamma)^3}{\pi g_0 kT} \right]^{1/4}. \tag{9}$$

It is worth noting that this result is obtained while neglecting the possibility of backward carrier jumps into initially occupied localized states. Similar to the situation in positionally random systems, such jumps should not be taken into account if one addresses the dc conductivity in positionally and energetically random systems.

At first glance, the problem of backward jumps in VRH can be solved on the basis of the same percolation ideas that were reviewed in the preceding section. However, there is an important difference between master equations governing carrier hopping in systems that are random both positionally and energetically, on the one hand, and only positionally, on the other hand. While the rates of direct and backward jumps of a carrier between any two localized states are equal to each other in a positionally random network of hopping sites, these rates are necessarily different in a positionally and en-

ergetically disordered system unless the two sites occasionally have the same energy. Therefore, it is not *a priori* clear whether accounting for backward carrier jumps in VRH would result in changing only numeric parameters as it is in positionally disordered systems, or whether the temperature dependence of the conductivity would also be different.

The rate-limiting step in VRH are thermally assisted carrier jumps from occupied states of energies around E_F to vacant hopping sites above the Fermi level. Such jumps do contribute to the dc conductivity only if subsequently the carrier jumps further rather than coming back to the initially occupied state. Therefore, one must exclude from consideration those vacant hopping sites from which carriers will most probably jump back to their starting sites. Consider a carrier that jumped from a starting site of the energy E_F over the distance r into a target site of the energy E_t. This jump will contribute to the dc conductivity only if the target site has at least one neighbor with hopping parameter less than $u_b = 2\gamma r$ *outside* the sphere of radius r centred at the starting site. The average number of such neighbors, $n_b(E,r)$, increases with increasing E and r as

$$n_b(E,r) = 2\pi \int_0^r dr' r'^2 \int_{\arccos(r'/2r)}^{\pi} d\vartheta \sin\vartheta \times \int_{E_F}^{E+2\gamma kT(r-r')} g(E')dE'. \tag{10}$$

The probability, $w(E,r)$ that there is at least one such neighbor is determined by the Poisson distribution,

$$w(E,r) = 1 - \exp[-n_b(E,r)]. \tag{11}$$

The function $w(E,r)$ essentially determines the probability for a carrier that is localized in a state at the Fermi level to find a hopping neighbor of the energy E over the distance r such that a jump to this neighbor will, most probably, *not* be followed by the return jump. The average number of such ''one-way'' neighbors $n(u)$ whose hopping parameters are not larger than u for direct carrier jumps from the starting site at the Fermi level, are given by

$$n(u) = 4\pi \int_0^{u/2\gamma} dr r^2 \int_{E_F}^{E_F + kT(u-2\gamma r)} dE[1 - \exp\{n_b(E,r)\}]. \tag{12}$$

If one accounts for the possibility of backward carrier jumps, the parameter $\langle u\rangle$ can still be used for the calculation of dc conductivity: $\sigma \propto \exp(-\langle u\rangle)$, where $\langle u\rangle$ is defined by Eq. (7) but with the function $n(u)$ as determined by Eq. (12). For a constant DOS distribution substituting Eqs. (10)–(12) into Eq. (7) yields

$$\begin{aligned}\langle u\rangle &= \int_0^\infty du \exp\left(-\left(\frac{u}{u_0}\right)^4 + \tfrac{48}{11}\int_0^1 \frac{dx}{x}\exp\left[-\frac{13}{20}\left(\frac{u}{u_0}\right)^4 x^4\right] \times\left\{1-\exp\left[-\tfrac{11}{4}\left(\frac{u}{u_0}\right)^4 x^3(1-x)\right]\right\}\right) \\ &= u_0\int_0^\infty d\nu \exp\left(-\nu^4 + \tfrac{48}{11}\int_0^1 \frac{dx}{x}\exp(-\tfrac{13}{20}\nu^4 x^4) \times\{1-\exp[-\tfrac{11}{4}\nu^4 x^3(1-x)]\}\right) \approx 1.183 u_0 .\end{aligned} \tag{13}$$

Despite the rather complicated form of Eq. (13) it predicts exactly the same temperature dependence for $\langle u\rangle$, as Eq. (8) for the traditional approach. Only the numeric coefficient is different. This proves that accounting for the possibility of ''round trips'' of carriers changes only the numeric coefficient in the exponent of the Mott $T^{-1/4}$ law while the functional dependence of the conductivity upon the temperature remains unaffected. This implies that the concept of a minimum number of bonds that is sufficient for the formation of the infinite percolation path, can be also applied to hopping systems with both energetic and positional disorder. This number can be evaluated from the following condition:

$$n_M(\langle u\rangle) = p_c , \tag{14}$$

where $n_M(\langle u\rangle)$ should be calculated with the average hopping parameter determined by Eq. (6) similar to the procedure of Sec. II. This calculation yields $p_c = 1.96$. This value is smaller than the minimum number of bonds providing for the infinite percolation cluster in a 3D positionally random hopping system ($p_c \cong 2.7$). This result is not surprising because the occurrence of energy disorder is virtually equivalent to an additional dimension in the r-E space and the minimum number of bonds is known to decrease with increasing dimensionality.[6–9]

Finally, we consider VRH with backward carrier jumps in a system with an exponential DOS distribution $g(E) = (N_t/\varepsilon_0)\exp(E/\varepsilon_0)$, where N_t is the total number of localized states and ε_0 is the characteristic energy of the distribution. This distribution is typical for band-tail states in inorganic disordered semiconductors. Substituting an exponential DOS function into Eqs. (7), (10)–(12) in order to calculate $\langle u\rangle$, and, respectively, into Eqs. (6) and (7) in order to calculate $\langle u\rangle_M$, leads to complex expressions for $\langle u\rangle$ and $\langle u\rangle_M$, that can be solved numerically. The temperature dependences of the average hopping parameters $\langle u\rangle$ and $\langle u\rangle_M$ are shown in Fig. 1 for different positions of the Fermi level, i.e., for different total carrier densities. If plotted as $\log\langle u\rangle$ vs $T^{-1/4}$ the curves are almost parallel to each other, implying that $\langle u\rangle(T) = \Theta(T)\langle u\rangle_M(T)$, whereby the function $\Theta(T)$ only weakly depends upon the temperature, as illustrated in Fig. 2. The factor $\Theta(T)$ also depends upon the Fermi-level position. If E_F is large enough, the system with an exponen-

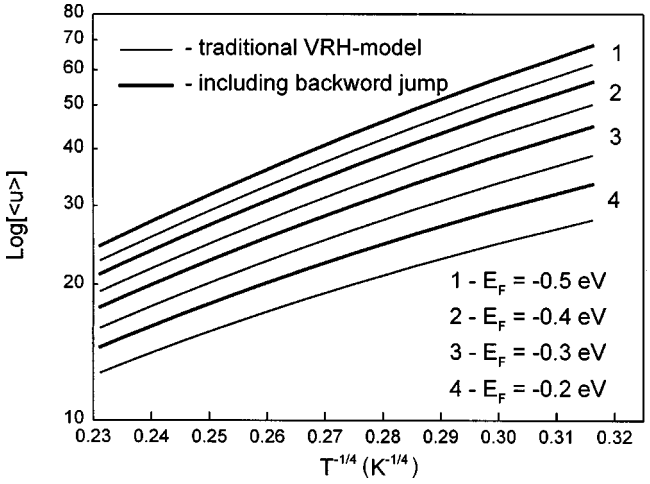

FIG. 1. Temperature dependences of the average hopping parameters $\langle u \rangle$ and $\langle u \rangle_M$ for an exponential DOS distribution parametric in the Fermi level position. The data are calculated for $\gamma = 5\ \mathrm{nm}^{-1}$, $\varepsilon_0 = 0.04$ eV, and $N_t = 10^{26}\ \mathrm{m}^{-3}$.

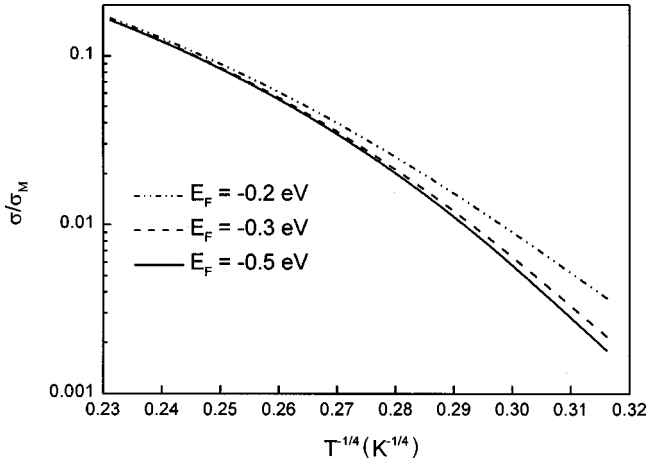

FIG. 3. The temperature dependences of the dark dc conductivity in materials with an exponential DOS distribution normalized to its value σ_M calculated without account for the backward carrier jumps. Material parameters are the same as in Fig. 1.

tial DOS function behaves rather similarly to that with a constant DOS. The effect of backward jumps on the dc conductivity is shown in Fig. 3 in which the ratio of σ's calculated with and without accounting for backward jumps, is plotted as a function of the temperature parametric in the Fermi energy. At low temperatures, the probability of backward jumps is high and, concomitantly, their effect on conductivity is strong: the difference in dc conductivities turns out to be very large, especially for systems with deeper Fermi levels.

IV. CONCLUSIONS

Theoretical analysis of charge-carrier transport in an energetically and positionally disordered hopping system must avoid the inclusion of an apparent contribution to the dc conductivity of multiple carrier jumps between pairs of occasionally close hopping sites. This effect is known to be essential when the dc conductivity in positionally random hopping systems is concerned. In such systems, the problem of apparently high conductivity can be resolved by the introduction of the concept of a minimum number of bonds required for the occurrence of the infinitely large percolation cluster.

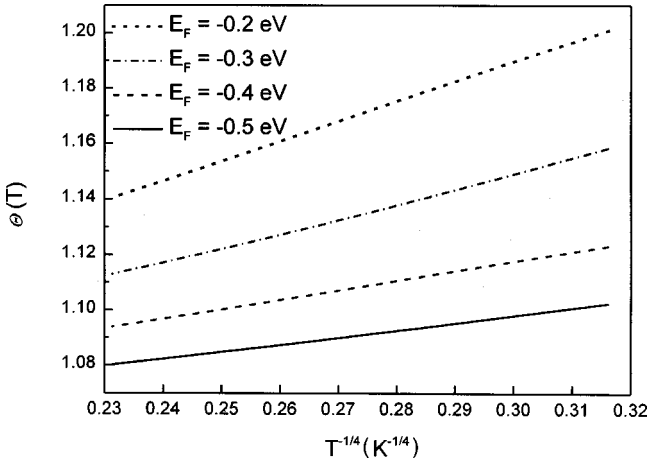

FIG. 2. The temperature dependences of the $\Theta(T)$ factor in a hopping system with an exponential DOS distribution. Material parameters are the same as in Fig. 1.

At variance with positionally random hopping networks, carrier transport in systems with both positional and energy disorder implies an interplay between the jump distance and the energy difference between starting and target sites. This interplay is traditionally considered in terms of the variable-range hopping models that disregard the possibility of carrier jumps from target sites back into starting sites. Since the rates of direct and backward jumps between any two sites are different in an energetically random hopping system, one may expect that the effect of return jumps could change the temperature dependence of the VRH dc conductivity. However, our consideration proves that the effect of return jumps does not affect the Mott $T^{-1/4}$ functional dependence of the conductivity for constant DOS distribution and only slightly changes the functional temperature dependence in a material with an exponential DOS function. This is revealed by the fact that, for a constant DOS, round-trip jumps lead only to a different numeric factor while this factor reveals only a weak temperature dependence in the case of an exponential DOS distribution. This result implies that the percolation concept of minimum bonding remains applicable for energetically random hopping systems as well.

ACKNOWLEDGMENTS

V. I. Arkhipov is grateful to IMEC for financial support. E. V. Emelianova acknowledges a financial support from the KU Leuven.

[1] H. Bässler, Phys. Status Solidi B **175**, 15 (1993).
[2] J. M. Marshall, Philos. Mag. B **38**, 335 (1978).
[3] N. F. Mott and E. A. Davis, *Electronic Processes in NonCrystalline Materials*, 2nd ed. (Clarendon, Oxford, 1979).
[4] H. Overhof and P. Thomas, *Electronic Transport in Hydrogenated Amorphous Semiconductors* (Springer-Verlag, Berlin, 1989).
[5] V. I. Arkhipov, E. V. Emelianova, and G. J. Adriaenssens, Phys. Rev. B **64**, 125125 (2001).
[6] B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer-Verlag, Berlin, 1984).
[7] G. E. Pike and C. H. Seager, Phys. Rev. B **10**, 1421 (1974).
[8] A. S. Skal and B. I. Shklovskii, Fiz. Tekh. Poluprov. **7**, 1589 (1973) [Sov. Phys. Semicond. **7**, 1058 (1973)].
[9] T. Odaki and M. Lax, Phys. Rev. B **36**, 3851 (1987).