A novel tunneling recombination regime for photocarriers in amorphous semiconductors

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A theory of low-temperature tunnelling recombination in amorphous undoped semiconductors under steady-state illumination is developed and the various regimes in which nonequilibrium populations form in the localized states (observed, e.g., using EPR) are analyzed. We discuss two limiting cases, where the mean distance $\bar{R}$ between geminate photoelectrons and photoholes is either larger or smaller than the mean spacing $N^{-1/3}$ between localized photocarriers. We show that for $\bar{R} < N^{-1/3}$ the often-discussed geminate recombination regime is replaced by a new regime due to photo-induced diffusion. This replacement occurs even in the absence of intrinsic diffusion; we refer to the new regime as "diffusive." In this regime the steady-state concentration N is due to widely-spaced pairs whose components are able to disperse over large distances by diffusion without recombining with each other, thereby forming a rarefied gas; these components only recombine after encountering a random particle of the other kind. The interpair recombination regime $\bar{R} > N^{-1/3}$ was modelled numerically; we found that in this regime partial spatial clustering of particles of the same kind can occur. We have established that some properties of the steady state can be investigated by non-steady-state methods. The theoretical results are compared to experimental data for α-Si:H.

I. INTRODUCTION

At present, the following picture is used to describe the generation of low-temperature photoluminescence in undoped amorphous hydrogenated silicon (see, e.g., Refs. 1 and 2): under optical excitation above the absorption edge, electrons and holes which are created in regions of high density of states are rapidly thermalized by phonon emission and come to occupy localized states in the "tails" of the conduction and valence band densities of states, respectively. In samples of α-Si:H with a low density of broken bonds, the basic recombination channel for localized photoelectrons and photoholes is tunnelling radiative recombination, which corresponds to the luminescence band at 1.2 to 1.4 eV. In this case it is assumed that at low temperature $T < 20$–30 K, diffusion of the localized photocarriers (thermally-activated or tunnelling) can be neglected during the short-time thermalization processes.

Usually it is assumed that a localized electron recombines with a localized hole separated by a distance R with a recombination time which depends exponentially on R:

$$\tau(R) = \tau_0 \exp(2R/R_0). \tag{1}$$

According to the estimates given in Refs. 1 and 3, we have $\tau_0 = 10^{-8}$, $R_0 = 11$–12 Å in α-Si:H. The probability $P_0(R)$ for creation of an electron-hole (geminate) pair with a separation R between the electron and hole (at the time when thermalization ends) is assumed to be Gaussian[4,5]:

$$P_0(R) = \frac{4R^2}{\pi^{1/2}\bar{R}^3} \exp\left(-\frac{R^2}{\bar{R}^2}\right). \tag{2}$$

In this case, the spatial correlation of geminate electrons and holes at the moment of their attachment to localized states is characterized by a single parameter, the length $\bar{R}$. The problem of determining the magnitude of $\bar{R}$, like the problem of calculating the function $P_0(R)$ from first principles, remains open; in analyzing the low-temperature experiments on α-Si:H one usually uses values of $\bar{R} \sim 50$–100 Å (55 Å in Ref. 3, 87 Å in Ref. 5).

The goal of this paper is to calculate the dependence of the steady-state concentration of localized electrons (or holes) $N(g)$ on the generation rate of electron-hole pairs per unit volume $g = K(I/\hbar\omega)$, where ω is the frequency, I the intensity and K the absorption coefficient of the excitation light, According to (1), (2), the function $N(g)$ is determined by three parameters: R_0, $\bar{R}$ and τ_0, on which we place no *a priori* limitations except that the inequality

$$R_0 \ll \bar{R}, \tag{3}$$

should hold. Therefore, the discussion given below is applicable to a larger group of problems than those which are specific to α-Si:H alone. We note that the value of N can be determined experimentally from the photo-induced EPR signal,[4,6,7]

Two models are used to describe photoluminescence in undoped α-Si:H: the model of geminate, or single-pair, recombination,[1,3,4] and the distant-pair recombination model.[2,5,7] In these models it is assumed that the primary contribution to the photoluminescence comes from recombination of pairs generated by the absorption of the same or of different photons, respectively. Obiously these two recombination models correspond to two different ranges of steady-states occupation of the density-of-states tails by photoelectrons and photoholes. Below, we will show that there is a third "diffusive" regime in which the photoluminescence is generated primarily by geminate recombination while the quantity $N(g)$ is determined by interpair recombination. Our analysis shows that this third regime applies to a large percentage of the experimental situations encountered in practice.

2. GEMINATE AND INTERPAIR RECOMBINATION REGIMES

It is clear that for weak steady-state illumination, the electron-hole pairs which are generated find themselves far

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from each other; consequently, they recombine independently, i.e., the recombination is geminate. In this case, obviously,

$$N(g)=g\int_0^\infty dR\,P_0(R)\,\tau(R)\approx 4\left(\frac{\bar{R}}{R_0}\right)^2 g\tau_0\exp\left(\frac{\bar{R}^2}{R_0{}^2}\right). \quad (4)$$

The basic contribution to (4) comes from pairs with large mutual separation lengths $\tilde{R}=\bar{R}^{\,2}/R_0$. Therefore, Eq. (4) is correct only for very small values of g, when these pairs do not overlap each other, i.e., for $N(g)\tilde{R}^{\,3}\ll 1$.

In the high-light-intensity limit, when

$$N\bar{R}^3\gg 1, \quad (5)$$

so that the mean spacing between geminate electrons and holes exceeds the mean distance between photocarriers in steady state, the correlations in spatial location of geminate electrons and holes obviously can be neglected. Then we can set $P_0(R)=$ constant and use the interpair recombination model.[2] In Ref. 2, a calculation of the function $N(g)$ was carried out numerically, including a number of simplifying assumptions. To exponential accuracy, the steady-state concentration N for $P_0(R)=$ constant satisfies the equation

$$N/\tau(R_N)=g, \quad (6)$$

where $R_N=bN^{-1/3}$ and b is a constant. Therefore, the regime discussed in Ref. 2 may be referred to as the interpair recombination regime with one spatial scale.

In the large intermediate region

$$\tilde{R}^{-3}<N<\bar{R}^{-3} \quad (7)$$

the results for large and small concentrations N can be "spliced together," using either an equation analogous to (6):

$$\frac{N}{\tau(R_N)}=g\int_{R_N}^\infty P_0(R)\,dR, \quad (8)$$

or one analogous to (4):

$$N=g\int_0^{R_N} P_0(R)\,\tau(R)\,dR, \quad (9)$$

These equations lead to the same estimate of $N(g)$ in order of magnitude. Therefore, it would appear that a complete qualitative picture of the steady-state occupation of localized states has been created. For small g, its most important feature is the anomalously long lifetime of pairs with $R\gg\bar{R}$, which leads to a rather large value of $N(g)$. In the following section we will show that by virtue of this long lifetime, even very weak diffusion destroys the picture described above.

3. DIFFUSIVE REGIME

The diffusion of electrons and holes can be related both to the finite temperature $T\neq 0$ of the sample (intrinsic diffusion) and to the very interesting phenomenon of effective photo-induced diffusion, which exists even at $T=0$. The mechanism of effective photodiffusion was first proposed by Kastner[8] to describe photo-induced bimolecular recombination of carriers localized on defects. As applied to undoped α-Si:H, this phenomenon can be described as follows: in the vicinity of, e.g., a solitary localized electron which belongs to a pair with an anomalously large mutual separation, an ordinary pair with separation $R\sim\bar{R}$ is generated whose hole recombines not with its partner but with the solitary electron. The electron left behind from the typical pair is found to be shifted in space by a distance l on the order of $\bar{R}$ relative to the electron that recombined. Since the frequency for such a shift is $\tau^{-1}\sim gR^{\,3}$, the result is diffusion of solitary carriers with a diffusion coefficient of $D\sim g\bar{R}^{\,5}$. More accurate estimates (see Appendix 1) give

$$\tau^{-1}={}^{16}/_3\pi^{1/2}g\bar{R}^3,\quad l\approx 2.2\bar{R},\quad D\approx 7.6g\bar{R}^5. \quad (10)$$

Diffusion of carriers, both intrinsic and photo-induced, makes it possible for carrier pairs with mutual separations larger than some length R_{bl} to continue to separate with appreciable probability without undergoing recombination. If diffusion occurs by hopping with $l\gg R_0$ and with a characteristic time $\tilde{\tau}$, then R_{bl} is determined by

$$\tau(R_{bl})=\tilde{\tau} \quad (11)$$

or

$$R_{bl}={}^1/_2R_0\ln(\tilde{\tau}/\tau_0).. \quad (12)$$

In the case of photo-induced diffusion, $\tilde{\tau}=\tau/2$, where τ is defined according to (10), since in this case both the hopping lengths and hopping times of electrons are the same. The meaning of estimate (11) can be interpreted as follows: if a pair succeeds in making one hop before recombination, thereby increasing R to l, then by virtue of the exponential dependence (*l*) the time for tunnelling recombination $\tau(R)$ must rise rapidly, and the carriers are able to separate further. From here one, we will assume that in our discussion of the diffusive regime the following inequality holds:

$$l<R_{bl}. \quad (13)$$

Let us introduce the probability $p_{\rm out}(R)$ that an electron-hole pair created with a separation R can migrate to infinity. Then the number of pairs broken by diffusion per unit time can be written in the form

$$g_{out}=g\int_0^\infty P_0(R)\,p_{out}(R)\,dR. \quad (14)$$

Electrons and holes from broken pairs form a rarefied gas of randomly-moving particles. A steady-state concentration of gas is established by virtue of the random encounters of the carriers around R_{bl}, which thus plays the role of the radius of a Smoluchowskii "black sphere."[11] In order to determine the concentration $N(g)$, we must set $g_{\rm out}$ equal to the number of such encounters per unit time:

$$g_{out}=4\pi R_{bl}\tilde{D}N^2, \quad (15)$$

where $\tilde{D}$ is the total diffusion coefficient for electrons and holes; in the case of photo-induced diffusion, $\tilde{D}=2D$, where the coefficient D is defined according to (10). Relation (15) is the basic equation for the diffusive regime; from it we find that

$$N(g)=(g_{out}/4\pi R_{bl}\tilde{D})^{1/2}. \quad (16)$$

Hence, the problem reduces to finding the function $p_{\rm out}(R)$. Solving the diffusion equation, we can easily show that for $R-R_{bl}\gg 1$,

$$p_{out}(R)=1-R_{bl}/R. \tag{17}$$

For $R<R_{bl}$, the probability $p_{\text{out}}(R)$ of breaking a pair is extremely small, whereas at the boundary of a sphere of radius R_{bl} when the inequality (13) holds this probability equals

$$p_{out}(R_{bl})=\alpha l/R_{bl}, \tag{18}$$

where the numerical coefficient satisfies $\alpha\approx 0.4$ (See Appendix 2).

In the low-intensity regions of optical excitation, i.e., those for which $R_{bl}>\tilde{R}=\bar{R}^2/R_0$, we can bound g_{out} from below; note that these intensities are less relevant from an experimental point of view. To make this estimate we need to substitute for $p_{\text{out}}(R)$ the function (17) for $R>R_{bl}$ and zero for $R<R_{bl}$, thereby increasing the value of R_{bl} compared to (12) by R_0. In the region of moderate intensities, for which $\tilde{R}>R_{bl}>1$, we can set $p_{\text{out}}(R)=0$ in (14) for $R<R_{bl}$, and in integrating over the region $R>R_{bl}$ the function $p_{\text{out}}(R)$ can be replaced by its value at $R=R_{bl}$. As a result of this we obtain for $R_{bl}>\tilde{R}$

$$g_{out}>\frac{1}{\pi^{1/2}}\frac{e^{-y^2}}{y}g, \tag{19}$$

$$N(g)>\left(\frac{g}{4\pi^{3/2}\bar{R}\tilde{D}}\right)^{1/2}\frac{e^{-y^2/2}}{y}, \tag{20}$$

and for $\tilde{R}>R_{bl}>1$

$$g_{out}=\frac{2}{\pi^{1/2}}xe^{-x^2}p_{out}(R_{bl})g, \tag{21}$$

$$N(g)=\left(\frac{\alpha g}{2\pi^{3/2}\bar{R}\tilde{D}}\frac{l}{\bar{R}}\right)^{1/2}\frac{e^{-x^2/2}}{x^{1/2}}, \tag{22}$$

where $x=R_{bl}/\bar{R}$, $y=(R_{bl}+R_0)/\bar{R}$.

Let us compare (20) with expression (4) for the concentration N in the geminate recombination regime, which can be recast in the form

$$N(g)=\frac{3}{8\pi^{1/2}}\frac{1}{\bar{R}R_0^2}\exp\left[\left(\frac{\bar{R}}{R_0}\right)^2-2\frac{\bar{R}}{R_0}x\right]. \tag{23}$$

Let us neglect intrinsic diffusion here and set $\tilde{D}=2D$, so that the ratio $g/\tilde{D}$ does not depend on the generation rate g [see (10)]. The exponents in (20) and (23) are comparable for $x\approx(2+2^{1/2})(\bar{R}/R_0)$. Estimates show that for $\bar{R}\geqslant 50$ Å, $\bar{R}/R_0\geqslant 4$, $\tau_0=10^{-8}$ sec, the values of (23) exceed those of (20) even at $g>1$ cm^{-3}sec^{-1}. From this it follows that in fact there is no steady-state geminate recombination region.

Hence, in the region $N<\bar{R}^{-3}$ we are in the diffusion regime. If the diffusion is intrinsic, i.e., if $\tilde{D}$ and R_{bl} do not depend on g, then it follows from (22) that $N(g)\propto g^{1/2}$. In the case of photo-induced diffusion

$$N(g)=\frac{C}{4\pi\bar{R}^3}\frac{e^{-x^2/2}}{x^{1/2}}, \tag{24}$$

where the numerical coefficient $C\approx 0.9$. As g increases up to the value where $x=R_{bl}/\bar{R}\sim l$, we obtain from (1) $N\sim(4\pi\bar{R}^3/e^{1/2})^{-1}$, i.e., it joins with the solution (6). According to (24)

$$\beta=\frac{d\ln N}{d\ln g}=\frac{R_0}{2\bar{R}}\left(x+\frac{1}{2x}\right). \tag{25}$$

Specifically, for $\bar{R}/R_0=5$, $x\sim 1$ we obtain $\beta\sim 0.15$.

Up until now we have discussed steady-state conditions. We now show that some properties of the stationary state can be investigated via nonstationary methods. Let us discuss two such methods: the first one consists of varying the generation rate g over a characteristic time which exceeds the elementary time $\tilde{\tau}$. In this case, in place of equation (15) we obtain for the concentration $N(t)$ the equation.

$$dN(t)/dt=g_{out}(t)-4\pi\tilde{D}R_{bl}N^2(t). \tag{26}$$

Let $g=g_0+\delta g(t)$, where $|\delta g(t)|\ll g_0$. Then in linear approximation for δg we obtain the following equation for the fluctuating component $\delta N(t)=N(t)-N_0$:

$$\left(\frac{d}{dt}+\frac{1}{\tau_\sim}\right)\delta N(t)=\frac{R_{bl}R_0}{\bar{R}^2}g_{out}(g_0)\frac{\delta g(t)}{g_0} \tag{27}$$

with characteristic time

$$\tau_\sim=(8\pi R_{bl}\tilde{D}N_0)^{-1}, \tag{28}$$

where $N_0=N(g_0)$ is determined by Eq. (24).

A second method, used, e.g., in Ref. 4, consists of measuring the time-dependent kinetics of $N(t)$ after the light is fully extinguished. Taking into account the pairwise character of tunnelling recombination, we obtain at $t=0$ the following decay time for $N(t)$:

$$\frac{1}{\tau_{off}}\equiv\left(\frac{1}{N}\frac{dN}{dt}\right)_{t=0}=\frac{g}{N(g)}. \tag{29}$$

If the basic contribution to $N(g)$ comes from isolated photocarriers, then the quantity dN/dt at $t=0$, as well as the photoluminescence intensity, is determined by the contribution from geminate pairs. The rapid deexcitation of the latter, along with pairs with separation $R<R_{bl}$ which form as a result of random encounters of isolated photocarriers, does not give rise to a noticeable change in N. Therefore it is of interest to investigate the kinetics of $N(t)$ for $t\gtrsim\tau(R_{bl})=\tilde{\tau}$, during which pairs with separation $R\gtrsim R_{bl}$ begin to recombine and $N(t)$ begins to change appreciably.

Let us introduce the function $\mathcal{N}(R)$, such that the value of $\mathcal{N}(R)dR$ determines the concentation of pairs which recombine with separations in the range $(R,R+dR)$. By using the function $\mathcal{N}(R)$ we can write the time-dependent kinetics of $N(t)$ for $t\gg\tilde{\tau}$ in the form

$$N(t)=\int_{R_{bl}}^{\infty}dR\,\mathcal{N}(R)\exp[-t/\tau(R)]\approx\int_{R_t}^{\infty}dR\,\mathcal{N}(R) \tag{30}$$

or

$$\frac{N(t)}{N_0}\approx 1-\frac{\mathcal{N}(R_{bl})R_0}{2N_0}\ln\frac{t}{\tilde{\tau}}, \tag{31}$$

where $R_t=(R_0/2)\ln(t/\tau_0)$, $N_0\equiv N(t=0)=N(g)$. Let us note that for the conditions under which (31) was derived, the second term on the right side of this approximate equation is small compared to unity. The quantity $\mathcal{N}(R_{bl})$ coincides with the value of the density distribution of electron-hole pairs with $R=R_{bl}$ under steady-state conditions preceding the switching off of the illumination. In calculating $\mathcal{N}(R_{bl})$ it is necessary to include not only the contribution of isolated photocarriers which encounter each other due to diffusion, but also the contribution of pairs generated with separation $R\approx R_{bl}$ which do not suceed in separating any further.

To conclude our discussion of the nonsteady conditions, let us note that the time it takes to establish a stationary regime when the illumination is suddenly switched off is determined the time $\tau_\sim$.

Let us briefly consider the problem of spin effects. When spin is included, a localized electron-hole pair can exist in four different states. In the case when the spin relaxation times of electrons and holes are comparable to or exceed the characteristic lifetime, spin effects related to the appearance of spatial correlations between electrons and holes are possible.[10] If, however, only one of the spin relaxation times is smaller than the elementary hopping time $\tilde{\tau}$ (in α-Si:H, the spin relaxation time for holes is the small one[11]), then spin effects in undoped amorphous material are unimportant, and the results of this section hold.

In Table I we present a comparison of theoretical results with the experimental data from Ref. 4. The values of g and $N_{\rm exp}$ were obtained by taking the values of the optical power and number of photoinduced spins in α-Si:H presented in Table I of Ref. 4 and dividing them by the effective volume of the illuminated region, i.e., 5×10^{-4} cm^{-3}. In calculating g we also took into account the reflection of light at the sample boundary, assuming a reflection coefficient of 50% (see Ref. 4). The values of $N_{\rm theor}$, $\tau_{\rm off}$ and $\tilde{\tau}$ were coupled using Eqs. (24), (29) and $\tilde{\tau}=\tau/2$, where the time τ was determined from (10). In the calculation we used the following parameter values: $\bar{R}=60$ Å, $R_0=12$ Å, $\tau_0=0.5\cdot10^{-8}$ sec. As is clear from Table I, we were able to get good agreement between the theoretical and experimental values of $N(g)$. This agreement is further reflected in the fact that the value of $\beta=d\,\ln N/d\,\ln g\approx0.2$ observed in experiment is close to the theoretical value $\beta\approx0.15$ obtained from (25) within the region of interest $x\gtrsim1$. We note that while the experimental value $\beta\approx0.2$ can be explained within the framework of photo-induced diffusion presented here, it disagrees completely with the dependence $N(g)\propto g^{1/2}$ obtained from (22) for the case of intrinsic diffusion.

The minimum value $\tau_{\rm min}$ was found in Ref. 4 by using a fit to the empirical formula $N(t)/N_0=A-B\,\lg t$, which coincides with (31), starting from the definition $A-B\,\lg\tau_{\rm min}=1$. According to (31), the time $\tau_{\rm min}$ must be compared with the time $\tilde{\tau}$. It is clear that these times do not differ by more than a factor of 2.

It must be emphasized that the basic theoretical formula (24) was derived under the assumption that $1<R_{bl}$, while the values of g given in the Table correspond to the case $R_{bl}\sim1$, which generally speaking requires a separate quantitative analysis. Nevertheless, we may expect that (24) admits extrapolarion to the case $R_{bl}\sim1$. Because the inequality $4N R^3_{bl}\ll1$ holds for all four values of g, we can infer that the experimental situation described in Ref. 4 is in fact one where the diffusion regime obtains (although the system is also not far from the transition to the interpair regime).

4. INTERPAIR RECOMBINATION REGIME

The diffusion regime described in the previous section determines the function $N(g)$ for a wide range of values of g in the region $N<\bar{R}^{-3}$. As is clear from (10), (12) and (24), N becomes of order $\bar{R}^{-3}$ for $g\tau(\bar{R})\bar{R}^3\sim1$. As g is increased further, the mean spacing between geminate electrons and holes $\bar{R}$ eventually exceeds the mean distance between neighboring photocarriers of either kind, i.e., $N^{-1/3}$. In this case, the function $N(g)$ is determined by the interpair recombination regime. The steady-state concentration N in this regime satisfies equation (6) to exponential accuracy. As an estimate, we can use the solution to this equation in the form

$$N\approx\left(\frac{2b}{R_0}\right)^3\left(\ln\frac{8b^3}{g\tau_0R_0^3}\right)^{-3}. \qquad (32)$$

Below we will determine the numerical constant b which relates R_N and $N^{-1/3}$. The value of b we find attests to nontrivial correlations in the spacings between electrons and holes in steady state.

The physical meaning of the quantity R_N is that there are practically no electron-hole pairs with spacings $R<R_N$ by virtue of the exponential dependence of the function $\tau(R)$ in the stationary state. In other words, the distribution function versus distance R of neighboring carriers of one sort relative to carriers of the other sort is sharply cut off on the small-R side at $R=R_N$; this dropoff occurs at a distance of order R_0. On the large-R side, for $R>R_N$ this function also falls off, although much more slowly, with a characteristic scale on the order of $N^{-1/3}$.

It is not possible to determine the distribution function analytically for all ranges of R or to calculate analytically the constant b. Therefore, in order to determine b we have undertaken to model the process of interpair recombination numerically, using the Monte-Carlo method. The modelling algorithm consists of the following: in a unit cube, particles of two kinds—"electrons" and "holes"—are "tossed in" one by one. The process of "tossing in," i.e., injection, of particles is implemented by generating three cartesian coordinates of a particle on the interval (0,1) using a random number generator. After being injected each particle undergoes a "survival check" as follows; whenever an electron (hole) is injected, the system is checked to see if it already has a hole (electron) at a distance $R<\mathcal{R}$ from the injected particle, where $\mathcal{R}$ is some previously-defined number. If such particles are present, then the one closest to the injected particle is chosen and its coordinates are erased from the computer memory while the coordinates of the injected particle are not stored in the computer memory. Hence, an injected particle of one kind "recombines" with a neighboring particle of the other kind, if it lies at a distance $R<\mathcal{R}$. If, however, there are no particle of the other kind in a sphere of radius $\mathcal{R}$ around the injected particle, then its coordinates are stored

TABLE I. A comparison of the theoretical results with experimental results[4] in α-Si:H.

g, sec^{-1} cm^{-3}	$N_{\rm exp}$, cm^{-3}	$N_{\rm theor}$, cm^{-3}	$\tau_{\rm off}$, sec	$\tilde{\tau}$, sec (theory)	$\tau_{\rm min}$, sec (exp)
$2.3\cdot10^{17}$	$3.6\cdot10^{16}$	$3.8\cdot10^{16}$	0.16	1.1	2
$1.3\cdot10^{18}$	$4.8\cdot10^{16}$	$5.5\cdot10^{16}$	0.04	0.2	0.4
$1.6\cdot10^{19}$	$8.2\cdot10^{16}$	$8.9\cdot10^{16}$	0.005	0.015	0.03
$9.8\cdot10^{19}$	$1.1\cdot10^{17}$	$1.2\cdot10^{17}$	0.001	0.0025	0.004

in the computer memory. Let us note that the quantity $\mathscr{R}$ introduced into the model corresponds to the physical quantity R_N in (6).

We studied the dependence of the steady-state concentration of particles of one kind of N on $\mathscr{R}$. In the simulation, the value of N rapidly attains its steady-state value. In Figure 1 we show the dependence of N on the number of injected particles M (which plays the role of time) for $\mathscr{R} = 0.08$ and 0.1. It is clear that a steady state is attained after injecting - 4000 particles; as $\mathscr{R}$ increases, this state is reached more rapidly. In the simulation, the values $\mathscr{R} = 0.1$; 0.09; 0.08, 0.07 were chosen. In all cases, the number of injected particles was no more than 10^4. For each $\mathscr{R}$, the values of N was averaged over the states of the system with $M \geqslant 8 \times 10^3$, and they were found to satisfy the relation $N = \mu/\mathscr{R}^3$, where $\mu \equiv b^3 \approx 0.25$.

For comparison with the computer model, we also solved a simpler problem, in which the particles that were injected into the system and recombined among themselves were all of one kind. In this case, it was found that the stationary concentration satisfies the relation $N = \nu/\mathscr{R}^3$ with $\nu \approx 0.17$. This result can be interpreted in an approximately analytic way: in the stationary state, the probability that an injected particle will not recombine immediately after injection equals 1/2, On the other hand, this probability coincides with the probability that there are no particles within an arbitrarily chosen sphere of radius $\mathscr{R}$. If we assume that the particles of the system are located randomly in space, then it is easy to estimate this probability by using a Poisson distribution. As a result, we obtain

$$\exp(-{}^4/_3\pi N\mathscr{R}^3)={}^1/_2, \tag{33}$$

from which it follows that

$$N=\frac{3\ln 2}{4\pi\mathscr{R}^3}\approx\frac{0.17}{\mathscr{R}^3}$$

in agreement with the computer simulation.

A comparison of the numerical values of the coefficients μ and ν shows that in the case of recombination of two kinds of particles, the steady-state particle concentration of each kind is approximately 1.5 times larger than the concentration for a single type of particle. This attests to the presence of correlations in the positions of the particles, i.e., spatial clustering of particles of each kind individually.

We also studied two- and one-dimensional systems with this kind of modelling. In these systems the clustering was still more marked. Thus, in the two-dimensional system $\mu/\nu \approx 3$, and for one dimension $\mu/\nu \approx 6$.

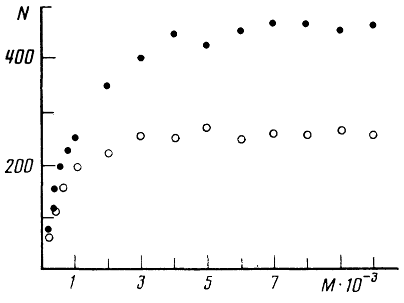

FIG. 1. Dependence of the concentration of one kind of particle on the number M of injected particles for $\mathscr{R} = 0.1$ (O) and $\mathscr{R} = 0.8$ (●).

5. CONCLUSION

In this paper, the dependence of the steady-state concentration of localized photocarriers on the intensity of excitation light was calculated neglecting nonradiative recombination. However, it is clear that the discussion given here of the diffusion regime admits a simple generalization taking nonradiative recombination into account. In order to determine the values of such parameters as $\bar{R}$, R_0 and τ_0 more precisely, in comparing theory with experiment it is necessary to analyze the experimental conditions carefully so as to clarify the photoluminescent quantum yield. It would be interesting to generalize the theory developed here by taking into account dispersion in the localization radius R_0, possible spin effects, Coulomb interactions between photocarriers, and also a more detailed analysis of the nonstationary problem under conditions of long-term stationary preillumination or periodic strongly-modulated illumination.

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APPENDIX 1

In a homogeneous isotropic material, the probability density per unit time of an effective hop from point **r** to point **r**′ by a localized carrier depends only on the distance between these points: $w_{\mathbf{r}',\mathbf{r}} = w(|\mathbf{r}' - \mathbf{r}|)$. Invoking the mechanism described in Section 3 for photo-induced diffusion, we have

$$4\pi R^2 w(R)=4\pi R^2 g\int_{R/2}^{\infty} P_0(R')\,\frac{1}{2}\left(1-\frac{R}{2R'}\right)dR'. \tag{A1.1}$$

Here, $R = |\mathbf{r} - \mathbf{r}'|$; R' is the electron-hole distance for a pair created in the vicinity of an isolated carrier located at the point **r**; the function $(2R' - R)/4R'$ in the integrand gives the probability that a hole belonging to a pair with separation R' is located at a distance less than R' from point

Here, $R = |\mathbf{r} - \mathbf{r}'|$; R' is the electron-hole distance for a pair created in the vicinity of an isolated carrier located at the point **r**; the function $(2R' - R)/4R'$ in the integrand gives the probability that a hole belonging to a pair with separation R' is located at a distance less than R' from point
r. For a Gaussian distribution [see (2)] we obtain

$$w(R)={}^1/_2 g[1-\Phi(R/2\bar{R})], \tag{A1.2}$$

where $\Phi(x)$ is the error function.

The time τ for an elementary hop, the elementary length l for an effective hop and the diffusion constant D are determined from the equations

$$\frac{1}{\tau}=\int_0^\infty w(R)\,4\pi R^2\,dR, \tag{A1.3}$$

$$l^2=\tau\int_0^\infty w(R)\,4\pi R^4\,dR, \tag{A1.4}$$

$$D={}^1/_6 l^2/\tau. \tag{A1.5}$$

Substituting (A1.2) into the integrands of (A1.3) and (A1.4) and performing the integrations over R, we obtain the estimates for τ^{-1}, l and D presented in (10).

APPENDIX 2

Since $R_0 \ll l$, the diffusion approximation cannot be used to calculate the probability $p_{\text{out}}(R)$ of breaking a pair for $R \approx R_{bl}$, and we must solve the kinetic equation

$$\int d\mathbf{r}'[\tilde{w}_{\mathbf{r}',\mathbf{r}}\rho(\mathbf{r}) - \tilde{w}_{\mathbf{r},\mathbf{r}'}\rho(\mathbf{r}')] + \frac{1}{\tau(r)}\rho(\mathbf{r}) = \frac{g}{4\pi R^2}\delta(r-R), \tag{A2.1}$$

where $\mathbf{r}$, $\mathbf{r}'$ are the positions of an electron in a pair relative to the hole, $\tilde{w}_{\mathbf{r}',\mathbf{r}}$ is the probability density for a transition $\mathbf{r} \to \mathbf{r}'$ (here both the hole and the electron can shift), $\rho(\mathbf{r})$ is the probability of finding an electron in the vicinity of the point $\mathbf{r}$; the function satisfies the boundary condition $\rho(\mathbf{r}) \to 0$ as $\mathbf{r} \to \infty$. The pair-breaking probability is related to $\rho(\mathbf{r})$ by the equation

$$p_{out}(R) = \frac{4\pi\tilde{D}}{g}\lim_{r\to\infty}\left(r^2\frac{\partial\rho}{\partial r}\right). \tag{A2.2}$$

Let us write $\rho(\mathbf{r})$ in the form

$$\rho(\mathbf{r}) = \frac{gT(R)}{4\pi R^2}\delta(r-R) + \frac{B}{r}\theta(r-R_{bl}) + \mathscr{P}(\mathbf{r}), \tag{A2.3}$$

where B is a coefficient independent of $\mathbf{r}$ and the function $\mathscr{P}(\mathbf{r})$ satisfies the condition $\mathbf{r}\mathscr{P}(\mathbf{r}) \to 0$ as $r \to \infty$. Substituting (A2.3) into (A2.1), we obtain an equation for the function $\mathscr{P}(\mathbf{r})$:

$$\mathscr{P}(\mathbf{r}) = T(r)\int d\mathbf{r}'\,\tilde{w}_{\mathbf{r},\mathbf{r}'}\mathscr{P}(\mathbf{r}') + f(r,R), \tag{A2.4}$$

where $T^{-1}(r) = \tilde{\tau}^{-1} + \tau^{-1}(r)$ and the inhomogeneous term f includes two components, proportional to $gT(R)$ and B respectively. The coefficient B in (A2.3) is found from the condition of conservation of particle number

$$J_{in}(R_{bl}) + 4\pi B\tilde{D} = g, \tag{A2.5}$$

where $J_{\text{in}}(R_{bl})$ is the particle current through a sphere of radius R_{bl} from outside to inside (the current through this sphere from inside to outside can be neglected for $R_0 \ll l$). The particles which contribute to $J_{\text{in}}(R_{bl})$ are those with separations $R_{bl} < R < R_{bl} + 1$. Equation (A2.4) can be solved by the method of successive approximations. It is especially easy to perform this calculation in the simplest case, when $\tilde{w}_{\mathbf{r}',\mathbf{r}} \propto \delta(|\mathbf{r}' - \mathbf{r}|^2 - l^2)$ holds. In this case, the coefficient α in (18) is found with high accuracy to equal the value 0.4. A close value is also obtained for the function $\tilde{w}_{\mathbf{r}',\mathbf{r}} = 2w|\mathbf{r}' - \mathbf{r}|)$, where the function $w(R)$ is defined in (A1.2).

(1) We note that for $R_0 \ll R_{bl}$, the definition of R_{bl} in (12) differs insignificantly from the black-sphere radius $R_{bl} = (R_0/2)\ln[(\gamma/2)^2 R_0^2/\tau_0\tilde{D}]$, introduced within the diffusion approximation picture ($\gamma = \exp[-\Gamma(1)]$, see Ref. 9).

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