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Geminate electron–cation recombination in disordered solids

Yu. A. Berlin,^{a)} N. I. Chekunaev, and V. I. Goldanskii

N. N. Semenov Institute of Chemical Physics of the USSR Academy of Sciences, Ulitsa Kossygina 4, 117977 Moscow, USSR

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A theory of a geminate electron–cation recombination has been developed using the percolation approach to the description of the electron transport in disordered solids. Following this approach all trapping sites are separated into two groups. The first group forms a diffusion cluster responsible for the macroscopic charge transfer in disordered media while the second group consists of isolated traps playing the role of origins and sinks for mobile electrons. In the framework of such a model an equation has been derived describing the electron motion in the Coulomb field of a parent cation. The solution of this equation in the long time limit shows that the recombination rate decreases vs time as $t^{-(1+\alpha/2)}$ with α being a positive constant or a very weak function of t . In the particular case of Gaussian diffusion $\alpha = 1$ and the kinetic law obtained reduces to that predicted by the well-known Onsager–Smoluchowski theory. However for the dispersive (non-Gaussian) transport in highly disordered systems $\alpha < 1$ and its value depends on the type of disorder, on the energy level structure of trapped electrons and on the specific mechanism of electron migration through the medium.

I. INTRODUCTION

It is generally acknowledged that ionization of disordered solids, particularly of low-temperature glasses, leads to an ensemble of isolated ion pairs in them, each such pair comprising as components a “parent” cation and an electron localized in the medium, initially localized much closer to each other than the neighboring like charges. As has been established, it is just such pairs that determine the regularities of indirect action of radiation in the course of radiolysis of condensed systems¹ and play an important, sometimes even decisive role in the mechanisms of such processes as radiation-induced electrical conductance of liquid and solid dielectrics,^{2,3} intrinsic photogeneration of charge carriers in molecular crystals⁴ and polymer photoconductors,⁵ isothermal and some other kind of luminescence of previously irradiated low-temperature matrices.^{3,6,7} No wonder that the dynamics of the behavior of ion pairs in the condensed phase has been the subject of intensive theoretical investigations for almost two decades (cf. for instance, reviews^{8,9}).

It should be noted however, that until recently this problem, as applied to disordered solids was treated only on the basis of a formally borrowed method employed in describing the geminate recombination kinetics in liquids, where the approach of an electron and a cation is believed to proceed in conformity with the laws typical for the classical (Gaussian) diffusion.⁸ Nevertheless, in spite of extensive application of such a technique, its being justification is somewhat doubtful in light of the results obtained in Refs. 10 and 11. The fact that in the case of electron hopping in disordered solids, the time of jump of said negative charge carrier between different pairs of neighboring traps may vary within a very wide range due to the absence of regularity in the deposition of structural traps (localization centers) and spread of

the latter in depth. As a result, the electron motion in such a situation and, consequently, the kinetics of “collapse” of ion pairs can no longer be described in terms of the conventional diffusion theory but should be considered within the framework of concepts of the non-Gaussian dispersion transport.^{12,13}

Recently an attempt to analyze the geminate recombination kinetics from this standpoint was made by Arkhipov, Nikitenko, and Rudenko¹⁴ as well as by Noolandi.¹⁵ All calculations were carried out, proceeding from two very specific assumptions. First, the authors of the abovementioned studies postulated the electron movement in the medium to be conditioned by thermoactivated transitions of charge carriers from the traps to the zone of delocalized states and back (mechanism of multiple retrapping). Second, the disorder of the medium was associated exclusively with the distribution of the electron localization centers in depth E (so-called site disorder). As has been shown by Noolandi¹⁵ these assumptions allow to describe the electron–cation recombination in amorphous materials with site disorder in terms of the multiple-trapping model of stochastic charge transport developed in Refs. 16 and 17. However, even in the particular case of the exponential distribution of traps in E the solution of the problem can be written down only with the help of a rather complicated series.¹⁴ As a result the calculation of the kinetic curves for the recombination of ion pairs may be obtained only in the numeric form, the qualitative analysis of the curves being quite difficult. Furthermore, in view of the abovementioned assumptions the theory developed in Refs. 14 and 15, as well as, by the way, earlier model calculations^{18,19} of the geminate recombination rate, fails to elucidate whether spatial, nonregularity of the disposition of the traps (so-called bond disorder) affects the kinetics of the process discussed in amorphous solids. Meanwhile, an answer to this question is of considerable interest, especially for the interpretation of some experimental data on the luminescence and electrical conductance of low-temperature glasses^{3,7} in

^{a)} Current address: Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973.

which the electron transfer proceeds by a mechanism different from its multiple retrapping and is caused by successive tunneling transitions between neighboring localization centers (hopping).

In connection with the above, here we present a theory of geminate electron-cation recombination in systems with both bond and site disorder. This theory is based on the concept of electron diffusion in a disordered medium developed in Refs. 10 and 20. The main features of the proposed theory and some general results following from it, equally suitable for both electron hopping and for the mechanism of electron transfer by means of its multiple trapping, are considered in Sec. II. In Sec. III these results are used to derive the kinetic law of decay of ion pairs in the long-time limit for amorphous substances possessing different types of disorder, involving the site disorder with the exponential and Gaussian distribution of structural traps over their depths. Section IV contains the main conclusions. Finally, in the Appendix we solve the equation for the time evolution of the electron concentration at the diffusion cluster (DC).

II. GEMINATE RECOMBINATION AND DIFFUSION OF ELECTRONS IN DISORDERED MEDIUM

Following previous results of Chekunaev, Berlin, and Flerov^{10,20} we consider electron hopping in disordered systems as trap-to-trap tunneling of an excess electron along the optimal trajectory (diffusion cluster). Such a trajectory has been defined previously¹⁰ and involves localization centers separated from their nearest neighbors by some distance $\xi < r_c + a$, where r_c is the percolation threshold and a is the radius of electron localization. The role of all other traps (so-called isolated centers) reduces merely to an exchange of electrons with the DC. As in the case of the mechanism of multiple retrapping there occurs an exchange of electron with the zone of delocalized states. Such a possibility of exchange with a spread of the electron exchange times between DC and isolated centers (IC) leads to the electron motion being described by a modified diffusion equation.^{10,20,21} To consider the electron transport in disordered media, we introduce a concentration n of "mobile" electrons (i.e., of those belonging to DC) and a concentration N of electrons located on isolated centers. It is apparent, that the total concentration of the electrons is $N_{\text{tot}}(t) = n(t) + N(t)$. Furthermore, the introduced values are related to

$$N(t) = \int_0^t \phi(t-\tau)n(\tau)d\tau + N_0Q(t), \quad (1)$$

where N_0 is the initial concentration of electrons at IC, $\phi(t)$ and $Q(t)$ are functions characterizing the rate of charge exchange between IC and DC, calculated in Refs. 10 and 20.

A modified diffusion equation describing the motion of an excess electron has the form^{10,20}

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial t} \int_0^t \phi(t-\tau)N(\tau)d\tau = D\Delta n - e\mu E \nabla n - N_0 \frac{\partial Q(t)}{\partial t}. \quad (2)$$

Here D and $\mu = eD/k_B T$ are the diffusion coefficient and the mobility of the electrons belonging to DC, respec-

tively, e is the electron charge, k_B is the Boltzmann's constant, T is a temperature, E is the electric field intensity created by the positive ion. To find the probability of electron recombination with the parent cation we assume initial spatial distribution of the electrons is given by

$$N_{\text{tot}}(0) = \frac{N_0 + n_0}{4\pi r_0^2} \delta(r - r_0). \quad (3)$$

The problem with an arbitrary spherically symmetrical initial distribution may be solved by averaging the solution of Eq. (2) with the initial condition Eq. (3) over r_0 . By introducing Laplace transform

$$\begin{aligned} \tilde{n}(p) &= \int_0^\infty n(t) \exp(-pt) dt, \\ \tilde{N}(p) &= \int_0^\infty N(t) \exp(-pt) dt, \end{aligned} \quad (4)$$

Eq. (2) may be rewritten in spherical coordinates as

$$\begin{aligned} D \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \tilde{n}}{\partial r} \right) + \frac{r_c}{r^2} \frac{\partial \tilde{n}}{\partial r} \right] + \frac{\delta(r - r_0)}{4\pi r_0^2} \\ \times [n_0 + N_0 - N_0 \tilde{Q}(p)] = \chi(p) \tilde{n}, \end{aligned} \quad (5)$$

where $r_c = e^2/(\epsilon k_B T)$ is the Onsager's radius, ϵ is the dielectric constant, $\chi(p) = p[1 + \tilde{\phi}(p)]$. Since the probability of finding an electron at long distances from the parent cation must tend to zero, one can write

$$\tilde{n}(p, \infty) = 0. \quad (6)$$

Equation (2) is valid at distances exceeding the correlation length of the diffusion cluster L . This length is at least an order of magnitude greater than the mean intertrap distance for the bond disordered systems and amounts to several intertrap distances for the site disorder medium.^{10,20} But if the reaction radius R exceeds the correlation length, Eq. (2) holds true at all distances, and as the second boundary condition the following relation may be used

$$\tilde{j}(R) = -D \left[\frac{\partial \tilde{n}}{\partial r} + \frac{r_c}{r^2} \tilde{n} \right]_{r=R} = -k \tilde{n}(R), \quad (7)$$

where the constant k characterizes the rate of electron reaction with the cation.

For sufficiently small p (and sufficiently large t) the asymptotic solution of Eq. (5) with boundary conditions (6) and (7) is given by (see the Appendix)

$$\begin{aligned} \tilde{n}(r) &= [n_0 + N_0 - N_0 \tilde{Q}(p)] \\ &\times \left\{ \frac{U(r_0) \exp(r_c/r) [1 - \exp(-r_c/r)]}{4\pi D r_c U(\infty)} \right. \\ &- \left[\frac{\chi(p)}{D} \right]^{1/2} \\ &\times \left. \frac{U(r_0) \exp(r_c/r) U(r)}{4\pi D U^2(\infty)} \right\}, \quad \text{for } r > r_0, \end{aligned} \quad (8)$$

$$\tilde{n}(r) = [n_0 + N_0 - N_0 p \tilde{Q}(p)] \times \left\{ \frac{U(r) \exp(r_c/r) [1 - \exp(-r_c/r_0)]}{4\pi D r_c U(\infty)} - \left[\frac{\chi(p)}{D} \right]^{1/2} \times \frac{U(r_0) \exp(r_c/r) U(r)}{4\pi D U^2(\infty)} \right\}, \text{ for } r < r_0, \quad (9)$$

where, similarly to Ref. 22, the following notation is used

$$U(r) = \exp(-r_c/r) + [D r_c / (k R^2) - 1] \times \exp(-r_c/r_0). \quad (10)$$

It should be noted that at $\tilde{Q} = 0$ and $\tilde{\phi} = 0$ (the Gaussian diffusion) Eqs. (8) and (9) reduce to results of Hong and Noolandi for small p .²²

The solution of Eq. (5) given by (8) and (9) makes it possible to calculate the quantities which are of physical interest, in particular, the rate of geminate recombination defined as $R(t) = -4\pi R^2 j(R, t) = 4\pi R^2 k n(R, t)$. From this expression and from Eq. (9) we can obtain the Laplace transform of $R(t)$ given by

$$\tilde{R}(p) = \left[\frac{1 - \exp(-r_c/r_0)}{U(\infty)} - \frac{U(r_0)}{U^2(\infty)} r_c \times (\chi(p)/D)^{1/2} \right] [n_0 + N_0 - N_0 p \tilde{Q}(p)], \quad (11)$$

while the proportion of survived electrons at DC may be written as follows:

$$\tilde{\Omega}(p) = 4\pi \int_0^\infty r^2 \tilde{n}(r, p) dr = \frac{n_0 + N_0 - N_0 p \tilde{Q}(p) + \tilde{R}(p)}{\chi(p)(n_0 + N_0)}. \quad (12)$$

Finally, to derive the expression for the total concentration of electrons separated from their cations by distance r at time t , all we have to do is to multiply Eqs. (8), and (9) by the factor $1 + \tilde{\phi}(p)$ and to carry out the inverse Laplace transform. The same mathematical operations with Eq. (12) allow to determine the survival probability. Results for different type of disorder will be presented in the next Section.

III. SOLUTION OF THE PROBLEM OF GERMINATE RECOMBINATION FOR DIFFERENT TYPES OF DISORDER

A. Site-disordered media with exponential distribution

In this case the number of traps with the energy depth between E and $E + dE$ is given by

$$f(E) = \frac{1}{k_B T_0} \exp(-E/k_B T_0), \quad (13)$$

where T_0 is a distribution parameter. Using this distribution one can show²⁰ that for electron hopping

$$p\tilde{\phi}(p) = A W_R (p/W_R)^\alpha, \quad (14)$$

$$p\tilde{Q}(p) = B (p/W_R)^\alpha, \quad (14')$$

$$\alpha = T/T_0. \quad (14'')$$

Here A and B are some numerical constants whereas W_R is an average frequency of electron transfer along DC. Note that $\chi(p)$ and $p\tilde{Q}(p)$ for the retrapping mechanism have the same form. However in the latter case instead of W_R Eqs. (14) and (14') contain the preexponential factor ν_0 appearing in the expression for the frequency of electron transitions from IC into the conduction band $\nu = \nu_0 \exp[-E/(k_B T)]$.

Substituting the expressions (14) into Eq. (8), (9), and (11) and taking the inverse Laplace transform one can easily derive formulas for $n(r, t)$, $R(t)$ and $\Omega(t)$ in the long time limit. If we omit the terms which decrease with t faster than $t^{-3/2}$, this yields

$$n(r, t) = \frac{\sin \pi \alpha / 2}{4\pi} \Gamma(1 + \alpha/2) (W_R/D)^{3/2} \times \frac{U(r_0) \exp(r_c/r) U(r)}{U^2(\infty) (W_R t)^{3/2}} A^{1/2} (n_0 + N_0), \quad (15)$$

$$R(t) = \frac{\sin \pi \alpha / 2}{4\pi} \Gamma(1 + \alpha/2) r_c [U(r_0)/U^2(\infty)] \times A^{1/2} W_R^{(1-\alpha)/2} D^{-1/2} t^{-(1+\alpha/2)} (n_0 + N_0), \quad (16)$$

$$\Omega(t) = U(r_0) [(W_R t)^{\alpha-1} + W_R r_c U^{-1}(\infty) \times D^{-1/2} (W_R t)^{\alpha/2-1}] / U(\infty). \quad (17)$$

The total concentration of the electrons and the survival probability are equal, respectively, to

$$N_{\text{tot}}(r, t) = \frac{U(r_0) \exp(r_c/r) [1 - \exp(-r_c/r)] W_R}{4\pi D r_c U(\infty) (W_R t)^\alpha (n_0 + N_0)^{-1}} \text{ for } r > r_0, \quad (18)$$

$$N_{\text{tot}}(r, t) = \frac{U(r) \exp(r_c/r) [1 - \exp(-r_c/r_0)] W_R}{4\pi D r_c U(\infty) (W_R t)^\alpha (n_0 + N_0)^{-1}} \text{ for } r < r_0, \quad (18')$$

$$\Omega_{\text{tot}}(t) = U(r_0) \left[1 + \left(\frac{W_R}{D} \right)^{1/2} \frac{r_c}{U(\infty) (W_R t)^{\alpha/2}} \right] / U(\infty). \quad (19)$$

B. Site disordered systems with normal distribution of traps in energy

The distribution of localization centers, in energy, is given by

$$f(E) = \frac{1}{\sigma_E (2\pi)^{1/2}} \exp[-E^2/(2\sigma_E^2)], \quad (20)$$

where σ_E is the energy distribution parameter. Using Eqs. (31) and (32) from Ref. 20, one can obtain

$$\chi(p) = W_R \exp \left[-\frac{(k_B T)^2}{2\sigma_E^2} \ln^2 \frac{W_R \sigma_E^2}{(k_B T)^2 p} \right] \text{ for } p > W_R \exp \left[-\frac{\sigma_E^2}{(k_B T)^2} \right], \quad (21)$$

$$\chi(p) = p \exp \left[\frac{\sigma_E^2}{2(k_B T)^2} \right] \quad \text{for } p < W \exp \left[- \frac{\sigma_E^2}{(k_B T)^2} \right]. \quad (21')$$

This yields formulas for $n(r, t)$, $R(g)$, and $\Omega(t)$ which are similar to Eqs. (15)–(19), but contain a time-dependent g given by

$$\alpha(t) = \begin{cases} \frac{(k_B T)^2}{2\sigma_E^2} \ln \frac{W_R t \sigma_E^2}{(k_B T)^2} & \text{for } t < t_0 = W_R^{-1} \exp \frac{\sigma^2}{(k_B T)^2}, \\ 1 & \text{for } t > t_0. \end{cases} \quad (22)$$

Note, however, that for highly site-disordered systems ($\sigma_E^2 \sim 0.1 \text{ eV}^2$, $W_R \sim 10^{10} \text{ s}^{-1}$, $r_c \sim 10^2 \text{ \AA}$, $D \sim 10^{-5} \text{ cm}^2/\text{s}$) t_0 exceeds the typical recombination time $t_1 \sim r_c^2/D$ even at room temperature. Therefore the second equality in Eq. (22) has no physical meaning. Moreover, taking into account that our asymptotic solution of Eq. (5) is valid only for $t > t_2 \sim r_0^2/D$ and that the typical mean initial separation distance r_0 is about a few tenths of r_c , one may neglect insignificant variations of α with t within the time interval $\Delta t = t_2 - t_1$.

C. Bond-disordered media

As has been mentioned above the equations employed earlier are valid, if R exceeds the correlation length L .¹⁰ This condition is satisfied for the site-disordered systems since L almost equals the average distance ξ_{av} between the localization centers. However for the bond disorder $L/\xi_{av} \approx (\xi_{av}/a)^{0.9} > 10$ (e.g., Ref. 10). For typical values $\xi_{av} \sim 10 \text{ \AA}$ and therefore $L > 10^2 \text{ \AA} \gg R = 5 \text{ \AA}$. Thus the boundary condition (7) becomes meaningless.

To solve the problem for bond-disordered media it is useful to note that according to Ref. 10, each isolated center is characterized by its distance \tilde{R} to DC and has its own frequency of electron exchange with DC defined as¹⁰ $W(\tilde{R}) = W_0 \exp(-\tilde{R}/a)$. The same quantities may be used to characterize a parent positive ion in the case, when $R > L$, although their values differ from those assigned to IC. This allows one to redefine the reaction radius and the rate constant k in the boundary condition (7) and permits us to

apply results obtained in Sec. II to the theoretical analysis of electron-cation geminate recombination in bond-disordered solids.

To prove the validity of this conclusion we introduce the distance \tilde{R}_i of a parent cation to DC and the frequency of the final electron transition from DC to its positive charged partner $W_{ic} = W_{oc} \exp(-\tilde{R}_i/a)$. For DC with the density of localization centers N_{DC} the flow I of electrons to a cation is equal to $W_{ic} n(L, t)/N_{DC}$, where $N_{DC} = a^{\beta}/\xi_{av}^{\beta+3}$ (see Ref. 10) and β is the critical index. On the other hand, $I = -4\pi L^2 D(\partial n/\partial r + (r_c/r^2)n)_{r=L}$ and hence

$$j(L, t) = - \frac{G W_{ic} \xi_{av}^{\beta+3}}{4\pi L^2 a^{\beta}} n(L, t), \quad (23)$$

where G is a factor which takes into account the complicated geometrical structure of DC. Putting now $k_{eff} = G W_{ic} \xi_{av}^{\beta+3}/(4\pi L^2 a^{\beta})$ and carrying out the Laplace transform we conclude that the result is of exactly the same form as the boundary condition (7). Thus in the case of bond disorder one can employ Eqs. (8) and (9) to find the asymptotic behavior of N_{tot} or Ω in the long time limit. As has been shown¹⁰ for systems with such a disorder

$$\chi(p) = W_R \exp[-(a/\xi_{av})^3 \ln^3(W_R/p)] \quad \text{if } p > W_R \exp[-(\xi_{av}/a)], \quad (24)$$

$$\chi(p) = p \quad \text{if } p < W_R \exp[-(\xi_{av}/a)]. \quad (24')$$

Corresponding relations (15)–(19) are derived with

$$\alpha(t) = (a/\xi_{av})^3 \ln^2(W_R t) \quad \text{when } t < W_R^{-1} \exp[(\xi_{av}/a)] \quad (25)$$

$$\alpha(t) = 1 \quad \text{when } t > W_R^{-1} \exp[(\xi_{av}/a)]. \quad (25')$$

Because of reasons already mentioned above in connection with Eqs. (22) we conclude that Eq. (25') has no physical meaning and that variations in α with increasing t are negligible.

Since W_{ic} has random values, to obtain a final result it is necessary to average Eqs. (15)–(19) over W_{ic} . After this procedure the time dependences for all the values of interest do not change, but instead of ratios $U(r)/U(\infty)$ and $U(r)/U^2(\infty)$ their mean values appear. For example, the quantity $U(r)/U(\infty)$ transform into the integral

$$\int \frac{\exp(-r_c/r) + [Dr_c a^{\beta}/(W_{ic}(\xi) \xi_{av}^{3+\beta}) - 1] \exp(-r_c/R)}{1 + [Dr_c a^{\beta}/(W_{ic}(\xi) \xi_{av}^{3+\beta}) - 1]} P(W_{ic}) dW_{ic}.$$

Here $P(W_{ic})$ is the distribution of the probability density for W_{ic} , which may be written in the excluded volume approximation as follows:

$$F(W_{ic}) dW_{ic} = \exp[-(\xi/\xi_{av})^3] d^3 \xi / \xi_{av}^3.$$

Averaging over this distribution immediately yields

$$\langle U(r)/U(\infty) \rangle = \frac{\exp(-r_c/r) + \phi(\xi_{av}) \exp(-r_c/L)}{1 + \phi(\xi_{av}) \exp(-r_c/L)}, \quad (26)$$

where $\phi(\xi_{av}) = Dr_c a^{\beta}/[W_{ic}(\xi_{av}) \xi_{av}^{3+\beta}] - 1$. For a similar

way one gets

$$\left\langle \frac{U(r)}{U^2(\infty)} \right\rangle = \frac{\langle U(r)/U(\infty) \rangle}{[1 + \phi(\xi_{av}) \exp(-r_c/L)]}, \quad (27)$$

if $\xi_{av}/a > \exp(\xi_{av}/a - r_c/L)$,

$$\left\langle \frac{U(r)}{U^2(\infty)} \right\rangle = \frac{\exp(-r_c/r) + \phi(a) \exp(-r_c/L)}{[1 + \phi(a) \exp(-r_c/L)]^2}, \quad (27')$$

if $\xi_{av}/a < \exp(\xi_{av}/a - r_c/L)$,

where $\phi(x) = Dr_c a^\beta / (W_{ic}(x) \xi_{av}^{3+\beta}) - 1$ and the notation $\langle \dots \rangle$ means averaging over W_{ic} .

IV. CONCLUSIONS

Here we have presented the theory of geminate electron-cation recombination in disordered solids taking into account the dispersion of positions and energy depths of trapping sites. Our theory is based on the percolation approach to the description of the electron transport in highly disordered media.

In the framework of this approach we derived new results for the long time behavior of the electron concentration, the recombination rate and the survival probability. As has been shown the latter quantity decreases vs time as a linear function of $t^{-\alpha/2}$ with α being a positive constant or a weak function of t . For $t \rightarrow \infty$ the survival probability tends to the nonzero and finite limit described by the formula which exactly coincides with the well-known expression for the ultimate escape probability.²²⁻²⁴ In addition, it has been found that the recombination rate is proportional to $t^{-(1+\alpha/2)}$. This analytical finding agrees with the kinetic law observed for the decay of the recombination luminescence in irradiated organic glasses (see, e.g., Refs. 6, 7, and 25) and with numerical results of a computer stimulation study of geminate recombination.^{18,19}

The physical origin of such kinetics is a dispersive character of the electron transport in highly disordered systems. Indeed, in the case of the Gaussian (nondispersive) diffusion there are no preferable trajectories of the electron motion and therefore all functions introduced here to take into account the charge exchange between isolated traps and the diffusion cluster become equal to zero. As a consequence in this particular case $\alpha = 1$ and our results reduce to those predicted by the Onsager-Smoluchowski theory for non-dispersive motion of charged reactive species.^{22,26} Thus the present treatment of geminate electron cation recombination may be considered as an extension of the classical theory mentioned above.

According to this extension the value of the exponent α depends on the type of disorder, the energy level structure of trapped electrons and on the specific mechanism of electron transfer (hopping or retrapping). The analysis of decay kinetics found for pulse-induced current in "time-of-flight" experimental conditions²⁷ gives for inorganic systems like low-temperature *a*-Se $\alpha \approx 0.4$ to 0.5. On the other hand, for site disordered organic crystals, α values evaluated from data on space charge limited current usually vary at $T = 300$ K within the range 0.1 to 0.5²⁸ and may be even less at low temperatures. This means that the contribution of disorder

to the evolution of the recombination process seems to be rather essential.

Finally, we would like to emphasize that our results may be applicable to geminate processes with the participation of other active species moving through the disordered medium by a sequence of transitions between traps. In particular, these results seem to be useful for the interpretation of kinetic data on some chemical reactions in low-temperature solids proceeding by the mechanism of quantum mechanical tunneling.¹³

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APPENDIX: LONG TIME BEHAVIOR OF ELECTRON CONCENTRATION AT DIFFUSION CLUSTER

Here we solve Eq. (5) with two boundary conditions (6) and (7) in the long-time limit. For $r \neq r_0$ the boundary value problem (5)-(7) has a form

$$\frac{\partial^2 \tilde{n}(r, p)}{\partial r^2} + \left[\frac{2}{r} + \frac{r_c}{r^2} \right] \frac{\partial \tilde{n}(r, p)}{\partial r} - \frac{\chi(p)}{D} \tilde{n}(r, p) = 0, \quad (A1)$$

$$k\tilde{n}(R, p) = D \left[\frac{\partial \tilde{n}(r, p)}{\partial r} + \frac{r_c}{r} \tilde{n}(r, p) \right] \Big|_{r=R}, \quad (A2)$$

$$\tilde{n}(\infty, p) = 0, \quad (A3)$$

$$\left| \frac{\partial \tilde{n}}{\partial r} \right|_{r=r_0+0} - \left| \frac{\partial \tilde{n}}{\partial r} \right|_{r=r_0-0} = -(4\pi r_0^2 D)^{-1} H(p), \quad (A4)$$

where $H(p) = n_0 + N_0 - N_0 \tilde{Q}(p)$.

Putting

$$\tilde{n} = CI_1(r, p) \quad \text{at } r > r_0 \quad (A5)$$

$$\tilde{n} = AI_1(r, p) + BI_2(r, p), \quad \text{at } r < r_0, \quad (A6)$$

where $I_1(r, p)$ and $I_2(r, p)$ are two linearly independent solutions of Eq. (A1), and substituting Eqs. (A5) and (A6) into Eqs. (A2)-(A4) one gets

$$\begin{aligned} CI_1(r_0, p) &= AI_1(r_0, p) + BI_2(r_0, p), \\ CI_1'(r_0, p) &= AI_1'(r_0, p) + BI_2'(r_0, p) \\ &= -(4\pi r_0^2 D)^{-1} H(p), \end{aligned} \quad (A7)$$

$$\begin{aligned} k[AI_1(R, p) + BI_2(R, p)] \\ = DA \left[I_1'(R, p) + \frac{r_c}{R} I_1(R, p) \right] \\ + B \left[I_2'(R, p) + \frac{r_c}{R} I_2(R, p) \right], \end{aligned}$$

where $I'_1(x, p) = dI_1/dr$ at $x = r$, $i = 1$ or 2 . Solving the set of Eqs. (A7) we have

$$\begin{aligned} A &= \frac{I_1(r_0, p) [\kappa I_2(R, p) + I'_2(R, p)]}{4\pi r_0^2 DZ(r_0) [\kappa I_1(R, p) + I'_1(R, p)]} H(p), \\ B &= I_1(r_0, p) / [4\pi r_0^2 DZ(r_0)] H(p), \\ C &= \frac{\kappa [I_1(r_0, p) I_2(R, p) - I_1(R, p) I_2(r_0, p)] + [I_1(r_0, p) I'_2(R, p) - I'_1(R, p) I_2(r_0, p)]}{4\pi r_0^2 DZ(r_0) [\kappa I_1(R, p) + I'_1(R, p)]} H(p), \end{aligned} \quad (\text{A8})$$

where $Z(r) = I'_1(r, p) I_2(r, p) - I_1(r, p) I'_2(r, p)$ and $\kappa = k / D(Dr_c/kR^2 - 1)$.

Note that $Z(r)$ must be a solution of the ordinary differential equation $Z' + (2/r + r_c/R^2)Z = 0$, since $I_1(r, p)$ and $I_2(r, p)$ satisfy Eq. (A1). Therefore

$$Z(r) = \text{const. } r^{-2} \exp(r_c/r). \quad (\text{A9})$$

Now we can proceed to the construction of two functions $I_1(r, p)$ and $I_2(r, p)$, which determine the evolution of the electron concentration at DC. For $r \gg r_c$ these functions depend on r either as

$$I = r^{-1} \exp[-(\chi(p)/D)^{1/2} r] \quad (\text{A10})$$

or as

$$I = r^{-1} \exp[(\chi(p)/D)^{1/2} r]. \quad (\text{A11})$$

On the other hand, for $r \ll [\chi(p)/D]^{-1/2}$ and $t \gg W_R^{-1} (\xi_{av}/r)^{2/\alpha}$ the last term in Eq. (A1) may be neglected. Then

$$I = C_1 \exp(r_c/r) + C_2. \quad (\text{A12})$$

Obviously, if $r_c \ll r \ll [D/\gamma(p)]^{1/2}$ both solutions are valid and must coincide. Therefore expanding Eqs. (A10) and (A12) in small parameters $[\chi(p)/D]^{1/2} r$ and r_c/r , respectively, and equating terms of the same order one can find C_1 and C_2 . As a result we have

$$I_1(r, p) = \frac{1}{r_c} [\exp(r_c/r) - 1] - [\chi(p)/D]^{1/2}. \quad (\text{A13})$$

The same procedure for Eqs. (A11) and (A12) yields

$$I_2(r, p) = \frac{1}{r_c} [\exp(r_c/r) - 1] + [\chi(p)/D]^{1/2}. \quad (\text{A14})$$

Expressions (A8), (A13), and (A14) define the approximate solution of the boundary value problem (A1)–(A4) in the long time limit $t > t_2 \sim r_0^2/D$.

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