Decay Dynamics in Disordered Systems: Application to Heavily Doped Semiconductors

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We have calculated, quantitatively, the time decay of donor-acceptor pair luminescence in compensated semiconductors, incorporating the effect of the potential fluctuations which exist in such materials. We show that the often-reported stretched-exponential decay law can here be derived rigorously, but only to a very close approximation, and, moreover, only provided that there is an alternate, activated, decay path. We also show that in the absence of such an alternate path, the decay is slower. We thus conclude that the stretched-exponential "law" provides good empirical fitting, but has no fundamental significance. [S0031-9007(98)05620-8]

PACS numbers: 71.55.Jv, 78.55.Et

It is well known that the decay dynamics in many disordered physical systems is generally slower than exponential decay. A very frequently reported dependence is that of stretched-exponential decay, the so-called Kohlrausch law. Examples include electrical response in disordered dielectrics and ionic conductors [1], hydrogen diffusion in hydrogenated amorphous silicon (*a*-Si:H) [2], persistent photoconductivity (PPC) in mixed semiconductors [3,4], and the decay of luminescence in disordered materials such as glasses, e.g., As_2S_3 [5] or ceramics, e.g., Cr^{3+}-doped β alumina [6].

It is usually assumed that fluctuations, for instance, in electric potentials, caused by some disorder in charge distributions, play a role in these slow decay phenomena. This view has recently been confirmed, quantitatively, by Bondarev and Pikhitsa [7], for conductivity phenomena in ionic glasses, where such phenomena result entirely from the behavior of ions. However, there exists another class of systems, including many showing PPC and/or luminescence, which contain carriers in addition to ions, and which show analogous slow decays. There is, to our knowledge, no quantitative treatment for such systems. In the present Letter, we analyze this case, specifically considering the time-resolved photoluminescence (TRPL) of donor-acceptor pairs (DAP) in heavily doped and compensated semiconductors. For these materials, potential fluctuations, because of electric fields resulting from some disorder in the distribution of ionized species, have long been predicted [8], and a number of experimental data on photoluminescence (PL) have been qualitatively interpreted on this basis (e.g., GaAs:Mg [9] and ZnSe:N [10,11]). We show, quantitatively and from basic principles, that TRPL in such systems can indeed give a stretched-exponential decay to a very close approximation. This type of decay, however, is obtained only if, in addition to the DAP radiative recombination, there are activated processes leading to alternate recombination paths (presumably nonradiative); we also show that in the absence of such an activation step (using a limit of zero

temperature) the decay is even slower than stretched exponential. We have confirmed this result experimentally, using heavily doped and compensated ZnSe:N. Moreover, we also compare our results to an earlier analysis [12] (THA model) of decay in compensated semiconductors, where fluctuations were not included; we show that there is a critical difference in the decay at a given emission wavelength, and explain this in terms of basic physics.

To obtain results on our DAP system, one must add the influence of fluctuations to "standard" DAP luminescence theory (see, e.g., Refs. [12,13]). Such PL results from recombination between an electron localized on a donor and a hole localized on an acceptor with probability $W(R) = W_{\max} \exp[-2R_B/R]$, where $W_{\max}$ is a constant, R is the donor-acceptor pair separation, and R_B is the Bohr radius of the shallower impurity; the energy of emission $h\nu$, in standard theory [12,13], is related to R by

$$h\nu = E_G - (E_A + E_D) + \frac{e^2}{\varepsilon R}, \qquad (1)$$

where E_G is the band gap, E_A and E_D are the acceptor and donor activation energies, respectively, e is the electron charge, and ε is the dielectric constant. In addition, there will also be thermal activation of carriers from the impurities into the appropriate band; considering only the shallower impurity, the donor in ZnSe, we can write a probability of such a process as

$$W_{nr} = W_{nr}^0 \exp[-E_D/kT], \qquad (2)$$

where W_{nr}^0 is a constant, k is the Boltzmann constant, and T is the temperature.

However, for systems of present (main) interest, i.e., those which have long-range—Coulomb—fluctuating internal electric fields, Eqs. (1) and (2) should be modified. Specifically, in this case, the system energies (relative to some absolute "reference energy") become dependent on a coordinate **r** through local values of the fluctuating potential $\varphi(\mathbf{r})$, which is the sum of the electric potentials at

r due to all ionized species in the material. Thus, a fluctuation term

$$U[\varphi] = e[\varphi(\mathbf{r}_D) - \varphi(\mathbf{r}_D + \mathbf{R})], \qquad (3)$$

because of the potential difference of the electron at the donor coordinate $\mathbf{r}_D$ and at the acceptor coordinate $(\mathbf{r}_D + \mathbf{R})$, where $|\mathbf{R}| = R$, must be added to the equation for the energy of the DAP emission, Eq. (1),

$$h\nu = E_G - (E_A + E_D) + \frac{e^2}{\varepsilon R} + U[\varphi]. \qquad (4)$$

While Eq. (1) gives a unique relation between $h\nu$ and R, an essential element in our theory is that the presence of $U[\varphi]$ breaks this unique relation. *In other words, DAPs with all possible separations as well as appropriate fluctuation energies can, in principle, contribute to the emission at a particular wavelength.*

We would like to emphasize that although fluctuations were considered in Ref. [7], the present physical system treats, in addition, charge carriers and their recombination properties [via Eqs. (2) and (4)], and is thus quite different from the case of ionic conductors treated earlier [7] (and, therefore, corresponding changes in the mathematical analysis are now also required).

Further, a fluctuation term

$$U_1[\varphi] = e[\varphi(\mathbf{r}_D + \mathbf{R}_i) - \varphi(\mathbf{r}_D)], \qquad (5)$$

containing a vector $\mathbf{R}_i$ ($|\mathbf{R}_i| = R_i$) that determines the "direction" of ionization, should be added to the donor activation energy in Eq. (2). This follows since, for an electron to be ionized, it must be removed from the vicinity of the donor, and thus the coordinate of the electron is effectively changed. In a system without fluctuations, a free electron would have an energy independent of its position in the material; however, with fluctuations, its energy becomes dependent on the value of the fluctuation potential at the new coordinate of the electron. Therefore, not all "directions" of ionization are equivalent, and, thus, the vector quantity characterizing such a process must be introduced.

For convenience of calculation we take the zero energy as $E_G - E_A - E_D$, defining an effective emission energy as $E = h\nu - E_G + E_A + E_D$. Including the required averaging over all possible realizations of the fluctuations, the mathematical generalization of the THA approach [12] for the time-dependent luminescence intensity $I_E(t)$ per unit energy interval near the value E, with the further inclusion of alternate paths, leads to the expression

$$I_E(t) = \langle Q(t) \rangle 4\pi(N_A - N_D) \int_0^\infty W(R) \exp[-W(R)t]$$
$$\times \left\langle \exp\left\{-W_{nr}^0 t \exp\left[-\frac{E_D + U_1[\varphi]}{kT}\right]\right\}\right.$$
$$\left.\times \delta\left(E - \frac{e^2}{\varepsilon R} - U[\varphi]\right)\right\rangle_{\{\varphi\}} R^2\, dR. \qquad (6)$$

Here, the δ function reflects the contribution of all suitable DAPs at the energy E, and $\langle\cdots\rangle_{\{\varphi\}}$ means

a normalized functional averaging over φ; Eq. (6) also contains the function $\langle Q(t) \rangle = \exp[4\pi(N_A - N_D) \int_0^\infty \{\exp[-W(r)t] - 1\}r^2\, dr]$, which is defined in [12] in such a way that the total light decay at $T = 0$ equals $-d\langle Q(t)\rangle/dt$. Note that in the absence of the fluctuations and alternate paths, Eq. (6) reduces to the corresponding equation in [12].

First, let us obtain the total light decay $I(t)$ by integrating Eq. (6) over all possible E. The functional average $\langle \exp\{-W_{nr}^0 t \exp[-\frac{E_D + U_1[\varphi]}{kT}]\}\rangle_{\{\varphi\}}$ left as a result of this procedure can be derived using the method developed in [7]. For the systems of present interest, the specific case of "frozen" fluctuations (with a temperature of "freezing," T_g [14]) has to be applied since the relevant charges are immobile at the temperatures where DAP PL can still be observed ($T < 100$ K). Further, it is important to note that electronic states with $E_D + U_1[\varphi] < 0$ are effectively delocalized, and thus, they do not contribute to the activated processes. Hence the functional average over fluctuations should be carried out only over the range $E_D + U_1[\varphi] \geq 0$. The explicit averaging gives a closed form for the intensity $I(t)$,

$$I(t) = -\frac{d\langle Q(t)\rangle}{dt} \frac{2[1 + \mathrm{erf}(\frac{E_D}{E_*})]^{-1}}{\sqrt{\pi}} \int_{-E_D/E_*}^\infty dy$$
$$\times \exp\left[-y^2 - W_{nr}^0 t \exp\left(-\frac{E_D + E_* y}{kT}\right)\right], \qquad (7)$$

where $\mathrm{erf}(z)$ is the error function, and $E_*^2 = \frac{4kT_g e^2}{\varepsilon R_i}[\frac{R_i}{R_s} - 1 + \exp(-\frac{R_i}{R_s})]$ is a parameter which is related to the magnitude of the fluctuations through the screening radius R_s [15] and the temperature T_g [14].

The integral factor in Eq. (7), as can be shown, gives, to a close approximation, the Kohlrausch-type decay, so that $I(t)$, for the most part, would follow this type of decay at relatively high temperatures, when the activation processes become significant. However, with decreasing temperatures, the influence of this integral factor decreases, and it will become noticeable only at very large t (usually larger than the experimentally observable region). In the low temperature region the factor $-d\langle Q(t)\rangle/dt$ would dominate, and it gives a decay which is slower than stretched exponential [12]. In the limit of $T = 0$, as can be seen from Eq. (7), the total light decay is the same as in the earlier treatment of THA [12]; this is as expected since potential fluctuations merely redistribute the intensities of emission at different wavelengths.

We next consider the case of emission at a particular wavelength, i.e., $I_E(t)$, and show that the result is now quite different from that in [12]. The direct averaging in Eq. (6), however, is not straightforward. But by approximating the average of the product by the product of the averages, then using the Fourier representation for a δ function, and finally following the method [7], it is possible to show, after a simple transformation of $\langle Q(t)\rangle$,

$$I_E(t) = \frac{\tilde{n}\xi^3}{2\sqrt{\pi}} \frac{W_{\max}}{E_*} \left[1 + \mathrm{erf}\left(\frac{E_D}{E_*}\right)\right]^{-1} \int_{-E_D/E_*}^{\infty} dy \exp\left[-y^2 - W_{nr}^0 t \exp\left(-\frac{E_D}{kT} - \frac{E_*}{kT}y\right)\right]$$

$$\times \exp\left\{-\frac{\tilde{n}}{6}\tilde{t}\int_0^{\infty} dx\, x^3 \exp[-x - \tilde{t}\exp(-x)]\right\} \int_0^{\infty} \frac{du\, u^{5/2}}{\sqrt{u - 1 + \exp(-u)}}$$

$$\times \exp\left\{-\xi u - \tilde{t}\exp(-\xi u) - \eta \frac{(\tilde{E}u - 1)^2}{u[u - 1 + \exp(-u)]}\right\}. \tag{8}$$

Here, we have introduced a dimensionless time $\tilde{t} = W_{\max}t$ and energy $\tilde{E} = \varepsilon R_s E/e^2$, as well as parameters $\xi = 2R_s/R_B$, $\eta = e^2/(4T_g\varepsilon R_s)$, and $\tilde{n} = \pi(N_A - N_D)R_B^3$, which have allowed us to have all integrals as dimensionless factors, so that only the prefactor carries information on the intensity units.

The fluctuations, in the presence of alternate paths, change $I_E(t)$ (at $T > 0$) to a predominantly stretched-exponential type, due to the first integral [see discussions of Eq. (7) above]. The radiative part (in the case $T = 0$, this is the only contribution to the intensity), however, is even slower than stretched exponential. These results are in sharp contrast to [12], which predicts an exponential decay of PL intensity at a particular wavelength [the result of [12] can be obtained from Eq. (8) in the limit when $R_s \to \infty$ and $W_{nr} \to 0$]. Note that the first integral in Eq. (8) at low temperatures would differ from $(\sqrt{\pi}/2)[1 + \mathrm{erf}(\frac{E_D}{E_*})]$ only at very large times [analogously to the previously discussed situation for $I(t)$; see Eq. (7)].

Let us now consider Eq. (8) in the limit $T = 0$. Deriving the asymptotic behavior ($\tilde{t} \to \infty$) of $\langle Q(t)\rangle$ as well as that of the fluctuation factor by the saddle point method, we obtain the time-dependent intensity of luminescence at given $\tilde{E}$

$$I_E(t) \propto \sqrt{\xi}\exp(-\eta\tilde{E}^2)\frac{(\ln\tilde{t})^2}{\tilde{t}}$$

$$\times \exp[-0.483(N_A - N_D)R_B^3(\ln\tilde{t})^3], \qquad \tilde{t} \to \infty. \tag{9}$$

It is to be noted that according to our theory, in disordered semiconductors, the asymptotic behavior of TRPL at all wavelengths follows the same law, i.e., all curves of the time dependence of PL intensity will be parallel. With decreasing magnitude of fluctuations (i.e., with the increase of R_s) the amplitude of $I_E(t)$ [Eq. (9)] will decrease. The asymptotic behavior of the total light decay, as easily verified by integration of $I_E(t)$ over all E, also will follow the temporal dependence of Eq. (9).

For comparison of our results to experimental data, which we do for $T = 10$ K, it must be noted that W_{nr} hardly contributes in this temperature range [16]. Thus, Eq. (8) at $T = 0$ can be used for accurate fitting of data. The fit to the data from ZnSe:N (at an emission wavelength of $\lambda = 4825$ Å) is shown in Fig. 1. The fit was obtained with $\xi = 3.9$, $\eta = 0.065$, $N_A - N_D = 5.7 \times 10^{17}$ cm^{-3}, and $W_{\max} = 3.4 \times 10^9$ s^{-1}. These values

are quite reasonable for our system, assuming $R_B = 24$ Å (which corresponds to the reported donor depth of 45 meV; see, e.g., Ref. [17]); also, the values of the dimensionless parameters are compatible with our estimates for R_s and T_g. Moreover, note that the fitting procedure is rather sensitive to the values of $W_{\max}$ and $N_A - N_D$; note that our value of $W_{\max}$ is in excellent agreement with a value of 2.7×10^9 s^{-1} predicted from scaling theory [18] based on results on ZnSe:Na [18]. Also, for comparison, in the inset of Fig. 1, we plot the experimental data in a double logarithmic scale, a scale in which the stretched-exponential function is a straight line; this clearly shows that the Kohlrausch function does not fit these data in all time intervals.

A very important conclusion of our work is that the PL decay in heavily doped materials will be of the stretched-exponential form, or slower, for decay at a given wavelength. This is in contradiction with earlier results [12]; this contradiction is not surprising since in the absence of fluctuations only pairs at a given separation contribute to the decay under these conditions, whereas fluctuations lead to an averaging over all decay pairs. A comparison to experimental data (Fig. 1) gives
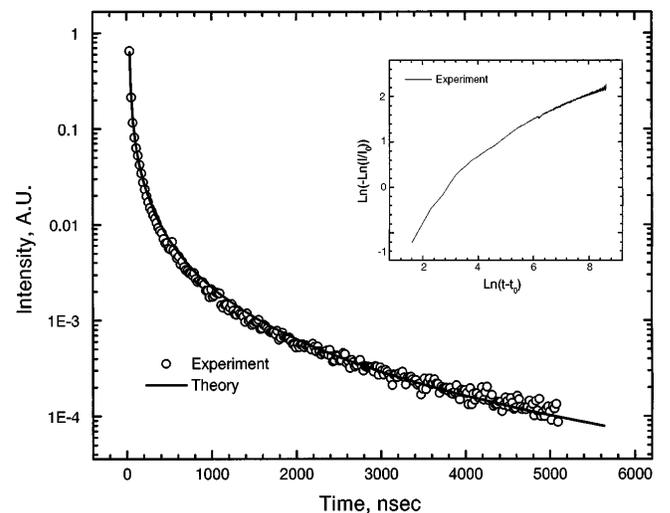

FIG. 1. Comparison of fluctuation theory to experimental time-resolved photoluminescence on ZnSe:N. Open circles are the experimental data; the solid curve is the theoretical fit with parameters $\xi = 3.9$, $\eta = 0.065$, $W_{\max} = 3.4 \times 10^9$ s^{-1}, and $N_A - N_D = 5.7 \times 10^{17}$ cm^{-3}. The inset shows the data in a double logarithmic scale, a scale in which the stretched-exponential function is a straight line.

good agreement, which we regard as an excellent proof of fluctuations. We also note that we have analyzed comparable data of THA [12] (their Figs. 3 and 10) and find that these data also show a decay which is slower than exponential; fluctuations are thus not unique to the ZnSe:N system but are present in compensated semiconductors in general, as expected.

Another important conclusion of this work is that PL at a particular wavelength at longer times has an identical decay. Further, we would like to emphasize that the present approach can, in principle, be applied to other similar phenomena. An example is PPC [3] in mixed semiconductors, where the recombination of electrons and holes in PPC is very similar to that for donor-acceptor pair PL.

In summary, we have shown that the frequently reported stretched-exponential decay law can be rigorously derived for DAP luminescence decay to a very close approximation in materials with potential fluctuations, provided that there is, in addition, an activated alternate decay path. Moreover, we have also shown that in the absence of such an alternate path, the stretched-exponential law does not hold, and the decay is even slower. Thus, an important conclusion is that this law has no fundamental significance, but merely often provides a good empirical fit; this point is reinforced by the results of Bondarev and Pikhitsa [7], who obtained similar results for conductivity phenomena in ionic glasses.

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[14] Note that one will obtain frozen fluctuations if the relevant charges are immobile. This is obviously the case, at usual temperatures, if the charges are ions, which was the situation considered in [7]. For the systems of present interest, the impurities, of course, are immobile, but there are, in addition, free carriers in the bands. However, as the temperature decreases, the (majority) carriers will be captured on the dopants (majority impurity). Once the remaining free carriers become fewer in number than the minority impurities, at a temperature we denote by T_g, the fluctuations will effectively be frozen. To obtain T_g one requires N_A and N_D, which are difficult to obtain for heavily compensated materials, but for such materials T_g can be estimated to be higher than 300 K.
[15] The role of the screening radius is discussed in Ref. [7], but this does not cover how to obtain it for the present system. For the present case, various approximations have been proposed in the literature, although we are not aware of any exact evaluations; however, approximations generally agree adequately, within their validity ranges. For the present ZnSe:N sample, we estimate R_s, according to G. F. Neumark, Phys. Rev. B **5**, 408 (1972), and get a value of 70–110 Å.
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