

Kinetics of low-temperature charge-carrier recombination in disordered hopping systems

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 6869

(<http://iopscience.iop.org/0953-8984/9/32/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 09:20

Please note that [terms and conditions apply](#).

Kinetics of low-temperature charge-carrier recombination in disordered hopping systems

V I Arkhipov[†] and G J Adriaenssens

Laboratorium voor Halgeleiderfysica, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Heverlee-Leuven, Belgium

Received 20 December 1996, in final form 16 June 1997

Abstract. Energetic relaxation and recombination of charge carriers are considered at low temperatures in disordered hopping systems, taking the increasing occupation of deep localized states into account. It is shown that, in the course of carrier relaxation controlled by monomolecular recombination, the occupational density of localized states does not change with time. If bimolecular recombination represents the dominant mode of the carrier-density relaxation, all deep localized states will sooner or later be occupied and the filling effect plays an important role in the process of relaxation.

1. Introduction

At low temperatures, charge-carrier recombination is one of the most important processes controlling the kinetics of photoconductivity, photo- and electroluminescence, photoinduced optical absorption, etc. in disordered materials. These materials are characterized by a broad energy spectrum and a random spatial distribution of the localized states which play the role of hopping sites for charge carriers [1, 2]. Carrier kinetics in such materials is normally considered as a random walk within a positionally and energetically disordered network of hopping sites [3–5]. In addition, some amorphous materials also have bands of extended states for electrons and holes. Trap-modulated band transport is then the dominant mode of carrier drift, diffusion, and recombination in such materials at high temperatures [6–8]. However, at sufficiently low temperatures thermally activated carrier jumps into the bands of delocalized states become very improbable and trap-controlled transport changes to carrier hopping [9, 10]. Hence, to understand electronic processes in disordered materials at low temperatures one should consider carrier tunnelling events in a random system of hopping sites.

Since, on the one hand, amorphous materials are characterized by a broad distribution of localized-state energies and, on the other hand, carrier jumps to shallower states are not very probable at low temperatures, downward hopping in that distribution will determine the kinetics of all low-temperature processes in disordered systems [11–14]. If the total density of carriers remains constant all deep states will sooner or later be filled and further downward jumps become impossible [15]. This leads to the establishment of a quasi-Fermi level whose position is determined by the interplay between the total density of carriers and the energy distribution of the localized states [15]. However, if the carrier density decreases with time due to recombination, the filling of deep states can be avoided provided

[†] Permanent address: Moscow Engineering Physics Institute, Kashirskoye shosse 31, Moscow 115409, Russia.

the decrease is sufficiently fast. Since the rate of recombination is controlled by carrier hopping, the problem must be considered in a self-consistent way. A relevant question is then: does recombination provide a sufficiently fast decrease of the total carrier density to allow for a weak-filling regime of carrier hopping, or should the filling effect always be taken into consideration?

While we discussed the process of low-temperature energy relaxation in one previous paper [14] and the influence of trap filling on that process in a second one [15], those studies did not take into account the effect of recombination. In the present paper we add this effect and investigate specifically the role of charge-carrier recombination on the energy relaxation. Both mono- and bimolecular modes of recombination are considered. It is shown that the monomolecular mode provides a sufficiently high rate of recombination and maintains a constant occupation of deep states independent of the initial degree of filling. The rate of bimolecular recombination is proportional to the square of the carrier density such that the ratio of the recombination rate to the total carrier density decreases with time. Concomitantly, the rate of recombination will sooner or later be too low to sustain the weak-filling regime of carrier hopping and the regime of high occupational density of deep localized states will be established even if the initial filling is arbitrarily weak.

2. Energetic diffusion in a disordered hopping system

Only downward carrier jumps are allowed at low temperatures and the energy distribution of localized carriers therefore always remains in non-equilibrium. In other words, most carriers occupy ‘metastable’ hopping sites. A state is called metastable when the carriers which were captured at a time $t' < t$ still have a high probability of being found in the same state at a given time t . At the initial time, $t = 0$, all sites are, obviously, metastable and the density of metastable states (DMS), $g_d(E, t)$, is simply equal to the total density of states (DOS), $g(E)$. In a spatially completely disordered system, distances to deeper hopping sites, accessible for the next jump, are characterized by a broad distribution such that some of the states remain metastable at any time. As already shown in [15] on the basis of the Poisson formalism, the probability $\varphi(E, t)$ for a hopping site with the energy E to be a metastable state at time t can be written in the following form:

$$\varphi(E, t) = \int_0^\infty dr \frac{dn(E, r, t)}{dr} \exp[-n(E, r, t)] \exp[-\nu_0 t \exp(-2\gamma r)] \quad (1)$$

where r is the spatial coordinate, γ the inverse localization radius, n the density of localized states available for a downward jump of a carrier from a localized state of energy E , and ν_0 the attempt-to-jump frequency. The energy scale assigns higher energies to deeper states. Equation (1) represents the integrated product of the number of states available for a downward jump in energy from E and the probability that no such jump has taken place up to time t . The latter is just the $n = 0$ term of a Poisson distribution. The energy-independent exponential term in the integrand of equation (1) represents a very steep function of the variable r around $r_j = (1/2\gamma) \ln(\nu_0 t)$ such that the following approximation becomes possible:

$$\begin{cases} \exp[-\nu_0 t \exp(-2\gamma r)] \approx 0 & r < r_j(t) \\ \exp[-\nu_0 t \exp(-2\gamma r)] \approx 1 & r > r_j(t) \end{cases} \quad r_j(t) = \frac{1}{2\gamma} \ln(\nu_0 t). \quad (2)$$

This approximation allows the evaluation of the integral in equation (1) as

$$\varphi(E, t) = \exp \left\{ -n \left[E, \frac{1}{2\gamma} \ln(\nu_0 t), t \right] \right\}. \quad (3)$$

In a completely disordered system the density function $n(E, r, t)$ takes the form,

$$n(E, r, t) = \frac{4\pi r^3}{3} \left\{ \int_E^\infty dE' [g(E') - \rho(E', t)] \right\} \quad (4)$$

where the function $\rho(E, t)$ describes the energy distribution of localized carriers. Concomitantly, the distribution function given by equation (3) reduces to,

$$\varphi(E, t) = \exp \left\{ -V(t) \left[\int_E^\infty dE' [g(E') - \rho(E', t)] \right] \right\} \quad (5)$$

where $V(t)$ is the volume of the sphere accessible for downward carrier jumps at the time t ,

$$V(t) = \frac{4\pi}{3} [r_j(t)]^3 = \frac{\pi}{6\gamma^3} [\ln(v_0 t)]^3. \quad (6)$$

It seems intuitively reasonable to assume that the energy distribution of localized carriers must mimic the DMS function. Nevertheless, this can be the case only if a carrier released from a hopping site (which then ceases to be a metastable state) can eventually make a jump onto another currently metastable state, independent of the energy of the latter. However, some hopping sites will cease to be metastable states while there are still sites with higher energies which remain metastable—all in agreement with the probability distribution of equation (5). As long as a carrier cannot jump upwards at low temperatures, this puts such metastable states 'out of reach'. This effect can, nevertheless, be disregarded since the density of 'shallow' metastable states is small compared to the total DMS. Under such conditions the energy distribution of localized carriers, $\rho(E, t)$ can be represented as a product of the DOS function, $g(E)$, the probability, $\varphi(E, t)$, for a site to be a metastable state, and a function $\chi(t)$ which represents the probability for a metastable state to be occupied at the time t :

$$\rho(E, t) = \chi(t)g(E)\varphi(E, t) \quad (7)$$

Substituting equation (5) into equation (7) yields an integral equation for the occupational probability $f(E, t) = \rho(E, t)/g(E)$:

$$f(E, t) = \chi(t) \exp \left\{ -V(t) \left[\int_E^\infty dE' g(E') [1 - f(E', t)] \right] \right\}. \quad (8)$$

The solution of equation (8) can be written [15] in the form

$$f(E, t) = \{1 + A(t) \exp[V(t)N(E)]\}^{-1} \quad (9)$$

where $N(E)$ is the density of localized states with energies, E' , exceeding E :

$$N(E) = \int_E^\infty dE' g(E') \quad (10)$$

and the function $A(t)$ must be found from the normalization condition,

$$\int_{-\infty}^\infty dE' g(E') f(E', t) = p(t) \quad (11)$$

where $p(t)$ is the total carrier density. Substituting equations (9) and (10) into equation (11) and integrating over energy yields the following relation between the functions $A(t)$ and $p(t)$:

$$f(\infty, t) = [1 + A(t)]^{-1} = \frac{1 - \exp[-p(t)V(t)]}{1 - \exp[-N_t V(t)]} \quad (12)$$

N_t being the total density of localized states. Since the probability to be a metastable state for a hopping site with the energy $E \rightarrow \infty$ approaches unity and the occupational probability for this site is given by $f(\infty, t)$ the latter must be equal to the function $\chi(t)$ —see equations (5) and (8). Therefore, the density of metastable states, $g_d(E, t) = \rho(E, t)/\chi(t)$, can be written as,

$$g_d(E, t) = g(E) \frac{1 - \exp[-N_t V(t)]}{1 - \exp[-p(t) V(t)]} \times \left\{ 1 + \frac{\exp[-p(t) V(t)] - \exp[-N_t V(t)]}{1 - \exp[-p(t) V(t)]} \exp[V(t) N(E)] \right\}^{-1}. \quad (13)$$

Integrating equation (13) over energy further yields an equation which relates the total density of metastable states, $N_d(t)$, to the total density of carriers as,

$$N_d(t) = \frac{1 - \exp[-N_t V(t)]}{1 - \exp[-p(t) V(t)]} p(t). \quad (14)$$

To write an equation for the carrier density $p(t)$ next, one should consider not only the kinetics of carrier jumps within the hopping system, but also take recombination jumps into account.

3. Kinetics of carrier recombination

A carrier can escape from a sufficiently deep hopping site only when this site ceases to be a metastable state. Therefore, the frequency, $\omega_{\text{out}}(E, t)$, of carrier jumps from states with energy E at time t can be written as,

$$\omega_{\text{out}}(E, t) = \frac{\rho(E, t)}{g_d(E, t)} \left| \frac{\partial g_d(E, t)}{\partial t} \right| = \frac{p(t)}{N_d(t)} \left| \frac{\partial g_d(E, t)}{\partial t} \right|. \quad (15)$$

The frequency, $\omega_{\text{in}}(E, t)$, of carrier jumps onto a metastable state is determined by the product of the total frequency of all carrier jumps at time t and the probability that a given site with energy E will be a target state for a particular jump:

$$\omega_{\text{in}}(E, t) = \left[\frac{g_d(E, t) - \rho(E, t)}{N_d(t) - p(t) + \alpha N_R(t)} \right] \left[\frac{p(t)}{N_d(t)} \left| \frac{dN_d(t)}{dt} \right| \right] \quad (16)$$

where N_R is the concentration of recombination centres and α accounts for the difference of jump probabilities to a metastable state and to a recombination centre. Note that the effect of trap filling is taken into consideration in equation (16). Combining equations (15) and (16) one obtains the following equation for the kinetics of the localized carrier density:

$$\frac{\partial \rho(E, t)}{\partial t} = \frac{p(t)}{N_d(t)} \left[\frac{g_d(E, t) - \rho(E, t)}{N_d(t) - p(t) + \alpha N_R(t)} \left| \frac{dN_d(t)}{dt} \right| - \left| \frac{\partial g_d(E, t)}{\partial t} \right| \right]. \quad (17)$$

Integrating equation (17) over energy yields an equation for the total density of carriers:

$$\frac{dp(t)}{dt} = - \frac{\alpha N_R(t) p(t)}{N_d(t) [N_d(t) - p(t) + \alpha N_R(t)]} \left| \frac{dN_d(t)}{dt} \right| = - \frac{\alpha N_R(t)}{1 - \frac{p(t)}{N_d(t)}} \frac{d}{dt} \left[\frac{p(t)}{N_d(t)} \right]. \quad (18)$$

Solutions for the above equation can be readily obtained in the cases of either monomolecular or bimolecular recombination, the two characteristic regimes which hold when the carrier density $p(t)$ is either small with respect to the intrinsic density of recombination centres, N_R , or large with respect to that density. In the latter case recombination occurs predominantly between carrier densities of opposing polarity.

Since monomolecular recombination is characterized by a constant value of the recombination centre concentration, $N_R(t) = N_R = \text{constant}$, equation (18) reduces to:

$$\frac{dp(t)}{dt} = -\frac{\alpha N_R}{1 - \frac{p(t)}{N_d(t)}} \frac{d}{dt} \left[\frac{p(t)}{N_d(t)} \right]. \quad (19)$$

By solving equation (19) with the initial condition $p(0) = p_0$, a transcendental equation relating the functions $p(t)$ and $N_d(t)$ is obtained:

$$p(t) = N_d(t) \left\{ 1 - \left(1 - \frac{p_0}{N_t} \right) \exp \left[-\frac{p_0 - p(t)}{\alpha N_R} \right] \right\}. \quad (20)$$

When finally the function $N_d(t)$ is eliminated between equations (14) and (20) the following equation is reached for the carrier density $p(t)$ under monomolecular recombination conditions:

$$\frac{1 - \exp[-p(t)V(t)]}{1 - \exp[-N_t V(t)]} = \left\{ 1 - \left(1 - \frac{p_0}{N_t} \right) \exp \left[-\frac{p_0 - p(t)}{\alpha N_R} \right] \right\}. \quad (21)$$

For bimolecular recombination, under the condition of neutrality when densities of electrons and holes are equal to each other, the concentration of recombination centres equals the charge-carrier density such that equation (18) reads,

$$\frac{dp(t)}{dt} = -\frac{\alpha p(t)}{1 - \frac{p(t)}{N_d(t)}} \frac{d}{dt} \left[\frac{p(t)}{N_d(t)} \right]. \quad (22)$$

Equation (22) can easily be solved, yielding

$$p(t) = p_0 \left\{ \frac{1 - [p(t)/N_d(t)]}{1 - (p_0/N_t)} \right\}^\alpha. \quad (23)$$

Substituting the function $N_d(t)$ from equation (14) into equation (23) one gets a transcendental equation for $p(t)$ under bimolecular recombination conditions,

$$p(t) = p_0 \left\{ \frac{\exp[-p(t)V(t)] - \exp[-N_t V(t)]}{\left(1 - \frac{p_0}{N_t} \right) \{1 - \exp[-N_t V(t)]\}} \right\}^\alpha. \quad (24)$$

Note that both equations (21) and (24) do not depend upon a particular choice of the DOS function. Therefore, these equations represent a very general tool to study kinetics of low-temperature recombination in various disordered hopping systems.

4. Results and discussion

4.1. Monomolecular recombination

For sufficiently long times of carrier-density relaxation, such that $N_t V(t) \gg 1$ is satisfied, a solution of equation (21) reads

$$p(t) = p_0 \frac{1 - \frac{\alpha N_R}{p_0} \ln \left(1 - \frac{p_0}{N_t} \right)}{1 + \alpha \frac{\pi N_R}{6\gamma^3} [\ln(v_0 t)]^3} \quad \frac{\pi N_t}{6\gamma^3} [\ln(v_0 t)]^3 \gg 1. \quad (25)$$

Substituting the long-time asymptotic form of equation (25), i.e. when $\alpha N_R V(t) \gg 1$, into equation (14) one gets

$$\frac{p(t)}{N_d(t)} = 1 - \left(1 - \frac{p_0}{N_t} \right) \exp \left(-\frac{p_0}{\alpha N_R} \right). \quad (26)$$

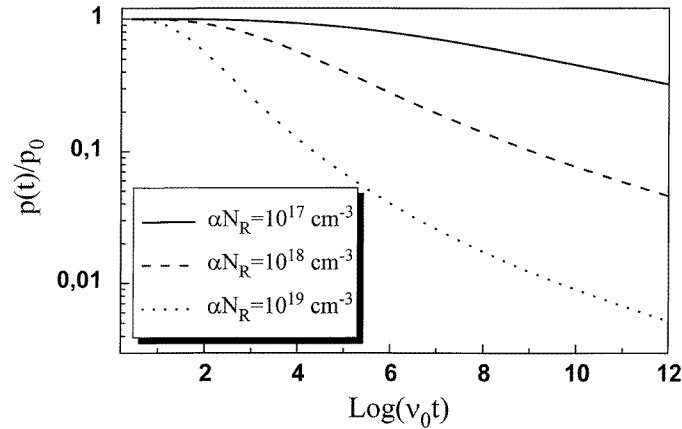


Figure 1. Time dependence of the charge-carrier density controlled by monomolecular recombination for different values of the effective recombination centre concentration αN_R . Further parameters are: $N_t = 10^{20} \text{ cm}^{-3}$, $6\gamma^3/\pi = 10^{21} \text{ cm}^{-3}$.

If the initial trap filling is sufficiently weak, $p_0/N_t \ll 1$ and $p_0/\alpha N_R \ll 1$, the ratio $p(t)/N_d(t)$ remains small at any time and the function $p(t)$ approaches its weak-occupation form which is similar to that obtained in [14]. It is very important to note that, in general, the ratio $p(t)/N_d(t)$ does not depend upon time if the total density of carriers is controlled by monomolecular recombination. In other words, monomolecular recombination maintains the trap-filling regime throughout the whole time interval of carrier relaxation and there is no transition from a weak-filling to a strong-filling regime or vice versa. Another interesting feature of the $p(t)$ function is its scaling-like dependence upon the initial density of carriers, p_0 for all realistic values of the other parameters. Indeed, the second term in the numerator of the right-hand side of equation (25) can be estimated as either $\frac{\alpha N_R}{N_t}$ if $p_0 \ll N_t$ or $\frac{\alpha N_R}{N_t} \ln(1 - \frac{p_0}{N_t})$ if $p_0 \approx N_t$. The regime of diffusion-controlled recombination, which is normally realized in disordered materials, implies $\alpha N_R \ll N_t$. The latter condition makes the second term small compared with unity and the ratio $p(t)/p_0$ becomes independent of p_0 . The time dependence of the carrier density obtained by the numerical solution of equation (21) is presented in figure 1.

4.2. Bimolecular recombination

We again consider charge-carrier kinetics at a time satisfying the inequality $N_t V(t) \gg 1$. Under this condition equation (24) reduces to

$$p(t) = p_0 \left(1 - \frac{p_0}{N_t}\right)^{-\alpha} \exp \left[-\alpha \frac{\pi p(t)}{6\gamma^3} [\ln(v_0 t)]^3 \right] \quad \frac{\pi N_t}{6\gamma^3} [\ln(v_0 t)]^3 \gg 1. \quad (27)$$

An approximate analytic solution of equation (27) can be written in the form

$$p(t) = \frac{6\gamma^3}{\pi\alpha} \ln \left\{ \frac{\pi\alpha p_0}{6\gamma^3} \left(1 - \frac{p_0}{N_t}\right)^{-\alpha} [\ln(v_0 t)]^3 \right\} [\ln(v_0 t)]^{-3}. \quad (28)$$

Substituting equation (28) into equation (14) shows that, at long times, the function $p(t)$ approaches the total density of deep states, $p(t) \approx N_d(t)$, $t \rightarrow \infty$, independent of the initial density of carriers. Thus, under the conditions of low-temperature bimolecular

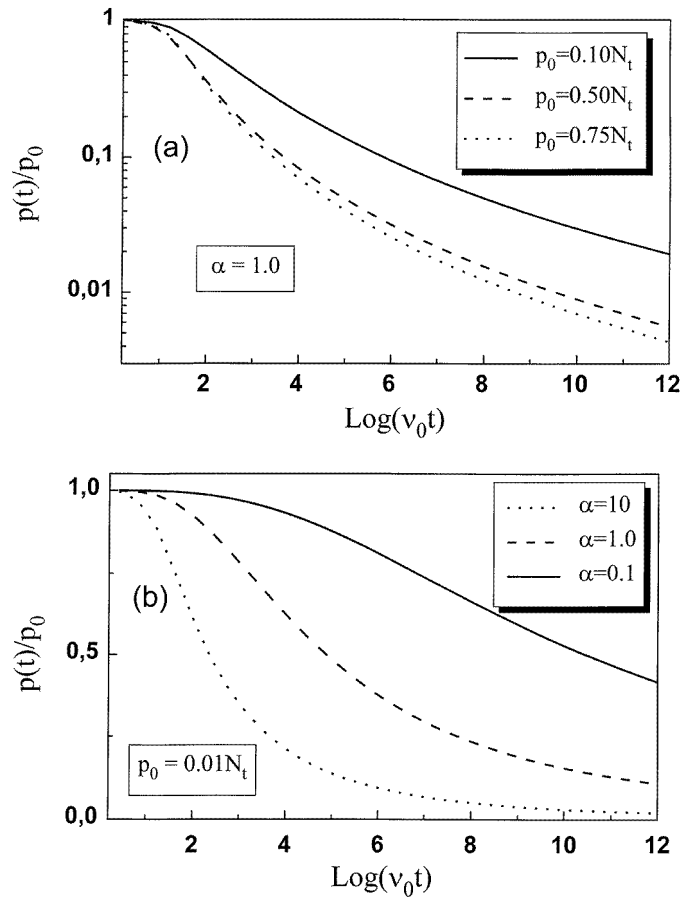


Figure 2. Time dependence of the charge-carrier density controlled by bimolecular recombination for different values (a) of the initial carrier density and (b) of the recombination cross section. Further parameters are identical to those of figure 1.

recombination, filling of deep localized states always occurs and this effect must be taken into consideration whenever any process controlled by bimolecular recombination at low temperatures is concerned. Time dependencies of the carrier density calculated from equation (24) are plotted in figure 2.

4.3. Practical implications

It will be realized that the above results refer to low-temperature hopping systems, and do not contain temperature as a parameter. One should therefore be cautious in applying the results to experimental situations. Only low-temperature, isothermal studies of carrier transport as a function of excitation or defect density would qualify. Nevertheless, the results do support the assumptions of filled deep traps and bimolecular recombination on which the theoretical descriptions of thermally stimulated current experiments are based [16], or which have been used in describing steady-state photoconductivity at low temperatures in terms of transport energy [17].

Acknowledgments

VIA acknowledges a fellowship from the K U Leuven. This work was supported by the Fonds voor Wetenschappelijk Onderzoek-Vlaanderen.

References

- [1] Mott N F and Davis E A 1979 *Electronic Processes in Non-crystalline Materials* 2nd edn (Oxford: Clarendon)
- [2] Scher H 1976 *Photoconductivity and Related Phenomena* ed J Mort and D M Pai (Amsterdam: Elsevier) p 71
- [3] Pautmeier L, Richert R and Bäessler H 1991 *Phil. Mag.* B **63** 587
- [4] Bäessler H 1993 *Phys. Status Solidi* b **175** 15
- [5] Arkhipov V I and Bäessler H 1993 *Phil. Mag.* B **68** 425
- [6] Arkhipov V I, Iovu M S, Rudenko A I and Shutov S D 1979 *Phys. Status Solidi* a **54** 67
- [7] Tiedje T and Rose A 1981 *Solid State Commun.* **37** 49
- [8] Orenstein J and Kastner M 1981 *Phys. Rev. Lett.* **46** 1421
- [9] Monroe D 1985 *Phys. Rev. Lett.* **54** 146
- [10] Arkhipov V I 1987 *Sov. Phys.-Semicond.* **21** 880
- [11] Shklovskii B I, Fritzsche H and Baranovskii S D 1989 *Phys. Rev. Lett.* **62** 2989
- [12] Grünwald M and Movaghar B 1989 *J. Phys.: Condens. Matter* **1** 2521
- [13] Arkhipov V I, Bäessler H, Deussen M, Göbel E O, Kersting R, Kurz H, Lemmer U and Mahrt R F 1995 *Phys. Rev. B* **52** 4932
- [14] Arkhipov V I and Adriaenssens G J 1996 *J. Phys.: Condens. Matter* **8** 7909
- [15] Arkhipov V I and Adriaenssens G J 1996 *J. Phys.: Condens. Matter* **8** L637
- [16] Zhu M and Fritzsche H 1986 *Phil. Mag.* B **53** 41
- [17] Baranovskii S D, Thomas P and Adriaenssens G J 1995 *J. Non-Cryst. Solids* **190** 283