CAPTURE AND RECOMBINATION OF CHARGE CARRIERS IN A STRONG ELECTRIC FIELD IN QUASI-ONE-DIMENSIONAL CRYSTALS WITH SCATTERING CENTERS

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UDC 621.315.592;621.383

The asymmetric random walk method is used to find the time dependence of the density of free charge carriers in a chain containing traps and neutral barriers, assuming a strong electric field. Fluctuations in the density of defects are taken into account exactly. The kinetics of the density decay has two stages: fast exponential decay at small times and slow decay ($\sim[\ln(t) + \text{const}]t^{-\alpha}$, where $\alpha \ll 1$ is a combination of the parameters of the system) at long times. It is also shown that in the presence of barrier defects the asymptotic forms of the decrease in the number of charge carriers due to capture by traps and due to germinal recombination are the same.

In a crystal with traps, an electric field applied along the direction of maximum conductivity enhances capture of free charge carriers by the traps. In the case of one-dimensional diffusion and small electric fields most of the charge carriers are annihilated due to capture by traps according to the equation $\sim\exp(-t^{1/3}-\eta^2 t)$ [1, 2] or $\sim\exp(-t^{1/2}-\eta^2 t)$ [3] ($\eta = eEa/2k_bT \ll c_{tr}$, e is the charge of the electron, a is the lattice constant, E is the electric field strength, T is the temperature, c_{tr} is the concentration of traps). In strong fields ($\eta \gg c_{tr}$) the number of charge carriers decreases as $\sim\exp(-\eta t)$ [1-3]. In theoretically predicted change in photocurrent kinetics with increase in the electric field has been observed in the crystal PDA-I-ON [4].

The enhancement of captures by traps in a strong electric field may not occur if scattering centers are present in the crystal along with traps. For example, broken bonds of polymer chains or impurities with high-lying electronic (hole) levels can play the role of scattering centers. The presence of barrier defects that restrict the motion of charge carriers and neutral particles differently can lead to the opposite effect: a marked slowing down of the decay in the density of charge carriers $\Delta\Omega(t)$ in a strong field. This was pointed out for the first time in [5, 6], where a power-law (rather than exponential) density decay $\sim t^{-\alpha}$, $\alpha = c/2\eta$, $c = c_{tr} + c_b$, was predicted (c_b is the concentration of barrier defects). The slowing effect is corroborated qualitatively in the present paper, but a different form is obtained for the function $\Delta\Omega(t)$. Our results are different as follows: 1) the complete time dependence $\Delta\Omega(t)$ is found; 2) a discrete model is used, where the field dependence of the kinetics can be obtained without assuming $\eta \ll 1$, which is characteristic of the diffusion model; 3) the field dependence of the time constant of the asymptotic form of $\Delta\Omega(t)$ is obtained for an arbitrary capture rate; 4) the asymptotic form of the decay in the number of charge carriers is established for geminal recombination in a chain with randomly distributed broken bonds.

We first consider the capture of diffusing charges by traps, assuming that the defects (traps and barriers) are randomly distributed on the chains along which the charge carriers move and are inpenetrable with respect to the charge carriers. The problem then reduces to first determining the probability of survival of a charge carrier $\Omega_n^{\nu}(t)$ in a given segment (cluster) of the chain consisting of n principal lattice points with defects on the ends, and then to calculating the average over cluster length

$$\Delta\Omega(t) = \langle\Omega(t)\rangle - c_b^2/c^2 = \sum_{n=1}^{\infty} n(1-c)^{n-1}\{c_{tr}^2\Omega_n^{(tr,tr)}(t) + c_b c_{tr}[\Omega_n^{(b,tr)}(t) + \Omega_n^{(tr,b)}(t)]\}. \tag{1}$$

Institute of Theoretical Physics, Academy of Sciences of the Ukrainian SSR, Kiev.
Translated from Teoreticheskaya i Éksperimental'naya Khimiya, Vol. 27, No. 2, pp. 129-133, March-April, 1991. Original article submitted May 21, 1990.

0040-5760/91/2702-0121$12.50

This equation gives an exact expression for the configuration average for the model considered here [7].

The probability of survival

$$\Omega_n^{\nu}(t) = n^{-1} \sum_{j,j_0=1}^{n} G_{j,j_0}^{\nu}(t) \tag{2}$$

is found assuming that the charge carriers in a cluster obey a dynamical equation of the Pauli type

$$\begin{gathered} dG_{j,j_0}^{\nu}(t)/dt = -[2\,\mathrm{Ch}(\eta) + (\omega_1^{\nu} - q)\,\delta_{j,1} + (\omega_n^{\nu} - q^{-1})\,\delta_{j,n}]\, G_{j,j_0}^{\nu}(t) + \\ + (1-\delta_{j,1})\, q^{-1} G_{j-1,j_0}^{\nu}(t) + (1-\delta_{j,n})\, q G_{j+1,j_0}^{\nu}(t), \\ G_{j,j_0}^{\nu}(0) = \delta_{j,j_0}, \quad \omega_1^{\nu} = \begin{cases} q\omega, \\ q\omega, \\ 0, \end{cases} \quad \omega_n^{\nu} = \begin{cases} q^{-1}\omega, & \nu = (\mathrm{tr},\mathrm{tr}), \\ 0, & \nu = (\mathrm{tr}, b), \\ q^{-1}\omega, & \nu = (b, \mathrm{tr}), \end{cases} \end{gathered} \tag{3}$$

whose solution has the form

$$G_{j,j_0}^{\nu}(t) = \frac{\exp[\eta(j_0 - j)]}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} g_{j,j_0}^{\nu}(s) \exp(st)\, ds, \tag{4}$$

where

$$g_{j,j_0}^{\nu}(s) = \begin{cases} \dfrac{[\mathrm{Sh}(j\xi) + \beta_1^{\nu}\,\mathrm{Sh}((j-1)\xi)]\,[\mathrm{Sh}((n-j_0+1)\xi) + \beta_n^{\nu}\mathrm{Sh}((n-j_0)\xi)]}{\mathrm{Sh}(\xi)\,[\mathrm{Sh}((n+1)\xi) + (\beta_1^{\nu} + \beta_n^{\nu})\,\mathrm{Sh}(n\xi) + \beta_1^{\nu}\beta_n^{\nu}\,\mathrm{Sh}((n-1)\xi)]}, \\ j \leqslant j_0, \\ j \leftrightarrow j_0, \quad j \geqslant j_0, \end{cases} \tag{5}$$

$$q = \exp(\eta), \quad \exp(\pm\xi) = s/2 + \mathrm{Ch}(\eta) \pm \sqrt{(s/2 + \mathrm{Ch}(\eta))^2 - 1},$$

$$\beta_{1(n)}^{\nu} = \omega_{1(n)}^{\nu} - \exp\left(\overset{+}{(-)}\,\eta\right),$$

ω is the frequency of particle jumps from principal lattice points to lattice points occupied by traps divided by the frequency W of particle jumps between principal lattice points of the chain in the absence of the field (i.e., the rate of diffusion). In (3) and (4) time is measured in units of W^{-1}.

Using (1)-(5) to calculate the average probability [8] in the case of a strong field and $c \ll 1$, we find

$$\Delta\Omega(t) = \frac{c_t c_{tr}}{c^2}\,\Phi(t) + \frac{c_{tr}}{c}\exp(-Kt), \quad \eta \gg c, \tag{6}$$

where the time constant of the function

$$\Phi(t) = \alpha\Gamma(1+\alpha)\,[\ln(t/\tau) + \alpha^{-1} + 0.5772]\,(t/\tau)^{-\alpha} \tag{7}$$

and the rate constant K are given by

$$\tau^{-1} = \frac{2\omega\,\mathrm{Sh}(\eta)}{1 + \omega/2\exp(\eta)\,\mathrm{Sh}(\eta)}, \quad K = 2\,\mathrm{Sh}(\eta)\begin{cases} c, & \omega \gg c \\ \omega, & \omega \ll c. \end{cases} \tag{8}$$

The function (6) suggests a sharp change may be observable in the kinetics of th charge-carrier density decay from an exponential to a power law or logarithmic power law. We see that the function $\Delta\Omega(t)$ may have the intermediate asymptotic form $\sim t^{-\alpha}$. The above results can be used to predict the concentration of charge carriers and the time corresponding to a particular form of the decay.

We next consider recombination of free charge carriers in a chain with randomly distributed barrier defects. In this case the average probability of survival of a pair of oppositely-charged particles originating at a distance $n_0 \ll c_b^{-1}$ is given by the sum

$$\langle\Omega^{e-h}(t')\rangle = c_b^2 \sum_{n=1}^{\infty} n\,(1-c_b)^{n-1}\Omega_{n,n_0}^{e-h}(t'), \tag{9}$$

where $\Omega^{e-h}_{n,n_0}(t')$ is the probability of survival of the pair up to the time t', averaged with respect to its initial position in a cluster of n principal lattice points with inpenetrable barriers on the ends.

The two-particle distribution function $\rho_{ij}(t')$ in a cluster is given by the system of equations

$$d\rho_{i,j}(t')/dt' = -[2\mathrm{Ch}(\eta) + (\omega' - q^{-1})\,\delta_{j,n-i} + q(\sigma_h\delta_{i,1} + \sigma_e\delta_{j,1})]\,\rho_{i,j}(t') + \\ + q^{-1}[(1-\delta_{i,1})\,\sigma_h\rho_{i-1,j}(t') + (1-\delta_{j,1})\,\sigma_e\rho_{i,j-1}(t')] + \\ + q(1-\delta_{j,n-i})\,(\sigma_h\rho_{i+1,j}(t') + \sigma_e\rho_{i,j+1}(t')), \tag{10}$$

where ω' is the analog of the parameter ω: It is the ratio of the rate of recombination of electrons and holes at the minimum distance *a* to the rate of relative diffusion of the pair of particles $W_e + W_h$; $\sigma_{h(e)} = W_{h(e)}/(W_e + W_h)$, $W_{e(h)}$ has the same meaning for electrons (holes) as W, and time is expressed in units of $(W_e + W_h)^{-1}$. The coordinates of the hole (i) and the electron (j) are chosen such that i = j = 1 corresponds to particles on the ends of the cluster (particles cannot pass by one another). According to (10), the field promotes charge separation. The sign of η must be switched in (10) when the field has the opposite direction.

The "slow" term in (6) is due to the contribution of clusters (b, tr) in (1) with lengths $n \gtrsim c^{-1}$ with reflecting and absorbing ends such that the charge carriers drift toward the reflecting end. It is not difficult to show from (4) and (5) that in clusters of this type the charge density is a maximum on the end of the cluster opposite to the trap and it decreases exponentially with increasing distance from the end. In the case of annihilation of charges by recombination the asymptotic form of (9) is determined by clusters in which opposite charges are confined near the reflecting boundaries by the field. The corresponding solution of (10) in a strong field ($n\eta \gg 1$) at large times is, to within exponentially small corrections

$$\rho_{i,j}(t') \sim \exp(-2\eta(i+j))\exp[-\exp(-2\eta n)\,t'/\tau'], \tag{11}$$

and so

$$\Omega^{e-h}_{n,n_0}(t') \sim \exp[-\exp(-2\eta n)\,t'/\tau'], \tag{12}$$

where τ' is given by (8) for τ, except that ω is replaced by ω'. Evaluating (9) with the help of (12) gives, for $c_b \ll 1$

$$\langle\Omega^{e-h}(t')\rangle = \int_0^\infty dx\,x\exp\left[-x - \frac{t'}{\tau'}\exp\left(-\frac{x}{\alpha'}\right)\right] \sim \left[\ln\left(\frac{t'}{\tau'}\right) - \alpha'^{-1} + 0.5772\right]\left(\frac{t'}{\tau'}\right)^{-\alpha'}, \quad \alpha' = c_b/2\eta. \tag{13}$$

In the absence of the field, binary recombination of charges in a chain with defects leads to a decay in the density of charge carriers at large times of the form $\sim\exp(-t^{1/3})$ [9]. In weak fields ($\eta \ll c_b$) one expects a change in the asymptotic form: $\exp(-t^{1/3}) \to \exp(-\eta^2 t)$, as in the case of capture of charges by traps. Comparison of these results with (13) shows that a strong electric field leads to an anomalous slowing of binary recombination of charges at large times, accompanied by a qualitative change in the form of the decay of the charge density.

Finally we note that for disordered systems where charge transport occurs in an isolated cavity in an inert solvent (i.e., in the subpercolation region) the asymptotic forms (7) and (13) remain valid for arbitrary dimensionality of the system.

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EFFECT OF THE LENGTH OF A POLYMER CHAIN ON THE RATE OF DONOR-ACCEPTOR ELECTRON TRANSFER

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UDC 537;577

We consider the dependence of the rate of activated and tunnel transfer of an electron between a donor and an acceptor separated by a chain of finite length on the energy and relaxation characteristics of the donor, the chain and the acceptor. It is found that the chain length is important for numbers of units not exceeding 5-7.

It is known that a polymer chain with structural groups having a considerable electron affinity is able to transfer an electron from a donor to an acceptor [1, 2]. This forms the basis for ideas about electron tunneling along special electronic pathways in individual proteins and in bimolecular protein complexes [3, 4], and also leads to the formulation of the concept of a soliton mechanism for the motion of an electron in soft polymers and biopolymers [5]. The finite nature of the chain determines the specific nature of the donor-acceptor electron transfer. Thus it has been shown [6] that on account of the discrete nature of the energy levels of the chain the probability of the tunneling of an excess electron can differ considerably from the value characteristic of a chain with a large number of units N.

In the present study we analyze further the dependence of the rate of activated and tunneling transfer between a donor and an acceptor separated by chains of finite length on the relaxation characteristics and the nature of the structural groups taking part in the electron transfer. As before [6, 13] we shall consider a donor—chain—acceptor (DCA) system in which the donor D is attached to the first unit, n = 1, and the acceptor to a later unit, n = N; we shall denote by $\bar{E}_0$, $\bar{E}_1$, and $\bar{E}_2$ the energy levels of the electron at any unit of the chain, at the donor and at the acceptor respectively, and by L, L_1, and L_2 the values of the resonance interactions characterizing the transfer of an electron between the units of the chain, between the donor and the unit of the chain with n = 1, and between the acceptor and the unit of the chain with n = N (Fig. 1). As in [2], the irreversibility of the process is allowed for by two types of relaxation processes. The first of these is indicated in Fig. 1 by the parameter K_1^{ν} (or K_2^{ν}), which signifies that the transfer of the electron between the donor and the chain unit with n = 1 (or between the acceptor and the chain unit with n = N) is accompanied by normal vibrations of frequency $\omega_{1\nu}$ (or $\omega_{2\nu}$). The second type of relaxation specifies the rapid irreversible removal of the electron from the acceptor state and can be allowed for by introducing the parameter $\Gamma/2$ ($\bar{E}_2$ is replaced by $\bar{E}_2 - i\Gamma/2$).

Institute for Theoretical Physics, Academy of Sciences of the Ukrainian SSR, Kiev.
Translated from Teoreticheskaya i Éksperimental'naya Khimiya, Vol. 27, No. 2, pp. 133-139, March-April, 1991. Original article submitted February 19, 1988.

 0040-5760/91/2702-0124$12.50