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ANOMALOUS SLOW-DOWN OF CHARGE CARRIER TRAPPING AND RECOMBINATION DUE TO A STRONG ELECTRIC FIELD IN QUASI-ONE-DIMENSIONAL CRYSTALS WITH SCATTERING CENTERS

A.I. Onipko

Institute for Theoretical Physics, Kiev-130, 252130, USSR

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An anomalous slow-down of trapping and recombination of charge carriers in one dimension with large bias is predicted. It is shown that for both processes the asymptotic time behaviour of the charge carrier density is $[\ln(t) + \text{const}]t^{-\alpha}$ (α is a certain combination of system parameters) and the electric field dependence of the characteristic time scale of the asymptotics is obtained without restrictions on the bias magnitude and the trapping (or recombination) rate. In cases of slow and fast trapping the full time dependence of the charge carrier density is also established.

IN CRYSTALS with traps an external electric field applied along the direction of the highest conductivity accelerates trapping of free charge carriers generated by light excitation and thus accelerates the photocurrent decay. Models of trapping of charged particles diffusing in one dimension predict the charge density decay law $\sim \exp(-t^{1/3} - \eta^2 t)$ in a small bias field E, $eEa/2k_BT = \eta \ll C_{tr}$; ($e$ is the magnitude of the electronic charge, a the lattice constant, k_B the Boltzmann constant, T the temperature, C_{tr} the trap concentration) whereas in strong fields the decay is $\sim \exp(-\eta t)$ [1–3]. This result refers to a so-called case of fast trapping, when the ratio between the trapping and the diffusion rates in zero bias, the parameter ω, is much greater than C_{tr}. In the opposite case, $\omega \ll C_{tr}$, the decay law in weak fields is $\sim \exp(-t^{1/2} - \eta^2 t)$ but in strong fields it remains $\sim \exp(-\eta t)$, differing only in the characteristic time scale [3]. Some of the predicted changes in the decay kinetics under the increasing magnitude of bias were observed in PDA-1-OH crystals [4].

A quite natural expectation of charge trapping acceleration in strong electric fields (large biases) may still not be justified if a crystal, in addition to traps, contains also the defects acting like scattering centers. Such a role can be played by broken bonds in polymeric chains or impurities with high-lying electron (hole) levels. The existence of these defects, restricting the charge carrier motion in finite chain segments or clusters can produce the opposite effect of a large bias, namely, the anomalous slow-down of charge trapping, resulting in an extremely slow decay of the charge density $\Delta\Omega(t)$. This possibility was first pointed out by Burlatsky and Ovchinnikov [5] who predicted a power (not exponential) asymptotics, $\Delta\Omega(t) \sim t^{-\alpha}$, $\alpha = C/2\eta$, $C = C_{tr} + C_b$, C_b is the concentration of scattering centers called below barriers. The effect of charge trapping slow-down in a large bias in the presence of barrier-type defects is confirmed here qualitatively but we came to another time dependence for $\Delta\Omega(t)$ at large times read as

$$\underset{\eta \gg C}{\Delta\Omega(t)} = \phi(t) = \frac{C_{tr}C_b}{C^2}\alpha\Gamma(1+\alpha)\frac{\ln(t/\tau) + \alpha^{-1} + 0.5772}{(t/\tau)^\alpha} \tag{1}$$

where $\Gamma(\alpha)$ is the gamma-function, the definitions of the time scale τ is given below.

The important distinctions between our and the previous results are as follows:

(i) The full time dependence $\Delta\Omega(t)$ is obtained for the cases of fast and slow trapping.

(ii) The use of the master equation formalism allows to trace the field dependence of trapping and recombination kinetics without restrictions on the parameter η, supposed to be small when the diffusion equation is used as it did in [1, 5, 6].

(iii) As a result we get the full field dependence of the characteristic time scale $\tau(\eta)$ (wrong limiting cases for $\tau(\eta)$ given in [6] are most likely due to misprints). At last it is claimed here that an asymptotic of pairwise charge recombination in a chain with barrier-type defects is also described by equation (1) with appropriately changed definitions of the parameters α and τ.

At first, let us consider the charge trapping in a chain assuming the chain defects, traps and barriers, to be distributed at random and not penetrable for charge carriers. Thus, under the assumption of a small charge carrier concentration the problem reduces to finding the survival probability (SP) of a charged particle in a single cluster built up of n host chain sites and with defected sites at its ends. Averaging this quantity over the cluster length distribution we obtain the exact expression for the configurationally averaged SP [7]

$$\Delta\Omega(t) = \langle\Omega(t)\rangle - \frac{C_b^2}{C^2} = \sum_{n=1}^{\infty} n(1-C)^{n-1} \times \{C_{tr}^2\Omega_n^{(tr,tr)}(t) + C_b C_{tr} \times [\Omega_n^{(b,tr)}(t) + \Omega_n^{(tr,b)}(t)]\}, \tag{2}$$

where the particle SP in a cluster is defined as

$$\Omega_n^v(t) = n^{-1}\sum_{j,j_0=1}^{n} G_{j,j_0}^v(t), \tag{3}$$

and $G_{j,j_0}^v(t)$ is the probability to find a particle on the jth site of a cluster v (with two traps at its ends — v = (tr, tr), with a barrier at the left end and with a trap at the right one — v = (b, tr) and vice versa — (tr, b)) at time t, given its initial position in the same cluster at the j_0-th site.

Using master equations

$$\frac{dG_{j,j_0}^v(t)}{dt} = [-2\,\mathrm{Ch}(\eta) + (q - \omega_1^v)\delta_{j,1} + (q^{-1} - \omega_n^v)\delta_{j,n}]G_{j,j_0}^v(t) + (1-\delta_{j,1})q^{-1}G_{j-1,j_0}^v(t) + (1-\delta_{j,n})qG_{j+1,j_0}^v(t),$$

$$G_{j,j_0}^v(0) = \delta_{j,j_0},$$

$$\omega_1^v = \begin{cases} q\omega \\ q\omega, \\ 0 \end{cases} \quad \omega_n^v = \begin{cases} q^{-1}\omega & v = (\mathrm{tr},\mathrm{tr}), \\ 0 & v = (\mathrm{tr}, b), \\ q^{-1}\omega & v = (b, \mathrm{tr}), \end{cases} \tag{4}$$

to describe the particle dynamics in a cluster, we get

$$G_{j,j_0}^v(t) = \frac{\exp[\eta(j_0 - j)]}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} g_{j,j_0}^v(s)\exp(st)\,ds, \tag{5}$$

where

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

$\beta_{\gamma 1(n)}^v = \omega_{1(n)}^v - \exp\left(\binom{+}{-}\eta\right)$ and the dimensionless time is used (the time unit is W^{-1}, W is the jumping rate of a charge carrier between the nearest-neighbour host chain sites in zero bias, i.e. the diffusion rate).

The calculation of the averaged SP in line with equations (2)–(6) (see for details [8]) leads to

$$\Delta\Omega(t)_{\eta \gg C} = \phi(t) + \frac{C_{tr}}{C}\exp(-Kt), \tag{7}$$

where the time scale of the function $\phi(t)$ given above and the rate constant K are defined by the following relations

$$\tau^{-1} = \frac{2\omega\,\mathrm{Sh}(\eta)}{1 + \dfrac{\omega}{2q\,\mathrm{Sh}(\eta)}},$$

$$K = 2\,\mathrm{Sh}(\eta) \times \begin{cases} C, & \omega \gg C \\ \omega, & \omega \ll C. \end{cases} \tag{8}$$

Note that equation (7) predicts a sharp change in trapping kinetics which is exponential at the initial stage $t \lesssim K^{-1}$, and the power or logarithmic-power type at large times, $t \gg K^{-1}$. As is seen from equation (1) the dependence $\sim t^{-\alpha}$ can be regarded as an intermediate asymptotic of $\Delta\Omega(t)$. It is also worth mentioning that equations (7) and (8) allows one to say definitely at what time the slow dependence of the charge density is "switched on" and what part of the initial number of free charge carriers escapes from being trapped at this time. Clearly, these are important questions to be answered if one tries to interpret experimental data (for instance, on photocurrent kinetics) using the dependence obtained above.

Let us turn now to geminate recombination assuming it to be the main path for free charge carriers to die. In this case the averaged SP of a pair of particles, say electron and hole, generated in a chain with barrier-type defects at the initial distance $n_0 \ll C_b^{-1}$ is defined by

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

where $\Omega_{n,n_0}^{e-h}(t')$ is the SP of a pair in a cluster with n

$$g_{j,j_0}^v(s) = \begin{cases} \dfrac{[\mathrm{Sh}(j\xi) + \beta_1^v\,\mathrm{Sh}((j-1)\xi)][\mathrm{Sh}((n-j_0+1)\xi) + \beta_n^v\,\mathrm{Sh}((n-j_0)\xi)]}{\mathrm{Sh}(\xi)[\mathrm{Sh}((n+1)\xi) + (\beta_1^v + \beta_n^v)\,\mathrm{Sh}(n\xi) + \beta_1^v\beta_n^v\,\mathrm{Sh}((n-1)\xi)]}, \\ j \leqslant j_0 \\ j \leftrightarrow j_0,\ j \geqslant j_0 \end{cases} \tag{6}$$

host sites and reflecting ends averaged over all possible initial positions of the pair in the cluster.

The two-particle distribution function $\rho_{i,j}(t')$ needed for calculations of $\Omega^{e-h}_{n,n_0}(t')$ satisfies master equations written as

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

where the parameter ω', an analogue of ω, represents the ratio of the electron–hole recombination rate, when the particles are separated by the minimal distance a, to the relative diffusion rate $W_e + W_h$, $\sigma_{e(h)} = W_{e(h)}/(W_e + W_h)$, $W_{e(h)}$ has the same meaning for an electron (hole) as the notation W used above, time t' is expressed in units $(W_e + W_h)^{-1}$. Coordinates of a hole (i) and an electron (j) in a cluster are chosen so that their position at the end host sites corresponds to $i = j = 1$ (particles cannot move one through another). In accordance with equation (10), an external field promotes charge separation. For the opposite field direction the opposite sign of η should be used.

Note here that the appearance of the "slow" term in equation (7) is due to the contribution into the average (2) from clusters with $n > C^{-1}$ and with reflecting and absorbing ends and only those of the latter where the charge drift is directed to the reflecting cluster end. In such clusters, as can be easily shown from equations (5) and (6), the charge density has at large times its maximum at the cluster end opposite to the absorbing one and decreases exponentially when going from the reflecting end.

By anology, the asymptotics of equation (9) is defined by those clusters, in which an electron and a hole are kept by the external field near the opposite cluster ends. The corresponding solution of equation (10) in strong fields and at large times takes the form (exponentially small corrections are neglected)

$$\rho_{i,j}(t') \sim \exp\,[-2\eta(i+j)]\,\exp\left[-\exp\,(-2\eta n)\,\frac{t'}{\tau'}\right] \quad (11)$$

that does not depend on n_0. The definition of τ' in equation (11) coincides with that of τ up to the replacement of ω by ω' in equation(8).

Thus,

$$\Omega_{n,n_0}(t') \sim \exp\left[-\exp\,(-2\eta n)\,\frac{t'}{\tau'}\right], \quad (12)$$

using which in equation (9) gives (for $C_b \ll 1$).

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

In zero field the asymptotics of the charge density decay due to a recombination is the same (for the nonideal chain considered) as for the case of trapping, i.e. $\sim \exp(-t^{1/3})$ [9]. In weak fields, $\eta \ll C_b$, one can expect the following change in the recombination kinetics at sufficiently large times, $\exp(-t^{1/3}) \to \exp(-t)$, similar to that characteristic of trapping kinetics, see above. The comparison of these dependences with equation (13) shows that the recombination process will slow down in strong fields and the slow-down accompanied with a considerable change in the charge density decay kinetics.

It should be emphasized that using the arguments similar to those given in [5, 6] one can show that the asymptotics (1) and (13) are also valid for a randomly disordered system of any dimension when host sites (molecules) form isolated cavities in an inert solvent.

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