Nonradiative recombination in noncrystalline semiconductors

S. D. Baranovskiĭ, V. G. Karpov, and B. I. Shklovskiĭ

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad

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A theory of nonradiative recombination of carriers is developed for the case of a quasicontinuous spectrum of localized states in the mobility gap of a noncrystalline semiconductor. The recombination rate is calculated as a function of the density of free carriers and of the temperature of the system. A study is made of the influence of the polaron effects on the recombination process. The results obtained account for the lux-ampere characteristics of amorphous semiconductors.

1. INTRODUCTION

It has been established experimentally[1-3] that the recombination of carriers in noncrystalline semiconductors is governed mainly by nonradiative processes. However, the mechanisms of these processes are still unclear. Standard concepts of the physics of crystalline semiconductors[4] relate the processes of nonradiative recombination to the emission of phonons the total energy of which is equal to the width of the band gap. The probability of this process decreases on increase in the number of the emitted phonons. Therefore, recombination is facilitated by the presence of deep impurity states (recombination centers), because this makes it possible to reduce the number of phonons emitted in one event. Consequently, the rate of recombination is governed by the nature and concentration of recombination centers in a crystal.

In the case of noncrystalline materials the role of the band gap is played by the mobility gap inside of which there is a quasicontinuous spectrum of levels associated with localized states. In this situation it is meaningless to speak of recombination centers having definite energy levels in the band gap.

We shall consider nonradiative recombination processes in the case of a quasicontinuous spectrum of localized states on the assumption that these states are due to a random spatial distribution of short-range centers, each of which can carry one electron. The main idea used in the present treatment was put forward in Ref. 5 and it postulates that the effective recombination channels are loose clusters of centers forming energy ladders with fairly small steps (Fig. 1). Such ladders facilitate greatly the processes of emission of phonons with the total energy equal to the mobility gap. Since the transitions between the levels are of the multiphonon nature, their probabilities increase on reduction in the height of the steps, i.e., on increase in the number of levels forming the ladder in question. On the other hand, the probability of formation of clusters of spatially close centers decreases rapidly on increase in their number. Therefore, there is an optimum in respect of the number of centers and the characteristic intercenter distance. Such optimal compact configurations are responsible for the recombination in noncrystalline materials. This idea was applied in Ref. 5 to surface recombination. We shall consider the more likely case of volume recombination in noncrystalline semiconductors. Moreover, in contrast to Ref. 5, we shall investigate the temperature dependence of the recombination rate and allow for the role played by the polaron effects. This variant of the theory is readily applied to the case of surface recombination.

We shall be interested in the dependence of the number of electron-hole pairs R recombining per unit time and per unit volume on their concentration n and on the temperature of the system T. With its aid we can find, for example, the steady-state nonequilibrium density as a function of the illumination intensity I. It is found that at low temperatures and in good agreement with the experimental results, this density is

$$n=n_0(I/I_0)^{\beta}, \quad \beta=\varepsilon_0/(\varepsilon_0+T), \tag{1}$$

where ε_0 is of the order of the characteristic phonon energy.

The present paper is organized as follows. In Sec. 2 we shall give the essential results from the theory of multiphonon transitions. In Sec. 3 we shall discuss recombination at zero temperature in a material characterized by a small polaron shift. In Sec. 4 we shall consider the case of finite temperatures. Recombination in the case of large polaron shifts will be considered in Sec. 5. Finally, a discussion of the results and a comparison with the available experimental data will be given in Sec. 6.

2. PROBABILITIES OF MULTIPHONON TRANSITIONS

We shall show below that the difference between adjacent energy levels forming a recombination ladder is many times greater than the characteristic phonon energy $\hbar\omega$. In this case each electron transition emits several phonons. A theoretical analysis of multiphonon transitions can be found in Refs. 6–8. We shall be interested mainly in the exponential dependence of the probabilities of transitions on the total energy ε of the emitted phonons, i.e., on the difference

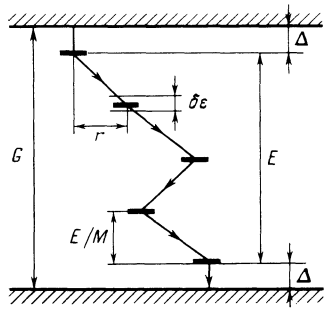

FIG. 1. Recombination channel consisting of a ladder of levels of height E with a number of steps $M = 4$ and with input and output of heights Δ.

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between those energy levels between which an electron transition takes place. We shall give these dependences without derivation.

The time for an electron transition from one localized state to another, located $\varepsilon \gg \hbar\omega$ lower on the energy scale, is given by the following expression valid at low temperatures[6-8]

$$\tau=\nu_0^{-1}\exp(2W/\hbar\omega-\gamma\varepsilon/\hbar\omega+2r/a),\quad \gamma=1-\ln(\varepsilon/2W), \tag{2}$$

where r is the distance between the centers; a is the localization radius of an electron at a center; ν_0 is the preexponential factor; W is the polaron shift, i.e., the gain in the total energy of the system due to relaxation of the atomic subsystem as a result of the appearance of an electron in the spectrum. It follows from Eq. (2) that if $\varepsilon > 2W$ the time for an electron jump between the centers rises exponentially on increase in ε:

$$\tau=\nu^{-1}\exp(\varepsilon/\varepsilon_0+2r/a),\quad \varepsilon_0=\hbar\omega/[\ln(\varepsilon/2W)-1]. \tag{3}$$

In the subsequent calculations we shall ignore the dependences of ε_0 on ε and assume that ε_0 is constant. In numerical estimates of the energies we shall use the value $\varepsilon_0 = 0.02$ eV, which is slightly less than the energy of the Debye phonons in amorphous semiconductors.[1] If $\varepsilon < 2W$, the transition time decreases exponentially on increase in ε. We can easily show that if $|\varepsilon - 2W| \ll 2W$, the transition time τ depends on ε in accordance with the law

$$\tau=\nu_0^{-1}\exp[(\varepsilon-2W)^2/2W\hbar\omega+2r/a] \tag{4}$$

and at a point $\varepsilon = 2W$ it has a minimum.

This applies to electron transitions between localized states. If one of the two states between which a transition takes is place is delocalized, the transition time is given by the expression

$$\tau=\nu^{-1}\exp(\varepsilon/\varepsilon_0) \tag{5}$$

irrespective of the relationship between ε and $2W$.

We are interested only in the exponential dependences of τ on ε and we shall not give explicit expressions for the preexponential factors ν_0 and ν. Both are of the same order of magnitude as the Debye frequency ω and the relationship between ν and ν_0 is readily established from Eqs. (2) and (3).

The present paper deals only with the case of low temperatures when $T \ll \hbar\omega$. In this case the probability of a downward transition on the energy scale is independent of temperature. The temperature dependences of the various quantities obtained later are not related to the temperature dependence of τ, but are due to other factors.

Finally, we note that the time τ' for an electron transition increasing the energy by ε is related to the energy transition time τ downward on the energy scale to the usual expression

$$\tau'=\tau\exp(\varepsilon/T). \tag{6}$$

3. RECOMBINATION IN MATERIALS WITH A SMALL POLARON SHIFT AT ZERO TEMPERATURE

We shall develop a theory of recombination when $T = 0$ on condition that the polaron shift W is small compared with the energy transferred by a phonon in one electron transition between the centers.

We shall discuss a set of parallel recombination channels, each of which represents a ladder of levels created by spatially close states. Such a channel is shown schematically in Fig. 1. It has $M + 2$ steps, the scatter of the step heights is $\delta\varepsilon$, and the typical jump length is r. It will be convenient to consider separately the first and last steps of the channel and to discuss at the same time a ladder of height $E = G - 2\Delta$, where G is the width of the mobility gap and Δ is the height of each of the outer steps in the channel. We shall call the first step of the channel the input and the last one the output.

Clearly, the maximum contribution to $R(n)$ is made by those channels for which the input and output frequencies τ^{-1} are equal to the reciprocal of the descent time τ_i^{-1} along a ladder of levels of height $E = G - 2\Delta$. This is because the time in which an electron-hole pair recombines in a channel is governed by the longest of these times. However, a reduction in the shortest of these times reduces the probability of a given configuration of the centers. The recombination flux is dominated by the channels with $\tau_i^{-1} \approx \tau^{-1}$, because the shorter time can always be increased readily and this increases the probability of a given configuration.

We shall consider the capture of electrons by the upper level of a ladder. We shall write down the time τ in which any particular carrier is captured by a given channel in the form

$$\tau=\frac{1}{n\sigma_c v}=\frac{1}{n\sigma v}\frac{\tau_c}{\tau_f}=\frac{\tau_c}{n\sigma^{3/2}}\equiv\frac{n_0}{n}\tau_c. \tag{7}$$

Here, σ_c is the capture cross section; v is the electron velocity; $\sigma \equiv n_0^{2/3}$ is the cross section of the region where an electron may be captured emitting phonons ($n_0 \approx 10^{18}$ cm^{-2}); τ_f is the transit time across this region; τ_c is the time for the capture of an electron in this region. It follows from Sec. 2 that

$$\tau_c=\nu^{-1}\exp(\Delta/\varepsilon_0). \tag{8}$$

We then have

$$\tau^{-1}=\nu\frac{n}{n_0}\exp\left(-\frac{G-E}{2\varepsilon_0}\right). \tag{9}$$

In turn the reciprocal time τ_i^{-1} for the descent of an electron along a ladder of levels of height E and with the number of steps M is, according to Eq. (3),

$$\tau_i^{-1}=\nu\exp(-E/M\varepsilon_0-\delta\varepsilon/\varepsilon_0-2r/a). \tag{10}$$

We shall assume that this time is governed by the slowest jump in the ladder. For this jump the initial center is usually filled and the final one is empty. Therefore, we shall ignore the factors associated with the occupancy numbers of the levels.

Equating τ^{-1} and τ_i^{-1}, we find that if $M \gg 1$ then

$$\Delta=G/M+\delta\varepsilon+2r\varepsilon_0/a-\varepsilon_0\ln(n_0/n). \tag{11}$$

We can determine $E = G - 2\Delta$ with the aid of Eq. (11) by substituting E in Eq. (10) and bearing in mind that $M \gg 1$, which gives the following expression for the reciprocal of the time for a carrier to pass along the channel:

$$\tau_i^{-1}=\nu\exp(-\tilde{G}/M\varepsilon_0-\delta\varepsilon/\varepsilon_0-2r/a), \tag{12}$$

where

$$\tilde{G}=G+2\varepsilon_0 \ln(n_0/n). \tag{13}$$

We shall write R in the form

$$R=\sum_i N_i\tau_i^{-1}, \tag{14}$$

where

$$N_i=r^{-3}(gr^3\delta\varepsilon)^{M+1} \tag{15}$$

is the number of channels of type i per unit volume and g is the density of states in the mobility gap, which we shall, for the time being, assume to be independent of energy. The quantity $N_i\tau_i^{-1}$ has a sharp maximum when considered as a function of M, r, or $\delta\varepsilon$ and this maximum occurs at

$$M_m=(\tilde{G}/L_0\varepsilon_0)^{1/2}, \quad \delta\varepsilon_m=\varepsilon_0 M_m, \quad r_m={}^3/_2 aM_m, \qquad L_0=\ln(8\varepsilon_0^{1/2}/27ga^3\tilde{G}^{1/2}). \tag{16}$$

This maximum appears because if $L_0 \gg 1$ (we shall assume that this inequality is satisfied) an increase in M reduces strongly the number N_i, but increases the frequency τ_i^{-1}. The optimal are the fairly rare but sufficiently "fast" channels with $\tau_i=\tau_m$, where

$$\tau_m^{-1}=\nu\exp(-\tilde{G}/M_m\varepsilon_0)=\nu\exp[-(\tilde{G}L_0/\varepsilon_0)^{1/2}]. \tag{17}$$

The argument of the exponential function in Eq. (17) is simplified by dropping the terms which are small in L_0^{-1} and which appear because of the last two terms in the argument of the exponential function in Eq. (10).

We can see from Eq. (16) that these channels are characterized by $\delta\varepsilon_m \ll E/M$, i.e., the levels in the optimal ladders are approximately equidistant on the energy scale. The reason is that the ladders in which some of the jumps have steps with a small height are much less probable than the ladders which are almost equidistant on the energy scale.

According to Eq. (16), the heights of M_m steps are distributed in a range $M_m\varepsilon_0$, so that the highest step differs by ε_0 from the one which is second on the height scale, i.e., the frequencies of the corresponding jumps differ approximately by the factor e. Therefore, in spite of the approximately equidistant distribution of the level, the hypothesis of the dominant role of the slowest jump is justified.

The substitution of Eq. (16) into Eqs. (14), (10), and (15) gives

$$R(n)\approx\frac{\nu}{a^3}\left(\frac{\varepsilon_0 L_0}{G}\right)^{3/2}\exp\left[-2\left(\frac{L_0}{\varepsilon_0}\right)^{1/2}\left(G+2\varepsilon_0\ln\frac{n_0}{n}\right)^{1/2}\right], \tag{18}$$

where—as in Ref. 17—the minor terms are dropped from the argument of the exponential function.

Equation (18) demonstrates the main advantage of the ladders: if $n=n_0$, instead of the factor $\exp(-G/\varepsilon_0)$, corresponding to the interband recombination process, the ladders give rise to the factor $\exp[-2(GL_0/\varepsilon_0)^{1/2}]$. If $G=1.5$ eV, $\varepsilon_0=0.02$, and $L_0=2$, the arguments of the first and second exponential functions are -75 and -24, respectively.

In the derivation of Eq. (18) it is assumed that g and a are independent of the energy ε ($\varepsilon=0$ applies in the middle of the mobility gap). We can readily show that even in the case of an exponential dependence $g(\varepsilon)$ the levels in a channel remain practically equidistant and the logarithm in Eq. (18) should be replaced by its average value

$$\frac{1}{G}\int_{-G/2}^{G/2} d\varepsilon \ln\frac{8\varepsilon_0^{1/2}}{27g(\varepsilon)a^3(\varepsilon)G^{3/2}}.$$

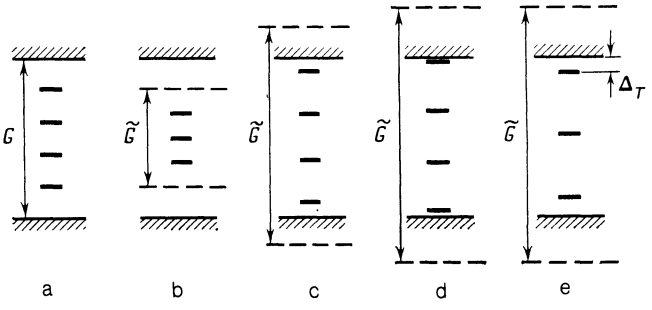

FIG. 2. Structure of the optimal recombination channels shown for different values of n and T: a) $T=0$, $n=n_0$; b) $T=0$, $n>n_0$; c) $T=0$, $n<n_0$; d) $T=0$, $n\lesssim n_c$; e) $0<T\ll\hbar\omega$, $n\lesssim n_c$.

We shall now interpret the results. It is clear from Eqs. (18) and (16) that if $n=n_0$, the whole channel (including the conduction and valence bands) forms an equidistant sequence of levels (Fig. 2a). If $n\neq n_0$, then the energies released at the input and output of the channel differ from the height of the ladder steps. The solution of Eq. (18) for this case can be represented in the following clear manner. The quantity $\tilde{G}$ defined in Eq. (13) will be called the renormalized width of the mobility gap. We can see that $\tilde{G}<G$ if $n>n_0$ (Fig. 2b), whereas $\tilde{G}>G$ in the more important case $n<n_0$ (Fig. 2c). The optimal channel divides the gap $\tilde{G}$ into a system of equidistant steps.

If $n>n_0$, the length of the ladder decreases on increase in n because of an increase in the heights Δ of the input and output. This occurs because in the expression (9) for the probability of input or output the smallness of $\tau_c^{-1}=\nu\exp(-\Delta/\varepsilon_0)$ is compensated by a large factor n/n_0. Then, in a wide range of n, when $\varepsilon_0|\ln(n_0/n)|\ll G$, it follows from Eqs. (18) and (16) that $R(n)\propto(n/n_0)^{2/M_m}$. In the limit of high n, when the factor n/n_0 is so large that the frequency of direct interband recombination is no longer small, such recombination becomes more effective. It is of bimolecular nature and the recombination flux is then proportional to n^2. (We must bear in mind that in the case of high densities the recombination mechanism described here may compete with the Auger recombination, which occurs either because of interband transitions or due to localized centers and ladders of such centers.)

In the much more likely case when $n\ll n_0$, a reduction in n reduces the height Δ of the input and output. Then, the highest (lowest) level of the ladder in the optimal channel approaches the bottom of the conduction band (top of the valence band) as shown in Fig. 2d. If $\Delta\lesssim\varepsilon_0$, the capture by the outer levels of the ladder ceases to be of multiphonon nature and its probability is practically independent of Δ. We then have $\tau_c\approx\nu^{-1}$ and $\tau\approx n_0\nu^{-1}/n$ [see Eqs. (8) and (9)]. This occurs at $n\approx n_c$, where n_c is given by the relationship

$$n_c=n_0\exp[-(GL_0/\varepsilon_0)^{1/2}]. \tag{19}$$

If $n < n_c$, Eq. (18) is no longer valid. We shall now consider this case in greater detail. The sum in Eq. (14) is still dominated by the channels with $\tau_i^{-1} \approx \tau^{-1}$. If $n < n_c$, these channels are characterized by $\tau_i^{-1} \approx \nu n/n_0$, i.e., according to Eq. (10) these are the channels characterized by

$$M = M_0(n) = \frac{G}{\varepsilon_0}\left(\ln\frac{n_0}{n}\right)^{-1}. \tag{20}$$

The channels with $M > M_0$ are faster, but not very effective because most of the time they remain empty. On the other hand, the channels with $M < M_0$ are usually occupied by carriers and are also ineffective in the recombination process. A calculation of the number of working channels gives

$$R(n) \approx \frac{\nu}{a^3 M_1^3}\left(\frac{27}{8} g a^3 \varepsilon_0 M_1^4\right)^{M_0+1} \frac{n}{n_0}, \qquad M_1 = \ln\left(\frac{n_0}{n}\right) \Big/ \ln\left(\frac{27}{8} g a^3 \varepsilon_0 M_1^4\right). \tag{21}$$

Therefore, if $n \ll n_c$ the recombination flux $R(n)$ rises sublinearly on increase in n. A reduction in n increases the width of the renormalized mobility gap $\tilde{G}$. As $\tilde{G}$ approaches $3G$ from below, the recombination channel becomes a pair of levels one of which is close to the conduction band and the other near the valence band. We can easily show that under steady-state conditions the probability of occupancy of the lower level of the pair by a hole (or of the upper level by an electron) is not low: it amounts to 2/3. The recombination via such pairs, the rate of which is proportional to the product of the concentration of pairs of levels N and the density n of carriers of one kind, will be more effective in the case when $n < N$ than the direct interband recombination of electrons and holes which are in delocalized states, the rate of which is proportional to n^2. Therefore, in the limit of low values of n the recombination flux $R(n)$ is a linear function of n.

We shall now consider the dependence of the logarithmic derivative $\alpha = d(\ln)r/d(\ln)n$ on n. As pointed out already, in the range $n \gg n_c$, it follows from Eqs. (18) and (16) that $\alpha = 2/M_m$.[1)] If $n \ll n_c$, ignoring the dependences of L_0 on n in Eq. (16), we find from Eqs. (21) and (20) that

$$\alpha = 1 - L_0 G \varepsilon_0^{-1} [\ln(n/n_0)]^{-2}. \tag{22}$$

Using Eq. (22) we can readily show that the value of n corresponding to $\alpha = 1/2$ is $n_0(n_c/n_0)^{\sqrt{2}}$, where n_c is given by Eq. (19) and the width of the range of values of $\ln(n/n_0)$ near $\ln(n_c/n_0)$ where M_0 becomes smaller than M_m by 2 is of the order of L_0. The general nature of the dependence of α on $\ln(n/n_0)$ is demonstrated in Fig. 3.

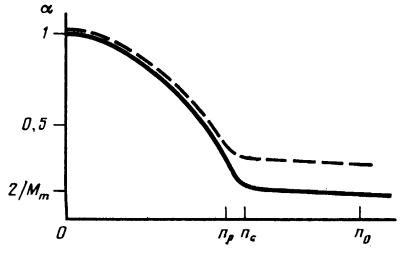

FIG. 3. Dependence $\alpha = d[\ln R(n)]/d[\ln(n/n_0)]$ on $\ln(n/n_0)$: the continuous curve represents the results in the absence of a polaron effect and the dashed curve corresponds to $n_p < n_c$.

The analysis presented in this section is valid as long as the energy interval between the levels forming a recombination ladder is considerably greater than $2W$, i.e., if $\tilde{G} > 2WM_m$. On the other hand, if $\tilde{G} \lesssim 2WM_m$, the above expression (3) for the multiphonon intercenter transition time is no longer valid. Moreover, the validity of the discussion in the present section is limited from above on the temperature scale by the temperature independence of the probabilities of multiphonon transitions and by the condition of ineffectiveness of thermally activated rise of carriers between the steps in a recombination ladder. If $n \ll n_c$, the latter condition may be more stringent. It will be discussed in the next section.

4. RECOMBINATION IN MATERIALS WITH A SMALL POLARON SHIFT AT FINITE TEMPERATURES

In this section we shall consider only the case when $n \ll n_c$. Then, as shown in Sec. 3, the input and output heights are smaller than the heights of the intermediate steps of the ladder (Fig. 2c). Therefore, at sufficiently low temperatures we can ignore the possibility of a rise of an electron up the ladder and allow only for the probability of its thermal activation from the first step of the ladder (entry into the channel). The only channels effective in the recombination process are those for which the transit time up the ladder of levels τ_i, equal to the input time τ into the channel, does not exceed the thermal activation time of an electron from the first step τ_T, where

$$\tau_T = \nu^{-1} \exp(\Delta/\varepsilon_0 + \Delta/T). \tag{23}$$

The condition $\tau_T = \tau$ represents the demarcation energy

$$\Delta_T = T \ln(n_0/n), \tag{24}$$

such that a carrier captured from a band at a depth $\Delta > \Delta_T$ recombines after dropping down the energy ladder, whereas at a depth $\Delta < \Delta_T$ it is released thermally back to the band. Among the channels satisfying the condition τ, $\tau_i \leqslant \tau_T$, those most likely to appear are characterized by $\tau \approx \tau_i \approx \tau_T$, i.e., they are channels for which the times of the input, passage along the ladder, and thermal activation were from the first step identical. For these channels the upper level coincides with the demarcation energy and the step height is $(\varepsilon_0 + T)\ln(n_0/n)$ (Fig. 2e). The reciprocal of the transit time of a carrier along the optimal channel is

$$\tau_i^{-1} = \nu \exp[-(T/\varepsilon_0 + 1)\ln(n_0/n)] = \nu(n/n_0)^{1+T/\varepsilon_0}. \tag{25}$$

The recombination flux is proportional to the carrier transit frequency and to the concentration of the optimal channels. We shall show that the temperature dependence of the concentration of the active channels is much weaker than the dependence of τ_i^{-1} on T described by Eq. (25), so that

$$R(n) \propto I_0(n/n_0)^{1+T/\varepsilon_0}, \tag{26}$$

where I_0 denotes the factors in R which are characterized by relatively weak temperature dependences.

Using Eq. (10), we find from Eq. (28) that

$$\frac{\tilde{G} - 2T\ln(n_0/n)}{M\varepsilon_0} + \frac{\delta\varepsilon}{\varepsilon_0} + \frac{2r}{a} = \left(\frac{T}{\varepsilon_0} + 1\right)\ln\frac{n_0}{n} \equiv \xi, \tag{27}$$

which relates M to $\delta\varepsilon$, r, and parameters of the problem.

Having determined M from Eq. (27), we can substitute it in Eq. (15) and find the optimal values of $\delta\varepsilon$ and r, i.e., those values of $\delta\varepsilon$ and r that ensure the maximum concentration of the channels satisfying the condition (27), which leads to the following expression for the recombination flux:

$$R(n,T)=\frac{\nu}{\xi a^3}\left(\frac{2L+3}{3}\right)^3\exp\left[-\xi-\left(\frac{\tilde{G}}{\xi\varepsilon_0}-2\right)(L+4)\right], \tag{28}$$

$$L=\ln[(2L+8)^4/54ga^3\varepsilon_0\xi^4].$$

If $n\ll n_c$, then the argument of the exponential function in the first expression of the system (28) is dominated by the first term, i.e., the temperature dependence of the concentration of the active channels is unimportant, whereas the temperature dependence of the recombination flux is indeed described by Eq. (26).

5. RECOMBINATION IN MATERIALS WITH A LARGE POLARON SHIFT

The theory presented in Secs. 3 and 4 applies to the case when the height ε of the steps in the ladder of the optimal channel exceeds $2W$, which is twice the polaron shift. Only then can we use Eq. (3) for the time of a jump of a carrier between two centers. If the height of the steps in the ladder is less than $2W$, it then follows from Eq. (2) that the probability τ^{-1} of a jump increases on increase in ε. It means that the channels with smaller numbers of steps are "faster." Therefore, in the case of substances with a large polaron shift the process of recombination is governed by the energy ladders for which the height of the steps is of the order of $2W$. In the case of the input to a channel and output from it, in the corresponding electron transitions one of the participating states is delocalized, whereas the time constant of such transitions is still described by Eq. (5).

As in the preceding sections, we shall consider separately the first and last steps of the channel and discuss also a ladder of levels of height $E=G-2\Delta$, where Δ is the height of the input (output). Each ladder is characterized by a typical jump distance r of an electron and by a scatter of the heights of the steps $\delta\varepsilon$ near the value $\varepsilon=2W$. In the optimal recombination ladders the value of ϵ may be slightly larger than $2W$, because this reduces the number of steps and makes the channel more probable. We shall therefore write down the energy separation between the neighboring levels in a ladder in the form

$$\varepsilon=2W+\varepsilon'+\mu,\quad \mu\ll W,\quad |\varepsilon'|<\delta\varepsilon$$

(if $\mu\gtrsim W$, we are dealing with the case of small polaron shifts, which are discussed in Secs. 3 and 4). Then, the number of steps in a ladder is

$$M=E/(2W+\mu). \tag{29}$$

The time for a jump between the levels of a ladder is now given by Eq. (4), where $\varepsilon-2W=\mu\pm\varepsilon'$. Assuming, as before, that the time for the carrier to travel along a ladder is determined by the time of the most difficult jump, we find from Eq. (4) that the frequency of transit along the ladder τ_i^{-1} is given by

$$\tau_i^{-1}=\nu_0\exp[-(\mu+\delta\varepsilon)^2/2W\hbar\omega-2r/a]. \tag{30}$$

We shall find the maximum recombination flux which can be provided by a set of ladders of height E, i.e., we shall determine those values of $\mu=\mu_m$, $\delta\varepsilon=\delta\varepsilon_m$, $r=r_m$, which ensure the maximum value of the quantity

$$r^{-3}(gr^3\delta\varepsilon)^{M+1}\tau_i^{-1}, \tag{31}$$

where M and τ_i^{-1} are given by Eqs. (29) and (30). Assuming, as in the preceding sections, that $M\gg 1$ and $L\equiv\ln(gr_m^3\delta\varepsilon_m)^{-1}\gg 1$, we can easily show that

$$\delta\varepsilon_m=2W/L-E\hbar\omega/4W,\quad \mu_m=E\hbar\omega L/4W-2W/L,$$
$$r_m={}^3/_2a(E/2W)(1-\mu_m/2W). \tag{32}$$

These formulas give positive values of $\delta\varepsilon_m$ and μ_m if

$$L_1\equiv 2W(E\hbar\omega/2)^{-1/2}<L<8W^2/E\hbar\omega\equiv L_2.$$

By definition, the quantity $\delta\varepsilon$ cannot be negative. As far as μ is concerned, it can be formally negative, but if $\mu<0$, the time for the most difficult jump τ_i in a ladder is not given by Eq. (30), but by the formula

$$\tau_i^{-1}=\nu_0\exp[-(\mu-\delta\varepsilon)^2/2W\hbar\omega-2r/a]. \tag{33}$$

In the range $\mu\leqslant 0$ the maximum of Eq. (31) subject to Eqs. (29) and (33) is observed for

$$\mu_m=0,\quad \delta\varepsilon_m=(E\hbar\omega/2)^{1/2},\quad r_m={}^3/_2aE/2W. \tag{34}$$

As already pointed out in Sec. 3, the most effective recombination occurs in the channels for which the input (output) time τ is equal to the time τ_i taken to pass along a channel. The time τ is given by Eq. (5) and the time τ_i is described by Eqs. (30) and (32) if $L\geqslant L_1$ and by Eqs. (33) and (34) if $L\leqslant L_1$. Equating τ and τ_i, we find that in both cases when ε_0, $\hbar\omega\ll W$ the expression for τ_i^{-1} should be modified by replacing E with $\tilde{G}=G+2\varepsilon_0\ln(n_0'/n)$, where $n_0'=\nu_0 n_0/\nu$.

Substituting in Eqs. (29)–(31) the values of the parameters given by the expressions in Eq. (34) when $L\leqslant L_1$ and by those in Eq. (32) if $L\geqslant L_1$, and also replacing these expressions the quantity E with $\tilde{G}$, we find that the recombination flux is now described by

$$R(n)=\frac{\nu_0}{({}^3/_4a\tilde{G}/W)^3}\times\begin{cases}\exp\left[-\dfrac{\tilde{G}}{2W}\left(\dfrac{7}{2}+L\right)\right], & L<L_1\\ \exp\left[-\dfrac{\tilde{G}}{2W}\left(L+4-\dfrac{\tilde{G}\hbar\omega}{16W^2}L^2\right)\right], & L\geqslant L_1\end{cases} \tag{35}$$

As L approaches from below the value $L_2=8W^2/\tilde{G}\hbar\omega$, we find that μ approaches $2W$. Then, the formulas in the present section cease to be valid and we have to use the results of Sec. 3. It must be stressed that Eq. (35) is meaningful only if $(\tilde{G}\hbar\omega)^{1/2}\ll W$. In the case of the opposite inequality, we always have the case of small polaron shifts.

We shall now establish the relationship between the results obtained in the present section and those deduced in Sec. 3. In the range of small values of $n<n_c$, where n_c is given by Eq. (19), the height of a step in the ladder is $\varepsilon=\varepsilon_0\times\ln(n_0/n)$, as shown already. If $\varepsilon>2W$, the results of Sec. 3 apply, whereas if $\varepsilon<2W$, we have to use the results of the present section. We must bear in mind that $\varepsilon_0\ln(n_0/$

$n) = 2W$ may be satisfied if $n = n_p < n_c$. Then, if $n > n_p$, we find from Eq. (35) that the logarithmic derivative $\alpha = d \ln R / d \ln(n/n_0)$ is

$$\alpha = \varepsilon_0 L / W. \tag{36}$$

Therefore, if $\ln(n/n_0) > \ln(n_p/n_0)$, the quantity α ceases to depend on $\ln(n/n_0)$ and is given by Eq. (36) (see Fig. 3). Like the rest of the theory given in the present section, Eq. (36) is valid if $L < L_2$. We can see that in this case we have $\alpha \ll 1$.

Finally, we note that the temperature dependence of the recombination flux is still given by Eq. (26) in the case of large polaron shifts. This can be demonstrated rigorously, but it is easy to understand it on the basis of the following qualitative considerations. The temperature dependence of Eq. (26) is obtained from Eqs. (23)–(25), which are of the same form as in the case of large polaron shifts, because the times for transitions from delocalized to localized states are given by Eq. (5) irrespective of the value of W. It follows that the recombination times are affected by the temperature of the semiconductor in the same way for all values of W. The number of the active channels depends, as in the case of small values of W, much less on temperature than does the recombination time. Therefore, the temperature dependence remains as before and it is still given by Eq. (26).

6. DISCUSSION OF RESULTS

The results of the above analysis demonstrate that effective recombination channels in noncrystalline semiconductors are clusters of spatially close centers the energies of which form almost equidistant ladders in the mobility gap. The high efficiency of these channels becomes obvious when a comparison is made of the recombination flux provided by them [given for various cases by Eqs. (18), (21), (28), and (35)] with the flux resulting from direct recombination across the mobility gap proportional to $\exp(-G/\varepsilon_0)$. We can see that the recombination channels ensure an exponentially large recombination flux. We considered above separately the cases of recombination in substances with small and large polaron shifts. We must bear in mind that the condition deciding whether the polaron shift is large or small is influenced not only by the properties of the material, but also by the carrier density n. When n is varied within a sufficiently wide range, there may be a change in the polaron shift. For example, in the case of sufficiently low densities $n \ll n_0$, the value of $\tilde{G}$ (representing the renormalized width of the mobility gap) is so large that the condition for a small polaron shift is obeyed, i.e., the height of a step in a channel is considerably greater than W. An increase in n reduces $\tilde{G}$ and if $\tilde{G} \lesssim 2W^2/\hbar\omega$, there is a change to the case of large polaron shifts. Typical values of the parameters obtained for different substances are such that both cases may be expected. For example, in the case of a-Si and a-Ge, we have $W \approx 0.2$ eV and $\hbar\omega \approx 300$ K, whereas in the case of chalcogenide glasses the value of W may reach 0.5 eV and we have $\hbar\omega \approx 150$ K (Ref. 1).

We shall compare the results obtained with the experimental temperature dependence of the photoconductivity (recorded at low temperatures $T < \hbar\omega/2$). We shall do this by writing down the condition for equality of the rates of optical generation I and recombination R [Eq. (26)]:

$$I_0 (n/n_0)^{1+T/\varepsilon_0} = I. \tag{37}$$

This relationship gives rise to the experimentally observed dependence (1). The dependence $\beta(T)$ has been explained so far by assuming a purely exponential fall in the tails of the density of states inside the mobility gap: $g(\varepsilon) \propto \exp(-\varepsilon/\varepsilon_0)$ (Ref. 9), where the parameter ε_0 is related to the characteristic energy scale of this distribution. Our interpretation makes it possible to avoid this assumption, because the relationship (1) applies to almost any continuous distribution $g(\varepsilon)$. In our approach the phonon energy plays the role of ε_0.

We have ignored completely the problem of how a carrier which is above the mobility edge reaches the input to a recombination channel. We shall assume that a carrier always finds rapidly the optimal channel. However, this assumption may be invalid in the case of noncrystalline materials with a low carrier mobility. The recombination process is then diffusion-limited.

We have also ignored the nature of the states in the mobility gap. If they are due to the polaron effect, if they appear because of the small elastic constants,[10] then generally it is incorrect to regard $\hbar\omega$ (and ε_0) are independent of the energy of the centers. However, our theory can easily be generalized to this case. We shall return to these problems in greater detail in future.

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[1)] In Ref. 5 the range of such low values of α is called incorrectly the region of saturation of $R(n)$. The maximum value of $R(n)$ is assumed to be $R(n_0)$.

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