Theory of low-temperature photoconductivity and photoluminescence in amorphous semiconductors

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A theory of the low-temperature tunnel radiative recombination of nonequilibrium carriers in an amorphous semiconductor is developed. Allowance is made for energy relaxation and spatial diffusion of carriers by hopping between localized states in the band tails. The problem of the fate of an isolated electron–hole pair is solved, i.e., a calculation is made of the probability $\eta(R)$ that the diffusing electron moves away from the hole to a distance exceeding R without recombining with it. It is shown that the solution of this problem is not affected by the actual form of the energy dependence of the density of states and of the localization radius or by the dependence of the hopping frequency on the energy of a phonon emitted in the course of a transition. At high values of R the probability $\eta(R)$ decreases as $R^{-\beta}$, where β is a critical exponent that depends only on the dimensionality of space and is equal to 1.15 in the three-dimensional case. It therefore follows that the electron and hole very readily separate in space in the course of energy relaxation. The function $\eta(R)$ is used to develop a steady-state theory of an amorphous semiconductor and to calculate its low-temperature photoconductivity and photoluminescence.

1. INTRODUCTION

Several experimental investigations had been made of the low-temperature photoluminescence[1,2] and photoconductivity[3,4] of hydrogenated amorphous silicon (a-Si:H). According to the experimental data of Refs. 1 and 2, the quantum efficiency of the photoluminescence is close to unity for a-Si:H samples with a low concentration of dangling bonds $N_s \lesssim 10^{16}$ cm^{-3}. Therefore, it is necessary to develop a theory of the photoconductivity and photoluminescence when nonradiative recombination is completely absent and then there is a single radiative recombination channel.

Photoluminescence is mainly due to what is known as twin recombination of electron–hole pairs in which an electron recombines with the hole which has been created simultaneously with the electron. On the other hand, photoconductivity is solely due to those carriers that have escaped twin recombination.[3] It therefore follows that photoluminescence and photoconductivity are competing processes. The key question is the quantum efficiency of the photoconductivity, i.e., the fraction of the optically created electron–hole pairs which avoid twin recombination. We develop a theory of the low-temperature tunnel radiative recombination of nonequilibrium carriers allowing for their energy relaxation and spatial diffusion by hopping between localized states in the band quasigap. We use this theory to calculate the characteristics of the photoluminescence and photoconductivity of an amorphous semiconductor.

In Sec. 2 we solve the problem of an isolated electron–hole pair. We calculate the probability $\eta(R)$ that a diffusing electron moves before recombination to a distance greater than a given value R from the hole. A very important feature of the problem is that its solution is not influenced by the actual form of the energy dependence of the density of states and of the localization radius or by the dependence of the probability of emission of a phonon on its energy. In all cases the probability $\eta(R)$ decreases at large values of R as $R^{-\beta}$, where the exponent β depends only on the dimensionality of space; in the three-dimensional case its value is 1.15 ± 0.02. In this sense the problem is completely universal.

In Sec. 3 we calculate the dependence of the steady-state density of nonequilibrium carriers on the rate of photogeneration of electron–hole pairs. In Sec. 4 we obtain analytic expressions for the static and dynamic photoconductivity of an amorphous semiconductor due to hopping energy relaxation of carriers between localized states. The results on the static photoconductivity are shown to agree well with the experimental data obtained for a-Si:H. The last part (Sec. 5) is devoted to a discussion of the low-temperature photoluminescence. Calculations are made of steady-state spectra and of the kinetics of the photoluminescence relaxation after the end of illumination.

Some of the results of the present study had been published earlier in a brief communication.[5]

2. ENERGY RELAXATION AND RECOMBINATION OF AN ISOLATED ELECTRON–HOLE PAIR

We consider the case when the photoconductivity and photoluminescence are excited with light of photon energy slightly less than the width of the mobility gap. Such light is absorbed mainly by pairs of closely spaced electron and hole localized states, since the matrix elements of a transition is proportional to the overlap integral which decreases exponentially with distance. It therefore follows that initially the electron and hole are located closely in space. We assume that the semiconductor is at absolute zero so that electrons jump only between localized states in the band quasigap. For simplicity, we assume that the hole is immobile and only the electron can tunnel from one localized state to another.

At each step in the process of relaxation along the density-of-states tail the electron can either recombine radiatively with the hole or it can jump nonradiatively to a localized state which is lower on the energy scale. Each of these processes involves the tunneling of the electron in space. The duration of a nonradiative transition to a localized state located at a distance f from the initial electron position is

$$\tau_d(r) = \nu_0^{-1} \exp(2r/a), \qquad (1)$$

where $\nu_0 \approx 10^{12}$ s^{-1} (Ref. 1) and a is the Bohr radius of a

localized state, which we shall assume is the shortest characteristic length of the problem. Equation (1) is written on the assumption that the transition probability is independent of the energies of the initial and final states. In this case, in view of the smallness of a the electron always jumps to the nearest localized state among those located lower on the energy scale. We shall show that the results are not greatly affected if this hypothesis is not made.

The time constant of radiative recombination of an electron with a hole located at a distance R is given by the expression

$$\tau_r(R) = \tau_0 \exp(2R/a), \tag{2}$$

where $\tau_0 \approx 10^{-8}$ s (Ref. 1); we are assuming here that the Bohr radius of an electron is considerably greater than the corresponding radius of the hole, so that the values of a are the same in Eqs. (1) and (2).

The diffusion of the electron during relaxation is very unusual. Let us consider an electron after the k th jump. We use N_k to denote the density of localized state accessible to the electron in the course of the $(k + 1)$ th jump, i.e., located below that localized state at which it is presented. We shall show that if no recombination takes place during this jump, then the new density N_{k+1} is distributed uniformly from zero to N_k. We therefore relabel all the localized states accessible in the course of the $(k + 1)$ th step in the order of increasing energy from 1 to M_k. In the $(k + 1)$ th step the electron jumps to the nearest localized state with a number M_{k+1} distributed at random between 1 and M_k. The states with numbers from M_k to M_{k+1} become inaccessible. Consequently, irrespective of the actual form of the density of states, we have

$$N_{k+1} = y N_k, \tag{3}$$

where y is a random quantity distributed uniformly between zero and unity. Therefore, after each jump the density of accessible localized states N decreases roughly speaking by a factor of 2 and the average distances between them increases by a factor of $2^{1/3}$. Consequently, the diffusion path is of the type shown in Fig. 1. If the directions of successive jumps are uncorrelated, then

$$\langle R_n^2 \rangle = \sum_{k=1}^{n} \langle r_k^2 \rangle, \tag{4}$$

where R_n is the distance of the electron from the hole after n steps, r_k is the length of the k th step, and the averaging is carried out over random realizations of the coordinates of 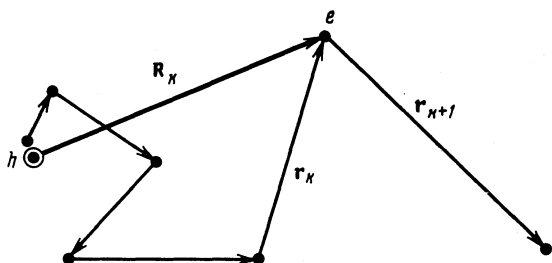a localized state which can have various energies. The situation is unusual because a constant increase in r_k makes the sum on the right-hand side of Eq. (4) a geometric progression. Consequently, R_k and R_{k+1} are of the same order of magnitude as the length of the last step r_k.

After the k th step the electron can either recombine with a hole localized at a distance R_k or it can undergo the next $(k + 1)$ th diffusion jump to a distance r_{k+1} (Fig. 1). Comparing the times (1) and (2), we find that if

$$R_k + R_c > r_{k+1}, \tag{5}$$

where

$$R_c = \frac{a}{2} \ln v_0 \tau_0, \tag{6}$$

then $\tau_d \ll \tau_r$, so that the electron is very likely to make the next jump. We shall assume that the electron is excited by light to a state close to the mobility edge, so that the density of states to which the electron can jump in the first step, N_0, is much greater than R_c^{-3}. It is therefore clear that during the first steps or jumps, as long as $R, r \ll R_c$, the inequality (5) is always satisfied and the electron continues to diffuse to a distance of the order of R_c. In other words, if $R, r \ll R_c$, the strong inequality $v_0 \tau_0 \approx 10^4 \gg 1$ ensures predominance of diffusion. This range of distance of R will be considered in detail later, whereas here we shall consider the case of large values of R.

For $R, r \gg R_c$, the diffusion process no longer predominates and the fate of the electron after the $(k + 1)$ th step is governed by the relationship between R_k and r_{k+1} (Fig. 1). If $R_k < r_{k+1}$, then the electron recombines, whereas if $R_k > r_{k+1}$, it continues to relax along the density-of-states tail.[2] It is very important to remember that the lengths R_k and r_{k+1} are of the same order of magnitude but they fluctuate up to 100%. Therefore, at each step in the case $R \gg R_c$ none of the processes mentioned earlier can have a parametric advantage over other processes. Moreover, the probability q that $r_{k+1} < R_k$, holds i.e., relaxation continues at the $(k + 1)$ th step, for $R \gg R_c$, cannot depend on the serial number of the step or jump because the number k alters only the scale of all the lengths and the pattern of behavior changes self-similar. The probability q is a certain number which is not close to zero or to unity. The probability of making M steps without recombination, beginning from $R \sim R_c$, is

$$q^M = \exp(-M|\ln q|). \tag{7}$$

A typical length R and M steps or jumps is of order

$$R \sim (2^{1/3})^M R_c. \tag{8}$$

Using M from Eq. (8) and substituting it into Eq. (7), we find that the probability that the electron traverses a distance R without recombination is given by

$$\eta(R) \sim (R_c/R)^\beta, \tag{9}$$

where $\beta \approx 3|\ln q|/\ln 2$ is a number of order unity. The recombination probability density at a distance R from a hole is $P(R) = -d\eta/dR$. According to Eq. (9), if $R \gg R_c$, then

$$P(R) \sim \frac{1}{R_c}(R_c/R)^{\beta+1}. \tag{10}$$

Therefore, the quantities $\eta(R)$ and $P(R)$ exhibit scaleless power-law behavior in the range $R \gg R_c$.

FIG. 1. Diffusion path of an electron.

We now consider the behavior of $P(R)$ at short distances $R < R_c$. As mentioned earlier, the probability $1 - \eta(R)$ that the electron recombines is low for $R \ll R_c$. In fact, the electron recombines in the $(k+1)$th step if the inequality (5) is no longer satisfied. It therefore follows that the distance r_{k+1} to the nearest localized state, accessible on the energy scale, is greater than R_c. However, in a typical case we have $r_{k+1} \sim R_k \sim R \ll R_c$. We can show that the quantity $1 - \eta(R)$ is then exponentially small: the probability that in a sphere of radius R_c there is no localized state with an average density $r_{k+1}^{-3} \sim R^{-3}$ is clearly equal to $\exp[-(4\pi/3)(R_c/R)^3]$. However, we shall soon show that this is not true. The problem is that the main contribution to the recombination during the $(k+1)$th step in the case when $R \ll R_c$ comes from the rare configurations in which the k th localized states are distributed at random so low on the energy scale that $N_k \sim R_c^{-3} \ll N_{k-1} \sim R^{-3}$ and the probability of loss is not exponentially small. According to Eq. (3), the probability of such a configuration is

$$1 - \eta(R) = \frac{N_k}{N_{k-1}} \sim \left(\frac{R}{R_c}\right)^3,$$

which leads to

$$P(R) \sim \frac{1}{R_c}\left(\frac{R}{R_c}\right)^2. \tag{11}$$

Comparing Eqs. (10) and (11), we can naturally assume that the function $P(R)$ is of universal validity

$$P(R) = \frac{1}{R_c} f\left(\frac{R}{R_c}\right), \tag{12}$$

where $f(x) \propto x^{-(\beta+1)}$ for $x \gg 1$ and $f(x) \propto x^2$ if $x \ll 1$.

We checked this hypothesis by rigorous numerical modeling of the problem using the algorithm described in Appendix 1. It was found that $R_c P(R)$ is indeed a universal function of R/R_c for all values of $R_c \geqslant 2N_0^{-1/3}$. This function is presented in Fig. 2. It has a maximum at $R/R_c \approx 1$ and the asymptotes follow Eqs. (10) and (11), where the critical exponent β is 1.15 ± 0.02.[3]

The results of simplified modeling of this problem are given in Ref. 5. They differ slightly from the function shown in Fig. 2. The simplification used in Ref. 5 is the approximate replacement of the non-Markovian process of energy relaxation by a similar Markovian process. It is assumed in Ref. 5 that the localized states accessible at each step are distribute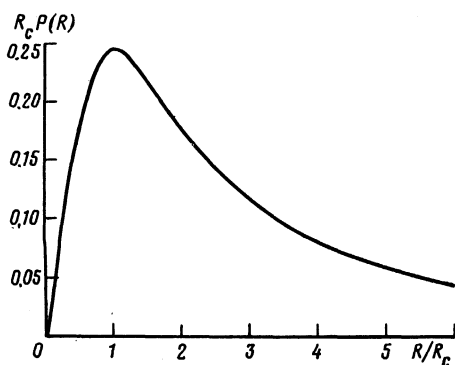d completely at random in space, irrespective of the path traveled by the electron before this step. Therefore, the vector for each possible diffusion step r_{k+1} can be determined by simply generating random values of N_k in accordance with Eq. (3), and then by generating a random distance r_{k+1} in accordance with the nearest-neighbor distribution for this density, and finally, by generating a random direction of r_{k+1}. We also checked the inequality (5) and either detected recombination or continued the process further.

It is clear, however, that in fact in the course of the $(k+1)$th step the electron can no longer be included inside a sphere with a center at the point $\mathbf{R}_{k-1}$ and radius $r_k = |\mathbf{R}_k - \mathbf{R}_{k-1}|$, because we know already that the localized state closest to the point $\mathbf{R}_{k-1}$ has a lower energy and is located at $\mathbf{R}_k$. Therefore, in the distribution of the sites accessible during the $(k+1)$th step there is an excluded volume along a path traversed by an electron, and the diffusion process is strictly speaking non-Markovian. The algorithm given in the Appendix 1 allows fully for this circumstance.

The function $P_M(R)$ is obtained in Ref. 5 in the range $R \lesssim 5R_c$ of importance in the experimental studies of photoluminescence and photoconductivity (here and below we shall use the index M to denote the quantities found in the Markov approximation). The critical exponent β_m has the value $\beta_m = 1.1$. Calculations of $P_M(R)$ at high values of R/R_c indicated that $\beta_M = |d \ln P_M/d \ln R| - 1$, and that this exponent rises slowly with increasing in R/R_c in the range $R/R_c > 5$ and for $R/R_c \gtrsim 15$ becomes equal to $\beta_M = 1.70 \pm 0.10$. The reason for this slow approach of β_M to the asymptote, in our opinion is the same as for the exact critical exponent β.

Thus the value of β_M is 1.5 times greater than β. This difference in our view, is due to the facts that an exclusion of a certain part of volume prevents jumps of the electron toward the hole. Therefore, the real motion of the electron in the radial direction is likely to resemble ballistic motion rather than diffusion. This naturally makes the separation between the electron and the hole easier and slows down the fall of $P(R)$ compared with $P_M(R)$.

We have not considered numerical modeling of $P(R)$. However, some important results can be obtained analytically for $P(R)$. Appendix 2 gives a rigorous proof that in the Markov approximation the value of $P_M(R)$ for $R \gg R_c$ is a power-law function of R. A method for analytic calculation of the power exponent β_M has been developed for a space of any dimension. In the three-dimensional case we obtain $\beta_M = 1.750$, in good agreement with numerical modeling. In the one-dimensional case we can also find the exact solution $\beta = 2$. In this case the exact formula simplifies, since allowance for the excluded volume has the effect that the electron moves in one direction and always away from the hole, i.e., the coordinate z_{k+1} is always greater than z_k and its distribution is independent of z_{k-1} (a chain of states is distributed along the z axis and the hole is located at $z = 0$).

We shall now discuss the universality of the results obtained. We have seen already that the approach does not depend on the nature of the density of states if the probability of a jump is independent of energy. We now use a simple but quite striking example to demonstrate that even a very strong energy dependence of τ_d has practically no effects. We assume that the density of states $g(\varepsilon)$ decreases with

FIG. 2. Dependence of $R_c P(R)$ on R/R_c in the range $R_c > 2N_0^{-1/3}$.

depth in the band in accordance with the law

$$g(\varepsilon) = g_0 \exp(-\varepsilon/\varepsilon_0), \tag{13}$$

whereas the maximum phonon frequency ω_D is low compared with $\varepsilon_0/\hbar$. Then, in Eq. (1) the time for a transition between localized states of energies ε_k and ε_{k+1} should be multiplied by $\exp[(\varepsilon_{k+1} - \varepsilon_k)/(\hbar\omega_D/\ln\Gamma^{-1})]$, which allows for multiphonon transitions (Γ is the dimensionless electron–phonon coupling constant). Therefore, in every jump an electron of energy ε_k and with a coordinate R_k selects in its environment a localized state $(\varepsilon_{k+1}, R_{k+1})$ for which the minimal sum is

$$r_{k+1} + a\frac{\varepsilon_{k+1} - \varepsilon_k}{2\hbar\omega_D}\ln\Gamma^{-1}. \tag{14}$$

As pointed out already, the quantities R_k and r_{k+1} are of the same order of magnitude and they fluctuate strongly, so that at distances from the hole obeying $R \gg R_{\mathrm{ph}} \equiv a\varepsilon_0 \ln\Gamma^{-1}/2\hbar\omega_D$ the second term in Eq. (14) is of little importance for almost all the localized states of energy $\varepsilon_{k+1} > \varepsilon_k$, so that the problem of selecting the next localized state is solved simply by its proximity in space. Thus, over distances $R \gg R_{\mathrm{ph}}$ the new situation does not differ in any way from that already investigated. Hence, it follows immediately that the asymptote of the function $P(R)$ in the case of sufficiently large values of R is always of the form given by Eq. (10) with the same power exponent $\beta = 1.15$. If $R_c > R_{\mathrm{ph}}$, the multiphonon factor simply results in the replacement of R_c with $R_c - R_{\mathrm{ph}}$.

We shall now consider the example of the opposite situation when the probability of a jump to a deep state is much greater than the probability of a typical jump. Such a situation arises if the constant of the coupling to optical phonons (of frequency close to ω_0) is $A \gg 1$ times greater than the constant of the interaction with acoustic phonons, where $\hbar\omega_0 \gg \varepsilon_0$. In this case at each step the electron has three possibilities: it can recombine with the hole, make a jump due to the interaction with an optical phonon, or jump emitting an acoustic phonon. Since in the interaction with an optical phonon the electron drops deep down on the energy scale, the density of states to which it can jump is low and in this process the nearest accessible localized state is generally located at a considerable distance. However, in the case of a transition due to the interaction with an acoustic phonon the localized state to which the electron jumps is located much closer and, because of the exponential dependence of the frequency of the jumps on the distance between the initial and final localized states, the process accompanied by the emission of an acoustic phonon is much faster. Consequently, the asymptotic form of $P(R)$ in the range $R \gg R_c$ is independent of A. Moreover, if $A \ll \nu_0\tau_0 \approx 10^4$, then neither the value of R_c nor the function $P(R)$ are affected.

Note also that the energy dependence of the localization radius does not influence the form of $P(R)$ either. In fact, when we compare the probabilities of recombination and diffusion jumps once again, we find that both probabilities contain the same localization radius a, which is governed by the instantaneous energy of the electron (on condition that this localization radius is greater than that of a hole). Consequently, the inequality (5) is of its previous form and the dependence $a(\varepsilon)$ is important only in the determination of R_c.

The deviation from the universal form of the function $P(R)$ appears only if we allow for the motion of the hole. If we assume that the radii of localization of the electron a_e or hole a_h are equal, we find that numerical simulation in the Markov approximation gives $\beta_M = 0.95 \pm 0.03$, instead of $\beta_M = 1.75$ in the case of a hole at rest. A reduction in the parameter a_h/a_e from 1 to 0 gradually increases the exponent β_M from 0.95 to 1.75.

We discussed above the process of spatial separation of an electron and a hole created in localized states. In fact, the majority of the experiments were carried out using interband excitation. An electron and a hole before capture by localized states can separate by a certain distance R_0. How does this affect the function $P(R)$? It follows from the above that for $R_0 < R_c$, this simply reduces $P(R)$ if $R < R_0$ and in no way affects the nature of the behavior of $P(R)$ in the range $R \gtrsim R_c$. However, for $R_0 > R_c$, then the functions $\eta(R)$ and $P(R)$ in the range $R > R_0$ are described by Eqs. (9) and (10), where we have to replace R_c with R_0.

3. STEADY-STATE DENSITY OF NONEQUILIBRIUM CARRIERS

In this section we calculate the dependence of the steady-state density n of nonequilibrium electrons on the rate of generation G, i.e., on the number of electron–hole pairs created optically per unit volume and per unit time. We consider the case of low values of G, when $n < R_c^{-3}$. The opposite situation characterized by $n > R_c^{-3}$ is considered in Ref. 6.

We can determine n in the case when $n < R_c^{-3}$ using the following equation[6]

$$G\eta(n^{-1/3}) = \frac{n}{\tau_0}\exp\left(-\frac{2n^{-1/3}}{a}\right). \tag{15}$$

The main idea behind the derivation of Eq. (15) is as follows. If we consider only twin recombination of electron–hole pairs, then the main contribution to the steady-state density of nonequilibrium carriers comes from pairs with the maximum internal separation, because the lifetime increases exponentially with increasing R and the concentration of those pairs $G\eta(R)$ which acquire high values of R per unit time decreasing with increasing R very slowly in accordance with the power law (9). Under conditions of steady-state illumination the maximum distance at which carriers recombine is $n^{-1/3}$. In most cases the recombination process at this distance is not of the twin type, but of the interpair type involving carriers created in different absorption events. Therefore, on the left-hand side of Eq. (15) we have the rate of generation of the longest-lived pairs, whereas on the right-hand side we have the interpair recombination rate.

Using Eq. (9) for $\eta(R)$ at $\beta = 1$, we find that the dependence $n(G)$ is described by

$$n(G) = \frac{8}{a^3}L^{-3}(G), \tag{16}$$

where the quantity $L(G)$ is the solution of the equation

$$L = \ln[\tfrac{1}{8}G\tau_0 L^2 a^3 \ln(\nu_0\tau_0)]. \tag{17}$$

Substituting the parameters $\tau_0 = 10^{-8}$ s, $\nu_0 = 10^{12}$ s^{-1}, and $a = 10$ Å in Eqs. (17) and (16), we find that at generation

rates $G = 10^{19}$–10^{21} cm^{-3}·s^{-1} the value of $L(G)$ varies from 17 to 13 and $n^{-1/3}$ from 85 to 65 Å. Under these conditions we have $R_c \approx 45$ Å. Therefore, under ordinary experimental conditions $n^{-1/3}$ is only twice as large as R_c.

The problem of determining the steady-state density n when the recombination is of tunnel radiative nature was discussed earlier.[7] It was assumed that electrons and holes photogenerated in a free state are captured by localized states and can no longer diffuse. Such a situation is in principle possible if there is a strong polaron effect that reduces the frequency ν_0 by many orders of magnitude and reverses the inequality $\nu_0\tau_0 \gg 1$ to a very strong opposite inequality $\nu_0\tau_0 \ll 1$.

It is shown in Ref. 7 that in this case the steady state of the system is controlled by what is known as photostimulated diffusion (PSD). This effect consists in the following. Due to the steady irradiation, new electron–hole pairs are created near existing electrons and holes and recombination of, e.g., an electron with a hole from a newly created pair effectively transfers it to a position of an electron in this pair. Such PSD not only separates twin pairs producing a gas of carriers of density n, but is also responsible for the recombination of carriers because of the random approach of electrons and holes.

We shall show that in the case we have studied, when $\nu_0\tau_0 \gg 1$ holds, the PSD process does not play a significant role. Since the majority of pairs recombine at a distance R_c, the PSD coefficient is of order $D \approx (GR_c^3)R_c^2 = GR_c^5$ (Ref. 8). The concentration of the pairs that recombine per unit time because of the PSD is $4\pi DR_r n^2$, where R_r is the radius of a sphere around a hole at which recombination occurs with a probability close to unity. Substituting the average distance $n^{-1/3}$ for R_r, we obtain an estimate of the upper limit for $(dn/dt)_{\mathrm{PSD}}$:

$$\left(\frac{dn}{dt}\right)_{\mathrm{PSD}} \lesssim G(nR_c^3)^{5/3}.$$

Comparing this quantity with the density of carriers, recombining per unit time due to ordinary diffusion, which according to Eq. (15) is $G\eta(n^{-1/3}) \approx G(nR_c^3)^{\beta/3}$, we can see that in the case under discussion described by $nR_c^3 \ll 1$ we can ignore the influence of the PSD.

4. LOW-TEMPERATURE HOPPING PHOTOCONDUCTIVITY

We begin by calculating the static photoconductivity due to carrier relaxation and recombination processes described above. Twin recombination of carriers makes no contribution to the steady-state photoconductivity,[3] so that the dipole moment p established as a result of spatial separation of an electron and a hole, because of the asymmetry of the directions of electron jumps on the energy scale in the presence of an electric field, disappears in the case of twin recombination. Then, in calculating the photoconductivity we need to allow only for the interpair recombination of carriers. The generation (and, consequently, recombination) rate for these carriers is $G\eta(n^{-1/3})$ per unit volume and, consequently, the current density j is of the form

$$j \approx pG\eta(n^{-1/3}), \tag{18}$$

where p is the dipole moment of a pair when interpair recombination occurs. In the calculation of p we need to know the

energy distribution of the localized states involved in the thermalization of the carriers. We shall assume that the density of states $g(\varepsilon)$ is described by Eq. (13), where ε is measured from the mobility edge into the mobility gap. Then the average dipole moment which appears in a jump of length r can be estimated from

$$p(r) \approx \frac{1}{3}\frac{e^2Er^2}{\varepsilon_0}. \tag{19}$$

Equation (19) is derived on the assumption that if the density of states is described by Eq. (13), the density of the localized states to which the electron can jump in the kth step is a function of the coordinate x along the direction of a field E obeying the law

$$N_k(x) = N_k(1 + eEx/\varepsilon_0),$$

where N_k is the density of the localized states accessible to an electron in the absence of the field. Consequently, the average value of the coordinate x of the nearest localized state is $eEr^2/3\varepsilon_0$, where r^2 is the mean square of the distance to the nearest localized state and the factor $\langle \cos^2 \vartheta \rangle = \frac{1}{3}$ is related to the average over the directions of jumps to the nearest neighbor. Since r_k increases with the serial number k of the step in accordance with a geometric progression, the dipole moment is given by the last step and amounts to

$$p \approx p(n^{-1/3}) \approx \frac{1}{3}\frac{e^2En^{-2/3}}{\varepsilon_0}. \tag{20}$$

Then, Eq. (18) together with Eqs. (20) and (9) are used to obtain the static photoconductivity $\sigma = j/E$ described by

$$\sigma \approx G\eta(n^{-1/3})\frac{e^2n^{-2/3}}{3\varepsilon_0} \approx G\frac{a^2e^2}{12\varepsilon_0}L(G)\ln\nu_0\tau_0, \tag{21}$$

where in the final expression we assume for simplicity that $\beta = 1$.

Determination of σ/Ge was reported in Ref. 3 and values of the order of 10^{-11} cm^2/V were obtained. Substituting in Eq. (21) the parameters $a = 10$ Å, $\varepsilon_0 = 0.025$ eV, $\nu_0\tau_0 = 10^4$, and $G = 10^{20}$ cm^{-3}·s^{-1}, we find that the ratio σ/Ge has the value 5×10^{-12} cm^2/V, in good agreement with the experimental results.

Using Eqs. (21) and (17), we find that the dependence of the photoconductivity on G can be represented in the form $\sigma \propto G^\gamma$, where

$$\gamma = 1 - L^{-1}(G). \tag{22}$$

Substituting in Eq. (22) the parameters given above, we find that for $G = 10^{19}$–10^{21} then we have $\gamma = 0.94$–0.92, which does not differ to greatly from the experimental values $\gamma = 0.97 \pm 0.03$ (Ref. 3).

We now consider the dynamic photoconductivity at a frequency ω. In this case the condition $\omega\tau_d(r_\omega) \sim 1$ can be used to find the maximum length

$$r_\omega = \frac{a}{2}\ln\left(\frac{\nu_0}{\omega}\right) \tag{23}$$

for those jumps which occur during one period of the field. We assume that $r_\omega \ll n^{-1/3}$; otherwise the photoconductivity is practically indistinguishable from that in the static case.

In calculating $\sigma(\omega)$ we can, following Pollak and Geballe,[8] calculate the number of resonant pairs of localized

states separated by a distance r within the range $r_\omega - a/2 < r < r_\omega + a/2$ and having one electron. This gives

$$\sigma(\omega) \approx e^2 n g(\varepsilon_G) r_\omega^4 a \omega = e^2 n^2 \varepsilon_0^{-1} r_\omega^4 a \omega. \tag{24}$$

Here, $g(\varepsilon_G) \equiv n/\varepsilon_0$ is the density of states in the region of ε_G, where a large number of electrons is concentrated under steady-state conditions. Then, using Eq. (16), we obtain

$$\frac{d \ln \sigma(\omega)}{d \ln G} = \frac{6}{L(G)}, \tag{25a}$$

$$\frac{d \ln \sigma(\omega)}{d \ln \omega} = 1 - \frac{4}{\ln(v_0/\omega)}. \tag{25b}$$

We now consider again the static photoconductivity and discuss its dependence on the frequency Ω of the exciting light. It is assumed above that $\hbar\Omega$ is only slightly less than the width of the mobility gap, so that electrons and holes are created in localized states close to the mobility edge.

We shall now consider the case of excitation by light of longer wavelengths which is characterized by $E_g - \hbar\Omega \gg \varepsilon_0$ and naturally, only the hopping photoconductivity exists in this case. The photoconductivity is estimated above on the assumption that electrons are created in localized states characterized by $\varepsilon \approx \varepsilon_0$, i.e., sufficiently close to the mobility edge to satisfy the inequality $N_0 R_c^3 \gg 1$, where N_0 is the density of the localized states accessible to electrons in the first step. Is this inequality disobeyed when $E_g - \hbar\Omega \gg \varepsilon_0$? The probability for an electron to appear with a given energy ε is proportional to the product of the density of states in the conduction and valence band tails:

$$g_e(\varepsilon) g_h(E_g - \hbar\Omega - \varepsilon). \tag{26}$$

If both densities of states are in the form of simple exponential functions of Eq. (13) with different characteristic energies ε_{0e} and ε_{0h}, where $\varepsilon_{0h} > \varepsilon_{0e}$, then even for $E_g - \hbar\Omega \gg \varepsilon_0$ the electrons mainly have energies $\varepsilon \approx \varepsilon_0$. Our theory is valid in this case, which is very realistic for amorphous silicon, and for $E_g - \hbar\Omega \gg \varepsilon_0$, the quantum efficiency of the photoconductivity is not specifically small.

The situation is different when the density of states as a function of energy falls faster than predicted by Eq. (13). We now consider a hypothetical case when the density of states is the same in both bands and is described by

$$g(\varepsilon) = g_0 \exp(-\varepsilon^2/\Lambda^2). \tag{27}$$

Then, Eq. (27) is maximal for

$$\varepsilon = \varepsilon_m \equiv \frac{E_g - \hbar\Omega}{2} \tag{28}$$

and at this point it is equal to

$$\exp\left[-\frac{(E_g - \hbar\Omega)^2}{2\Lambda^2}\right]. \tag{29}$$

The contribution to the absorption by electrons characterized by $\varepsilon \sim \Lambda$ is much less than that given by Eq. (29) and is proportional to

$$\exp\left[-\frac{(E_g - \hbar\Omega)^2}{\Lambda^2}\right]. \tag{30}$$

We consider the photoconductivity associated with typical electrons which are created with the energy described by Eq. (28). The density

$$N_0(\varepsilon_m) \equiv \int_{\varepsilon_m}^{\infty} g(\varepsilon) d\varepsilon$$

of the localized states accessible in the first step in the case when $E_g - \hbar\Omega \gg \Lambda$ can easily become much less than R_c^{-3}, i.e., the condition for our theory to be valid may be violated. In this case the photoelectron recombines with its own hole as a rule without making a single step. The main contribution to $\eta(n^{-1/3})$, which is a quantity necessary in the calculation of the photoconductivity, comes from pairs of closely spaced localized states such that for each of them there is a random low-probability chain of localized states ("conductor") which allows an electron to reach the average distance $N_0^{-1/3}(\varepsilon_m)$ between the accessible localized states by dropping slightly on the energy scale. Further relaxation and diffusion of such an electron occur in accordance with our theory. The probability that such a conductor will appear is calculated in Ref. 9 and for the case of interest to us is proportional to

$$\exp\left[-\frac{1}{6\ln 2} \ln^2 \frac{1}{N_0(\varepsilon_m) R_c^3}\right]. \tag{31}$$

This exponential factor occurs in $\eta(n^{-1/3})$. Consequently, the quantum efficiency of the photoconductivity per absorbed photon becomes exponentially small and falls rapidly as $\hbar\Omega$ is reduced. The factor (31) remains in the expression for the photoconductivity until the product of the exponential functions (31) and (29) becomes comparable with that given by Eq. (30). At lower values of $\hbar\Omega$ the main contribution to the photoconductivity comes from electrons which are created with an energy $\varepsilon \sim \Lambda$, and the photoconductivity is proportional to the factor (30).

5. LOW-TEMPERATURE PHOTOLUMINESCENCE OF AMORPHOUS SEMICONDUCTORS

We first consider the photoluminescence kinetics after the end of illumination. In experimental investigations it is usual to plot the dependence of the luminescence intensity on the logarithm of time. It is assumed in Ref. 2 that the observed luminescence decay curve is governed by the distribution of the internal distances R in the recombining twin pairs. Then, the experimentally determined density of the distribution of the logarithm of the lifetime

$$\Psi[(a/2)\ln(\tau/\tau_0)]$$

should be identical with $P(R)$. Strictly speaking, this is not quite correct, because the lifetime can in some cases be governed not by the recombination jumps, but the longest of the diffusion jumps. We used numerical simulation to calculate both functions and to show that $\Psi(R)$ differs from $P(R)$ by no more than 5%. This means that the time τ is usually governed by the recombination time and not by the diffusion time in the course of cooling. We checked this directly by a numerical calculation of the fraction of cases when the slowest is the diffusion rather than the recombination jump. It was found that the fraction was indeed small and amounted to about 9%.

We were therefore able to compare the theoretical curve $P(R)$ with the observed dependence $\Psi[(a/2)\ln \tau/\tau_0]$. It follows from Fig. 2 that the maximum of the lifetime distribution function occurs at $R \approx R_c$, i.e., at the luminescence

time

$$\tau_{max} \approx \tau_r(R_c) = v_0\tau_0{}^2. \tag{32}$$

Using the values $\tau_0 \approx 10^{-8}$ s and $v_0 \approx 10^{12}$ s^{-1}, we obtain $\tau_{max} \approx 10^{-4}$ s, in good agreement with the experimental data.[1] However, if we plot the dependence $\Psi[(a/2)\ln \tau/\tau_0]$ on the basis of the experimental results and ensure that the maximum of $\Psi(R)$ is equal in amplitude to the maximum of $P(R)$, we find that the $\Psi(R)$ curve is considerably narrower than the theoretical curve $P(R)$. The steeper slope of $\Psi(R)$ to the left of the maximum is most likely due to the diffusion of electrons between delocalized states in the band discussed at the end of Sec. 2. The steeper slope to the right of the maximum may, in principle, be due to nonradiative recombination processes, which are also ignored by our theory.

Another possible reason for the steep slope of $\Psi(R)$ at high values of R may be a high concentration of electron–hole pairs n. This is because even in the case of pulsed excitation in a real experimental situation the value of $n^{-1/3}$ is slightly higher than R_c. Obviously, the function $P(R)$ calculated in Sec. 2 can be used only up to $R \sim n^{-1/3}$. We shall show that if $R > n^{-1/3}$, when the interpair recombination predominates, we have $\Psi(R) \propto R^{-4}$, which is in good agreement with the experimental results. In fact, the interpair recombination process has the effect that the density of the electron–hole gas decreases and the gas eventually becomes practically homogeneous. Clearly, if the average distance between carriers reaches R, then their density is of order R^{-3}. All these carriers recombine by forming jumps of length exceeding R. We therefore obtain

$$\int_R^\infty \Psi(R')dR' \propto R^{-3} \quad \text{and} \quad \Psi(R) \propto R^{-4}.$$

Clearly, we can observe (in the absence of nonradiative channels) a region characterized by $R > R_c$ where the fall of $P(R)$ in accordance with Eq. (10) is slow, if we use much lower excitation intensities.

We are interested in the photoluminescence intensity integrated over the spectrum and independent of the actual nature of the density of states $g(\varepsilon)$ in the band quasigap. The photoluminescence spectrum naturally depends on $g(\varepsilon)$, but the calculation can be completed for any density of states. Let us assume that $F(\varepsilon)$ is the probability for an electron to recombine from a localized state with an energy exceeding ε. We first calculate the asymptotic form of $F(\varepsilon)$ at high values of ε, i.e., the fraction of electrons that have dropped anomalously far down on the energy scale. As pointed out in Sec. 2, in the case of energy relaxation of an electron its energy and the distance to a hole are related by

$$N(\varepsilon) \propto R^{-3}, \tag{33}$$

where

$$N(\varepsilon) = \int_\varepsilon^\infty g(\varepsilon')d\varepsilon' \tag{34}$$

is the number of localized states with energies in excess of ε (the values of ε are measured into the band quasigap). We therefore have

$$F(\varepsilon) \sim \eta[R(\varepsilon)] \sim [R_c/R(\varepsilon)]^\beta = Z^{\beta/3}(\varepsilon), \tag{35}$$

where

$$Z(\varepsilon) \equiv \frac{4\pi}{3}N(\varepsilon)R_c{}^3. \tag{36}$$

Equation (35) is valid for $R \gg R_c$, i.e., when $Z \ll 1$.

We can easily find the asymptotic form of $F(\varepsilon)$ also in the opposite case when $Z \gg 1$. In this case an electron at a distance R from a hole can recombine so that the energy is ε in none of the sites, the concentration of which is $N(\varepsilon)$, accessible to electrons is in a sphere of radius $R + R_c$ surrounding an electron. The probability of such an event (in the Markov approximation) is

$$W(\varepsilon,R) = \exp\left[-\frac{4\pi}{3}N(\varepsilon)(R+R_c)^3\right]. \tag{37}$$

In the case of the values of $Z \gg 1$ of interest to us, when the argument of the exponential function in Eq. (37) is large, the main role in the recombination process is played by pairs characterized by $R \ll R(\varepsilon)$. The density of the probability that an electron is found at a given point in the case when $R \ll R(\varepsilon)$ is of order $R^{-3}(\varepsilon)$, so that the recombination probability is described by the expression

$$1-F(\varepsilon) \approx \int_0^\infty \frac{4\pi R^2}{R^3(\varepsilon)}W(\varepsilon,R)dR \approx \frac{4\pi}{27}\frac{\exp[-Z(\varepsilon)]}{Z^2(\varepsilon)}. \tag{38}$$

Since the function F has two asymptotic forms which depend only on Z and not on $N(\varepsilon)$ and R_c separately, it follows that $F(\varepsilon)$ may be determined uniquely by the value of $Z(\varepsilon)$ for any $R_c \gg N_0{}^{-1/3}$. Computer modeling supports this hypothesis completely: for $R_c \gtrsim 2N_0{}^{-1/3}$, the $F(Z)$ curves are indistinguishable from one another. Then, for $Z \ll 1$ and $Z \gg 1$, we find that the asymptotes described by Eqs. (35) and (38), respectively, are accurate apart from a numerical factor.

The spectral density of the steady-state photoluminescence is readily expressed in terms of $F(\varepsilon)$:

$$I(\varepsilon) = \frac{dF}{d\varepsilon} = \frac{dF}{dZ}\frac{dZ}{d\varepsilon} = \frac{g(\varepsilon)}{N(\varepsilon)}\varphi[Z(\varepsilon)], \tag{39}$$

where

$$\varphi(Z) = Z\frac{dF}{dZ}. \tag{40}$$

A plot of the function $\varphi(Z)$ obtained from numerical modeling is shown in Fig. 3.

In the case when $g(\varepsilon)$ is described by Eq. (13), we have

$$Z(\varepsilon) = \exp\left(\frac{\varepsilon_c-\varepsilon}{\varepsilon_0}\right), \quad \varepsilon_c = \varepsilon_0\ln\left(\frac{4\pi}{3}R_c{}^3N_0\right), \tag{41}$$

$$I(\varepsilon) = \frac{1}{\varepsilon_0}\varphi[Z(\varepsilon)], \tag{42}$$

and according to Eqs. (35) and (38), the asymptotic expressions for $I(\varepsilon)$ become

$$I(\varepsilon) \approx \frac{4\pi}{27}\frac{\exp[-Z(\varepsilon)]}{\varepsilon_0 Z(\varepsilon)} \quad \text{when} \quad \varepsilon \ll \varepsilon_c, \tag{43}$$

$$I(\varepsilon) \sim \frac{1}{\varepsilon_0}\exp\left[\frac{0.38(\varepsilon_c-\varepsilon)}{\varepsilon_0}\right] \quad \text{when} \quad \varepsilon \gg \varepsilon_c. \tag{44}$$

It follows from Eqs. (41) and (42) that in this case the plot in Fig. 3 also represents $I[(\varepsilon-\varepsilon_c)/\varepsilon_0]$. The maximum value of I corresponds to $\varepsilon_c + 4.5\varepsilon_0$ and the asymptotes given
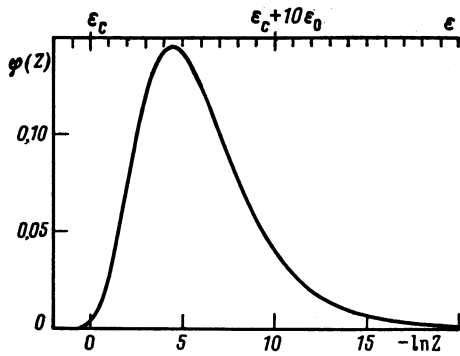
FIG. 3. Function $\varphi(Z)$ found by numerical modeling. According to Eq. (39) this function determines the steady-state photoluminescence spectrum. The top abscissa scale gives the energy of the emitted photons; each division on this scale represents ε_0. The values of Z and ε_c were found using Eq. (41).

by Eqs. (43) and (44) provide satisfactory descriptions for $\varepsilon \leqslant \varepsilon_c$ and $\varepsilon \geqslant \varepsilon_c + 7\varepsilon_0$, respectively.

In comparing our spectra with the experimental results we must bear in mind that, as in the case of $P(R)$, the asymptotic form given by Eq. (44) can be observed only in the case of a very low pumping rate and under real experimental conditions the nontwin recombination should result in truncation of the long-wavelength part of the spectrum. The same effect results from the nonradiative recombination which we have ignored. Moreover, some of the experimentally observed large Stokes shifts of the photoluminescence may not be associated with the hopping relaxation of electrons, but with the polaron shift of hole levels.[1] The dispersion of the polaron shifts then may also influence the form of the photoluminescence spectrum.

We may then find that the energy of the maximum of the photoluminescence line $\varepsilon_m = \varepsilon_c + 4.5\varepsilon_0$ we have found can not correspond to a real experimental situation, since the recombination time at such energies should be very long and steady-state conditions cannot be attained. In fact, the density of localized states characterized by $\varepsilon > \varepsilon_m$ is

$$N(\varepsilon_m) = R_c^{-3} \exp(-4.5),$$

and the average distance between them is

$$r_m \approx R_c \exp(1.5) \approx 4.5 R_c.$$

At a distance r_m the recombination time is very long. However, this conclusion is wrong because the recombination characterized by the energy ε is dominated by electrons which recombine at a distance shorter than $R(\varepsilon)$. This is due to the fact that the recombination probability rises steeply if an electron is accidentally at a point characterized by $R \ll R(\varepsilon)$. We can readily show that at $\varepsilon = \varepsilon_c$, the integral in Eq. (38) is dominated by the contribution from the region $R \lesssim R_c/4\pi$ and not $R_c \approx R(\varepsilon_c)$. We are therefore of the opinion that the dependence (42) should provide a satisfactory description of the photoluminescence line profile in the region of its maximum. A more serious analysis of this topic should include a numerical study of the kinetics of the photoluminescence spectrum.

APPENDIX 1. DESCRIPTION OF THE SIMULATION

The idea of modeling of the process of electron relaxation is as follows: assuming a random realization of coordinates and energies of localized states, study jumps an electron undergoes between them in accordance with the "rules of behavior" for an electron described in Sec. 2. We now repeat these rules briefly:

1) Initially the electron and hole are at the same point in space, at the origin of a coordinate system, and the electron energy is $\varepsilon = 0$;

2) If at a distance smaller than $R + R_c$ [see Eq. (5)] there is no localized state lower on the energy scale than the state at which an electron is residing, recombination takes place and the history of such an electron ends;

3) If there are localized states of this kind, the electron drops to the nearest of them and then stages 2 and 3 are repeated.

If we store the information on the distance R from the origin and on the energy ε of the recombining electron, we can use a large number of such histories to calculate the distribution functions of R and ε and then applying them to determine the quantities $\eta(R)$, $P(R)$, $I(\varepsilon)$ of interest to us, as well as the index β, and so on.

In spite of the great simplicity of the rules stated above, the problem of developing a working program is not trivial, because the lengths of the electron jumps increase geometrically, in accordance with Eq. (8). If 30 electron jumps (and the probability of this many jumps is not that low) takes place, the electron is at a distance of order $2^{10} N_0^{-1/3} \approx 10^3 N_0^{-1/3}$ from the hole. In a sphere of this radius there are about 10^9 localized states. Information on such a number of localized states cannot be put in any computer memory and the search for the nearest out of 10^9 states would require hours of computer time. On the other hand, it is obvious that there is no need to calculate the probability of a transition to such a giant number of states since in the course of relaxation of the electron there are only $R^3(\varepsilon)N(\varepsilon) \sim 1$ states accessible in a sphere of radius $R(\varepsilon)$ inside which the electron is located. Therefore, the only way of writing a working program involves taking into account new regions of space only when they become accessible to the electron and to generate in these regions only those localized states which are lower on the energy scale than that at which the electron is residing when these regions become accessible to it. If this program is followed literally, it becomes necessary to handle a very complex geometric object in the form of a sequence of intersecting spheres of different radii "threaded" on the electron path. A reasonable compromise is to find the solution by considering first a region in space in the form of a minimal parallelepiped containing all such spheres.

We now describe the algorithm derived on the basis of the above considerations:

1. The initial state of the system is generated with the electron located at the origin of a coordinate system where the hole is also located. A parallelepiped used in the above program is located symmetrically relative to the origin of the coordinate system; its dimensions are $1.3 N_0^{-1/3}$ along the y and z axes and zero along the x axis (the reason for this selection will become obvious later). Since the volume of the "investigated" region of space is initially zero, the number of localized states in this region can naturally be also assumed to be zero.

2. We can then determine the distance r_{min} from the localized state at which an electron is residing to the nearest

localized state within the investigated region of space (if there is such a space); We then find the distance r_b of the electron to the nearest face of this parallelepiped. If it contains localized states characterized by $r_{min} < r_b$, the algorithm goes over to step 4, but if the opposite inequality applies it goes to the next step 3.

3. In the direction to the nearest face the size of the region in space being investigated increases by $|\ln q_1|/N(\varepsilon)S$, where ε is the energy of the localized state in which the electron is located, S is the area of the face which has moved away, and q_1 is a random number distributed uniformly between 0 and 1. At a random point directly on the face which has moved away there is a new localized state of energy ε' such that $N(\varepsilon') = q_2 N(\varepsilon)$, where q_2 is a different random number from the interval $(0,1)$. The program then returns to step 2.

4. If $r_{min} > R + R_c$, the electron is lost, its history is finished, and the program goes over to step 5. In the opposite case the electron is transferred to the nearest state and all the localized states with energies below that at which the electron is residing are removed from the computer memory because a transition to any of these localized states is no longer possible. The program then returns to step 2.

5. For each lost electron the distance to the origin of the coordinates R at the moment of recombination is stored as well as the length of the slowest jump during its history $R_l = \max(R, r_m - R_c)$, where r_m is the maximum length of the jump between the localized states, are recorded in the computer memory. Moreover, the value of $N(\varepsilon)$ at the energy at which the electron is lost and the number of jumps performed by the electron are also stored in the memory. At the end of the run these stored data are used to calculate $P(R)$ (the density of the distribution of R), $\Psi(R)$ (the density of the distribution of R_l), and $I(\varepsilon)$ {for the density of states described by Eq. (13), this is the density of the distribution of the quantity $\varepsilon_0 \ln[N_0/N(\varepsilon)]$}.

APPENDIX 2

This Appendix is concerned with calculation of the function $\eta(R)$, which represents the probability that the electron travels away from the hole to a distance exceeding R when $R \gg R_c$. We make the assumption already discussed in the main text: we postulate that the probability of an electron jump from a point $\mathbf{R}_k$ to a point $\mathbf{R}_{k+1}$ is independent of its previous position $\mathbf{R}_{k-1}$ This means that we shall ignore the presence of an excluded volume formed by a set of spheres with their centers at the points $\mathbf{R}_{i-1}$ and with radii $|\mathbf{R}_i - \mathbf{R}_{i-1}|, i \leqslant k$, which the electron cannot enter from the points $\mathbf{R}_k$, because there are no accessible sites in this region.

Since at each step k we have not only a random electron coordinate $\mathbf{R}_k$, but also a random concentration of accessible sites N_k, the problem suggested here requires introduction of a function $p_k(\mathbf{R},N)$, which is the density of the probability that an electron reaches $\mathbf{R}$ after k jumps and is not lost; the concentration is then N. In the case of the function $p_k(\mathbf{R},N)$ in the d-dimensional case we have the recurrence relation

$$p_k(\mathbf{R},N) = \int_0^1 dx \int_0^\infty dN' \int_\Omega d^d R' \delta(N - xN')$$

$$\times W(\mathbf{R}|\mathbf{R}',N') p_{k-1}(\mathbf{R}',N'), \qquad (A2.1)$$

where $W(\mathbf{R}|\mathbf{R}',N')$ is the probability of finding a site nearest to the point $\mathbf{R}'$ at the point $\mathbf{R}$, given by

$$W(\mathbf{R}|\mathbf{R}',N') = N' \exp[-\alpha_d N' |\mathbf{R}-\mathbf{R}'|^d], \quad \alpha_d = \frac{\pi^{d/2}}{\Gamma(1+d/2)}.$$

$$(A2.2)$$

The length of the jump from a point $\mathbf{R}'$ should not exceed R' [in accordance with condition (5) where we have ignored R_c]. Therefore, integration in Eq. (A2.1) is carried out over the volume Ω defined by the condition $|\mathbf{R}' - \mathbf{R}| < R'$. Since the function $p_k(\mathbf{R},N)$ obviously depends only on the absolute value of $\mathbf{R}$, in Eq. (A2.1) we can go over from integration using cylindrical coordinates and direct the z' axis along $\mathbf{R}$. Trivial integration with respect to x then gives

$$p_k(R,N) = \int_N^\infty dN' \int_{R/2}^\infty dz' \int d^{d-1}\rho'$$

$$\times \exp\{-\alpha_d N'[(z'-R)^2 + \rho'^2]^{d/2}\} p_{k-1}(R',N).$$

$$(A2.3)$$

The method during subsequent calculations can be illustrated most conveniently by considering the one-dimensional case $d = 1$. First of all, we note that in the one-dimensional case there is no need for any simplification: allowance for the excluded volume reduces to the assumption that an electron jumps always in one direction, i.e., that we always have $z_{k-1} < z_k$. Therefore, a recurrence relationship similar to Eq. (A2.3) is

$$p_k(z,N) = \int_N^\infty dN' \int_{z/2}^z dz' \exp[-N'(z-z')] p_{k-1}(z',N'). \quad (A2.4)$$

The required function $\eta(z)$ is expressed in terms of $p_k(z,N)$ as follows:

$$\eta(z) = \sum_{k=0}^\infty \int_0^\infty dN' \int_z^\infty dz' p_k(z',N'). \qquad (A2.5)$$

Equation (A2.4), like Eq. (A2.3), has a characteristic scaling property: if the functions $p_i(z,N)$ satisfy this equation, it is satisfied also by the functions $\tilde{p}_i(z,N) = p_i(Cz,N/C)$, where C is an arbitrary constant. In other words, Eq. (A2.4) is the difference equation for $\ln(z/N)$. We shall introduce new variables $u = \ln(z/N)$ and $v = zN$ and seek the solution of Eq. (A2.4) in the form

$$p_k(z,N) = \int_{-\infty}^\infty d\omega e^{-i\omega u} f_{i\omega}^{(k)}(v). \qquad (A2.6)$$

Substitution of Eq. (A2.6) into Eq. (A2.4) allows us, as can easily be shown, to obtain a recurrence relation separately for each value $s = i\omega$:

$$f_s^{(k)}(v) = v^{-s} \int_0^\infty dt\, t^{2s-1} \int_{t/2}^t \frac{dw}{w^s} e^{v-t} f_s^{(k-1)}(w). \qquad (A2.7)$$

Substituting Eq. (A2.6) into Eq. (A2.5) and going over to integration with respect to du' and dv' in Eq. (A2.5), we obtain

$$\eta(z) = \frac{1}{2} \int_{-\infty}^\infty d\omega \int_{-\infty}^\infty du' e^{-i\omega'} \int_{z^2 e^{-u'}}^\infty dv' \sum_{k=0}^\infty f_{i\omega}^{(k)}(v'). \qquad (A2.8)$$

Hence, the derivative $d\eta(z)/dz$ can be found by the substitution $v = z^2 e^{-u'}$:

$$\frac{d\eta}{dz} = \frac{1}{z} \int_{-\infty}^{\infty} d\omega \exp(-2i\omega \ln z) F(i\omega), \qquad (A2.9)$$

$$F(s) = \int_{0}^{\infty} dv \, v^s \sum_{k=0}^{\infty} f_s^{(k)}(v). \qquad (A2.10)$$

The behavior of $\eta'(z)$ at high values of z is governed by the properties of the function $F(i\omega)$, which we shall show to be associated with the convergence of the above series with respect to k.

If k is large, the solution of Eq. (A2.7) becomes

$$f_s^{(k)}(v) = A_s [\varkappa(s)]^k \Psi_s(v), \qquad (A2.11)$$

where $\varkappa(s)$ and ψ_s are the largest eigenvalue and the corresponding eigenfunction of the equation

$$\varkappa(s) \Psi_s(v) = v^{-s} \int_{v}^{\infty} dt \, t^{2s-1} \int_{t/2}^{t} \frac{dw}{w^s} e^{w-t} \Psi_s(w), \qquad (A2.12)$$

and the constant $A_s \sim 1$ depends on the initial function $f_s^{(0)}(v)$. We can easily show by direct substitution that Eq. (A2.12) satisfies

$$\Psi_s(v) = v^{-s} e^{-v}, \quad \varkappa(s) = \frac{1}{1-2s}(1-2^{2s-1}). \qquad (A2.13)$$

Substituting Eq. (A2.11) into Eq. (A2.10), we can see that the convergence of the series in Eq. (A2.10) is governed by the convergence of the sum of the geometric series

$$\sum_k [\varkappa(s)]^k,$$

so that at the point $s = s_0$, where $\varkappa(s_0) = 1$ holds, the series diverges and the function $F(s)$ has a pole. Therefore, at high values of z it follows from Eq. (A2.9) that

$$\frac{d\eta(z)}{dz} \propto z^{-1-2s_0}, \quad \varkappa(s_0) = 1 \qquad (A2.14)$$

[this is not true for arbitrary values of z, because we have to allow for the poles $s_i > s_0$ associated with other eigenvalues of Eq. (A2.12)]. It is clear from Eq. (A2.13) that $s_0 = 1$. Therefore, we obtain a power law for $\eta(z)$ and the exponent is $\beta = 2s_0 = 2$.

The power-law asymptote $\eta(z)$ for a space with arbitrary dimensions d can be calculated in exactly the same way if we begin with Eq. (A2.3). Then $\varkappa(s)$ occurring in Eq. (A2.14) represents an eigenvalue of the equation

$$\varkappa(s) \Psi_s(v) = d(d-1)\alpha_{d-1} v^{-s} \int_{v}^{\infty} dt \, t^{2s-1} \int_{t/2}^{t} dz$$

$$\times \int_{0}^{\infty} d\rho \, \rho^{d-2} r^{-s} \exp\{-\alpha_d [(z-t)^2 + \rho^2]^{d/2}\} \Psi_s(r). \qquad (A2.15)$$

In contrast to the one-dimensional case described by Eq. (A2.12), we cannot solve Eq. (A2.15) analytically and, therefore, we have to use a computer. We found that the power exponent in Eq. (9) is $\beta_M = 1.750$ for $d = 3$ and $\beta_M = 3.576$ for $d = 1$.

The latter value is obtained if we omit integration with respect to ρ from Eq. (A2.15) and replace $(d-1)\alpha_{d-1}$ with 1; it corresponds to the situation when an electron can move along a chain in either direction. This hypothesis has no physical meaning, because it postulates that on the hole side there is continuous creation of sites accessible to an electron, but this result illustrates well the difference between ballistic motion (i.e., when the motion is in one direction, as is indeed found in the one-dimensional case) and diffusive motion of electrons: in the latter case the value of β_M is 1.8 times larger. This illustration allows us to understand the difference (discussed in body of the paper) between the value $\beta_M = 1.75$ obtained in this Appendix for $d = 3$ and the result of numerical modeling, $\beta = 1.15 \pm 0.01$. The difference is due to the fact that our calculation is based on diffusion, whereas in reality an electron is more likely to move ballistically in the radial direction.

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[2]We must stress once again that the categorical nature of this conclusion is based on the smallness of the Bohr radius compared with other spatial scales of the problem.

[3]We note that the index β reaches 1.15 only if R/R_c is sufficiently large (of the order of 30), whereas for $3 \leqslant R/R_c \leqslant 5$ the value of β is close to 0.8. The reason for such a late rise of $P(R)$ to the asymptotic value is readily identified. Therefore, β is closely related to the probability of finding an accessible localized state in a sphere of radius $R + R_c$. The function $P(R)$ reaches the asymptotic value if in calculation of the volume of this sphere $4\pi(R + R_c)^3/3$ we can ignore R_c. We can do this if $R \approx 4R_c$ and this in turn leads to halving of the volume. Therefore, in this range of R the index β should differ significantly from its maximum value and in fact the value should be smaller, i.e., the probability of the loss of an electron should be higher.

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