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An effective-medium theory has been developed to describe the nondispersive charge carrier transport in a disordered organic material containing extrinsic traps. The results of calculations are compared to predictions of the Hoesterey and Letson formalism, which has been widely used before to describe trapping. We argue that our theory describes more adequately charge transport in the presence of traps since it accounts for the effects of disorder. Also it was found that both the relaxation of the ensemble of majority charge carriers within the combined intrinsic and extrinsic density of state distribution and the occurrence of trap-to-trap migration alters the temperature dependence of the charge mobility significantly, notably at lower temperature.

Keywords: effective-medium approach; organic materials; transport; traps

1. INTRODUCTION

Charge carrier transport phenomena in disordered organic solids have been the subject of intensive research for many years (for reviews, see [1–4]) that was stimulated by the use of these materials in modern

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electronic techniques. Many recent studies have been described within the framework of the Gaussian disorder model of Bässler and coworkers [4,5]. The model is premised on the argument that charge carrier transport occurs by hopping through a Gaussian density of transport states (DOS) of energetic width σ. In the framework of this model, an analytical Effective-Medium Approach (EMA) was recently developed [6] for effective drift mobility. One of the most important limitations of the disorder formalism is, however, that it does not address carrier transport in the presence of traps. Traps in disordered media are the extrinsic localized states that differ from the majority of hopping (transport) states in that they require substantially larger energy input to release the charge carriers back to the intrinsic DOS. To obtain the relationship of the trap-controlled to trap-free mobility, the Hoesterey and Letson expression [7] has usually been used and is based on a discrete trap depth argument without disorder effects.

In the present work, the EMA is formulated to describe charge transport in the presence of traps. We consider here the dependence of mobility on the temperature in trap-containing materials. The results of the EMA calculation are found to be in good agreement with experimental data.

2. THEORETICAL FORMULATION

This work extends the recently suggested EMA [6] to describe charge transport in the presence of trapping. The disordered medium is replaced by an effective ordered medium (cubic lattice of sites with spacing a which is equal to the average distance between all localized states). Each lattice site can be either a trap or intrinsic transport (hopping) site with a relative concentration c or $1 - c$, respectively. We take into account only the site energetic disorder. We assume a Gaussian density-of-states (DOS) distribution of intrinsic transport sites. Trap states are also distributed in energy according to a Gaussian function, but they are offset to lower energies with respect to the center of the intrinsic DOS by $-E_t$ ($E_t > 0$). Thus, the cumulative DOS in this case is a superposition of two Gaussians. The case $c = 0$ implies a trap-free disordered system, while $c = 1$ means that charge carrier transport occurs only via the traps.

A self-consistent EMA theory based on a two-site cluster approach was formulated [6] to describe nondispersive charge carrier transport in a trap-free disordered organic system. This theory involves transcendental equations that allow the calculation of the effective parameters W_e^+ and W_e^- which describe the effective jump rates along

and opposite to the electric field (**E**) direction. By definition, the effective drift mobility is

$$\mu_e = a\frac{W_e^+ - W_e^-}{E} \tag{1}$$

In the case of large energetic disorder, one has [6,8]:

$$W_e^+ = \langle W_{12}^+ \rangle, \qquad W_e^- = \langle W_{21}^- \rangle, \tag{2}$$

where the angular brackets denote configuration averaging. In this case, the parameters W_e^+ and W_e^- must be determined using the Miller-Abrahams expression for the jump rate between sites with energies ε_j and ε_i:

$$W_{12}^+ = W_0 \exp\left(-\frac{|\varepsilon_2 - \varepsilon_1 - eaE| + (\varepsilon_2 - \varepsilon_1 - eaE)}{2k_BT}\right), \tag{3}$$

$$W_{21}^- = W_0 \exp\left(-\frac{|\varepsilon_1 - \varepsilon_2 + eaE| + (\varepsilon_1 - \varepsilon_2 + eaE)}{2k_BT}\right), \tag{4}$$

where $W_0 = v_0 \exp(-2a/b)$, and b is the localization radius of a charge carrier. An essential point is that the value of W_0 was taken in the derivation of (2) as being equal for all neighbor sites (the absence of positional disorder).

When traps are present in a disordered system, the calculation of W_e^+ and W_e^- becomes much more complicated. The problem is that the parameter W_0, which describes a tunneling transition of a carrier between neighbor sites, could in principle be different for the cases of (i) transitions between intrinsic transport sites, (ii) transitions between an intrinsic transport- and a trap site, and (iii) trap-trap transitions. Therefore, the present analysis will be restricted to the case of equal W_0 parameters for all the above-mentioned types of transitions. With this approximation, (2) remains unchanged for the trap-containing systems as well. The presence of traps has to be taken into consideration at the configurational averaging stage of the analysis.

First let us calculate the parameter W_e^+. One has to choose the distribution functions for the target and starting states. As was demonstrated [6,8], one should perform the configurational averaging over the energy distributions of the starting state, ε_1, and the target state, ε_2. In this case, the target and starting states are described by the density-of-states (DOS) distribution, $P(\varepsilon_2)$, and occupational density-of-states (ODOS) distribution, $P(\varepsilon_1)$, respectively. Let us

choose the normalized cumulative DOS distribution function for a trap-containing disordered system as follows:

$$P(\varepsilon_2) = \frac{1-c}{\sigma_0\sqrt{2\pi}}\exp\left(-\frac{1}{2}\left(\frac{\varepsilon_2}{\sigma_0}\right)^2\right) + \frac{c}{\sigma_1\sqrt{2\pi}}\exp\left(-\frac{1}{2}\left(\frac{\varepsilon_2+E_t}{\sigma_1}\right)^2\right). \quad (5)$$

Here, it is assumed that the energy distributions of the density of transport and trap states are described by Gaussian functions of width σ_0 and σ_1, respectively. To obtain an expression for $P(\varepsilon_1)$ in the form of an ODOS, one should normalize the product of $P(\varepsilon_1)$ [presented in the form similar to (8)] and $\exp(-\varepsilon_1/k_BT)$ to unity. When calculating W_e^-, one should take into account that the energies ε_2 and ε_1 in the expression for $\langle W_{21}^- \rangle$ correspond to a starting and a target state, respectively.

In the case of a large degree of energetic disorder ($\sigma_0/k_BT >> 1, \sigma_1/k_BT >> 1$), we obtain a final expression for the non-dispersive drift mobility (1)

$$\mu_e = \mu_2 \frac{Y_e^+ - Y_e^-}{f}, \quad (6)$$

where

$$Y_e^\pm = A\{(1-c)^2 i_1^\pm + (1-c)c\left(i_2^\pm + i_3^\pm \exp(xy)\right) + c^2 i_4^\pm \exp(xy)\}, \quad (7)$$

$$i_1^\pm = \frac{1}{2}\exp\left(\frac{x^2}{2}\right)\left\{\left(1-erf\left(\frac{\pm f}{\sqrt{2}}\right)\right)\exp\left(-\frac{x^2}{2}\pm xf\right) + \left(1-erf\left(\frac{x\mp f}{\sqrt{2}}\right)\right)\right\}, \quad (8)$$

$$i_2^\pm = \frac{1}{2}\exp\left(\frac{x^2}{2}\right)\left\{\left(1-erf\left(\frac{\pm f+y}{\sqrt{2}}\right)\right)\exp\left(-\frac{x^2}{2}+x(\pm f+y)\right) + \left(1-erf\left(\frac{x\mp f-y}{\sqrt{2}}\right)\right)\right\}, \quad (9)$$

$$i_3^\pm = \frac{1}{2}\exp\left(\frac{x^2\eta^2}{2}\right)\left\{\left(1-erf\left(\frac{\pm f-y}{\eta\sqrt{2}}\right)\right)\exp\left(-\frac{x^2\eta^2}{2}+x(\pm f-y)\right) + \left(1-erf\left(\frac{\eta^2 x\mp f+y}{\eta\sqrt{2}}\right)\right)\right\}, \quad (10)$$

$$i_4^\pm = \frac{1}{2}\exp\left(\frac{x^2\eta^2}{2}\right)\left\{\left(1-erf\left(\frac{\pm f}{\eta\sqrt{2}}\right)\right)\exp\left(-\frac{x^2\eta^2}{2}\pm xf\right) + \left(1-erf\left(\frac{\mu^2 x\mp f}{\eta\sqrt{2}}\right)\right)\right\}, \quad (11)$$

$$x = \frac{\sigma_0}{k_B T}, \quad \eta = \frac{\sigma_1}{\sigma_0}, \quad y = \frac{E_t}{\sigma_0}, \quad f = \frac{eaE}{\sigma_0}, \quad \mu_2 = \frac{ea^2 \nu_0}{\sigma_0} \exp\left(-2\frac{a}{b}\right), \quad (12)$$

where $erf(z) = (2/\sqrt{\pi}) \int_0^z dt \exp(-t^2)$ is the error function.

In the limiting case where $f \to 0$ ($E \to 0$) and $y >> 1$, i.e. in the case of deep traps, relations (6–12) yield

$$\mu_e = \mu_e(0) \frac{\left[1 + c^2 \exp(xy)\right]}{1 + c\left\{\exp\left[xy + \frac{1}{2}x^2(\eta^2 - 1)\right]\right\}}, \quad (13)$$

where $\mu_e(0) = \mu_e(c = 0) = \mu_2 x \exp\left(-x^2/2\right)$.

Let us find a trap concentration $c_{1/2}$ at which the charge mobility drops by a factor of 2, $\mu_e/\mu_e(0) = 1/2$, under the condition $c << 1$. It is easy to see that

$$c_{1/2} \cong \exp\left[-\frac{E_t}{k_B T} - \frac{1}{2}\left(\frac{\sigma_0}{k_B T}\right)^2 (\eta^2 - 1)\right]. \quad (14)$$

Then, at $c >> c_{1/2}$, one has

$$\mu_e = \mu_e(0) \frac{1 + c^2 \exp(xy)}{c} \exp\left[-xy - \frac{1}{2}x^2(\eta^2 - 1)\right]. \quad (15)$$

From (15), one can obtain the critical trap concentration c_{cr} at which the effective charge carrier mobility reaches the minimum value μ_e^m

$$c_{cr} = \exp\left(-\frac{1}{2}\frac{E_t}{k_B T}\right), \quad (16)$$

$$\mu_e^m = \mu_e(0) 2 c_{cr} \exp\left[-\frac{1}{2}x^2(\eta^2 - 1)\right]. \quad (17)$$

Let us rewrite (15) in the form

$$\mu_e = \mu_e(0) c \frac{1 + \left(\frac{c}{c_{cr}}\right)^2}{\left(\frac{c}{c_{cr}}\right)^2} \exp\left[-\frac{1}{2}x^2(\eta^2 - 1)\right]. \quad (18)$$

For trap concentrations in the range of $c_{1/2} << c << c_{cr}$, relation (18) and the expression for $\mu_e(0)$ yield

$$\mu_e = \mu_2 c^{-1} \left(\frac{\sigma_0}{k_B T}\right) \exp\left[-\frac{E_t}{k_B T} - \frac{1}{2}\left(\eta \frac{\sigma_0}{k_B T}\right)^2\right]. \quad (19)$$

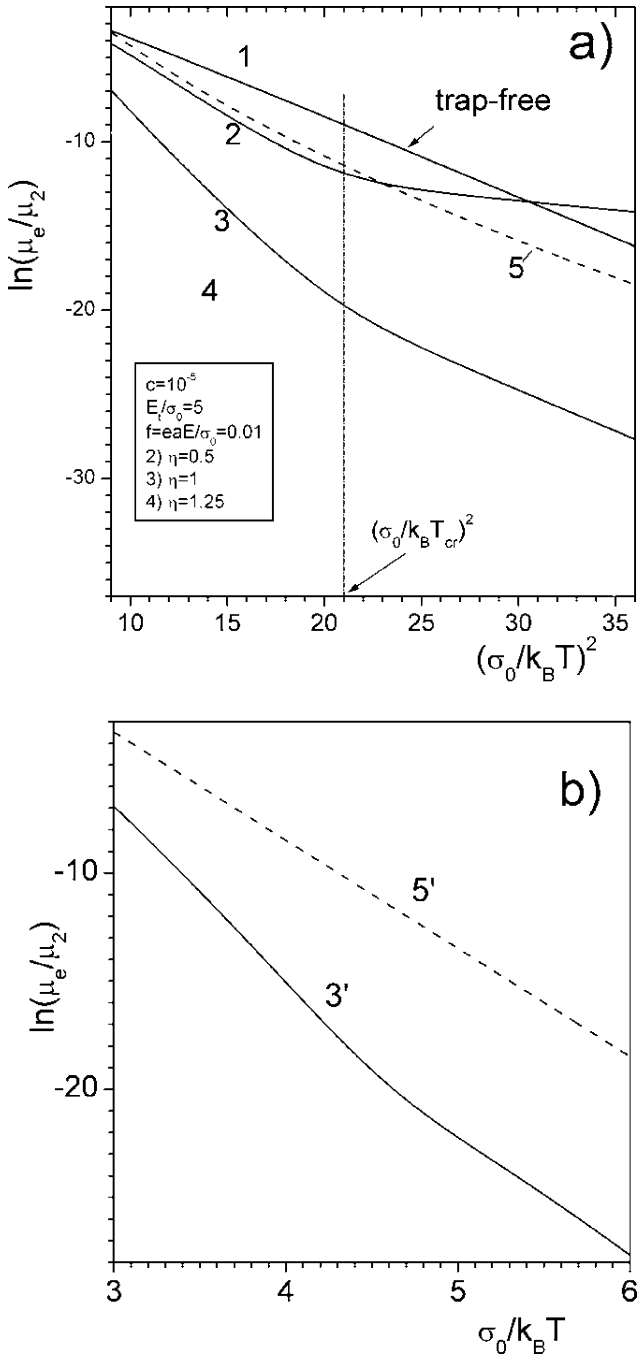
Further, for trap concentrations in the range of $c_{cr} << c \leq 1$, relation (18) leads to

$$\mu_e = \mu_2 c \left(\frac{\sigma_0}{k_B T}\right) \exp\left[-\frac{1}{2}\left(\eta \frac{\sigma_0}{k_B T}\right)^2\right]. \quad (20)$$

Thus, at c_{cr}, one expects a transition from trap-controlled to the trap-to-trap hopping transport, i.e. c_{cr} is the transition point between trap-controlled and trap-to-trap hopping transport which are described by (19) and (20), respectively.

3. TEMPERATURE DEPENDENCE OF CHARGE MOBILITY IN TRAP-CONTAINING DISORDERED SYSTEMS

Let us consider the temperature dependence of drift charge carrier mobility in a disordered material containing traps. Theoretical treatment of mobility over a broad temperature range reveals a critical temperature T_{cr} at which the transition from trap-controlled to trap-to-trap hopping transport regime occurs. The expression for T_{cr} at a concentration c can be obtained from (16) as $T_{cr} = -E_t/2k_B \ln(c)$. The temperature dependence of charge carrier mobility calculated by (6)–(12) for different parameters η is presented in Figure 1. The asymptotic behavior of the mobility in the temperature range $T > T_{cr}$ (trap-controlled transport regime) and in the range $T < T_{cr}$ (trap-to-trap transport regime) can be described by (25) and (26), respectively. One can see from (19) that the activation energy of charge mobility has two contributions in the range of $T > T_{cr}$. The first contribution is determined by the average trap depth E_t, and the second one by the width of the trap distribution in energy, $\sigma_1 = \eta\sigma_0$. For the parameters used in Figure 1a, T_{cr} corresponds to $(\sigma_0/K_B T_{cr})^2 \cong 21$. By using (19), one can estimate E_1 and σ_1 from the experimental data on the temperature dependence of charge mobility. On the other hand, it can be seen from (20) that, for $T < T_{cr}$, the activation energy of charge mobility contains only the contribution from the width of the energy trap distribution $\sigma_1 = \eta\sigma_0$, because transport proceeds at such temperatures via traps. From Figure 1a, one can see that the temperature dependence of charge mobility in the trap-containing disordered system depends considerably on the parameter η. For instance, at $\eta < 1$, i.e. when the width of the energy distribution of traps σ_1 is smaller than the width of the energy distribution of intrinsic hopping sites σ_0, the decrease of mobility with decrease in temperature in the range $T < T_{cr}$ (curve 2 in Fig. 1a) becomes less pronounced in comparison



to that for a trap-free system (curve 1). This can lead to a situation where the charge mobility in a trap-containing system at a certain temperature might even exceed that in the trap-free material. For purposes of comparison, curve 5 on Figure 1a shows the temperature dependence of charge mobility calculated from the Hoesterey-Letson formalism [7] neglecting the energetic disorder. In this case, for trap concentrations $c >> c_{1/2}$, one has $\ln(\mu_e/\mu_2) = -\ln(c) - (E_t/\sigma_0)\sqrt{(\sigma_0/k_BT)^2}$. Here, the activation energy of the mobility E_a is equal to the trap depth $E_a = E_t$. On the other hand, the present EMA theory, which accounts for the disorder effects, predicts the apparent activation energy of charge mobility to exceed $E_a = E_t + \eta^2\sigma_0^2/k_BT$ over the trap concentration range $c_{1/2} << c << c_{cr}(T > T_{cr})$. For trap concentrations $c_{cr} << c \leq 1$ $(T < T_{cr})$, one gets $E_a = \eta^2\sigma_0^2/k_BT$. This is illustrated by Figure 1b, where curves 3 and 5 of Figure 1a are replotted in the Arrhenius coordinates (curves 3′ and 5′, respectively).

An example comparing experiment and theory is given in Figure 2. This shows the temperature dependence of the zero-field hole mobility (symbols) measured in polyphenylenevinylene-ether (PPV-ether) [9] and that calculated by the above theory (solid line). To calculate the temperature dependence of charge mobility, we used the parameters σ_0, σ_1, E_t, and c obtained recently by TSL measurements [10] of an alkoxy-substituted PPV derivative (DOO-PPV). Assuming $\sigma_1 < \sigma_0$, i.e. $\eta < 1$, with $T_{cr} = 325\,K$, a reasonably good agreement between the theoretical calculation and experimental data is obtained.

4. CONCLUSION

The important message is that the effect of deep traps in a disordered organic photoconductor cannot be described in terms of the conventional Hoesterey and Letson model [7], which predicts an Arrhenius-type temperature dependence of charge carrier mobility, where the activation energy is simply the trap depth E_t. It turns out that both the relaxation of the ensemble of majority charge carriers within the

FIGURE 1 a) The calculated temperature dependence of charge mobility in the trap-free (curve 1) and trap-containing disordered system for different parameters $\eta = \sigma_1/\sigma_0 : 0.5$ (curve 2), 1 (curve 3), and 1.25 (curve 4) plotted in $\ln(\mu_e/\mu_2)$ vs. $(\sigma_0/k_BT)^2$ representation. The $\mu(T)$-dependence calculated with the Hoesterey-Letson formalism is given for comparison (curve 5). b) The same curves 3 and 5 but replotted in $\ln(\mu_e/\mu_2)$ vs. σ_0/k_BT representation (curves 3′ and 5′, respectively).

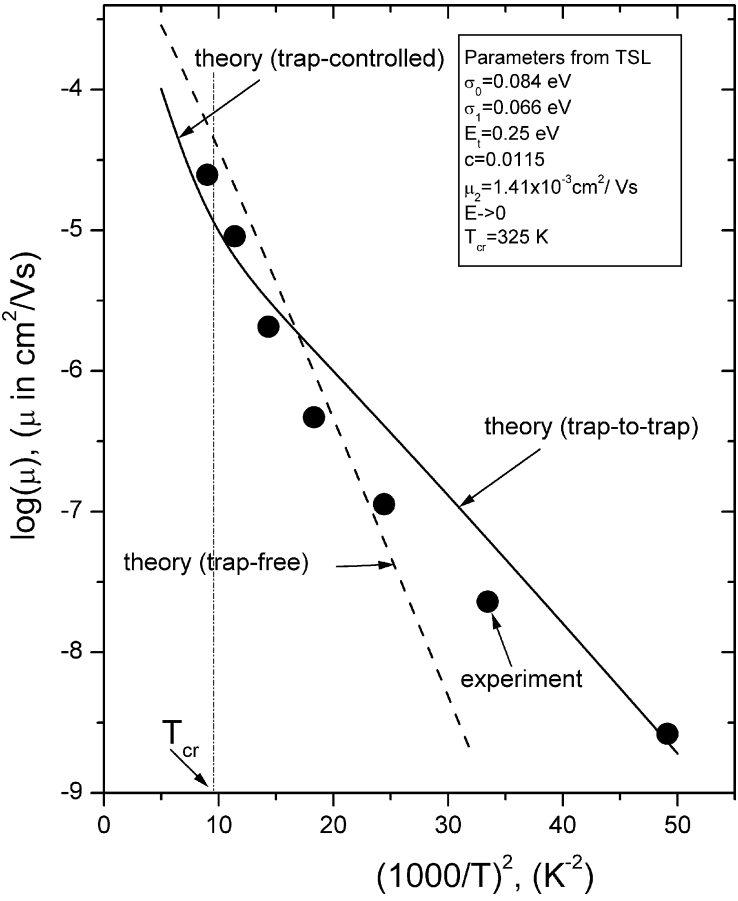


FIGURE 2 The temperature dependence of the zero-field hole mobility (symbols) measured in PPV-ether [9] and that calculated by the above theory (solid line) using parameters from TSL measurements [10].

combined intrinsic and extrinsic density of state distribution and the occurrence of the trap-to-trap migration alter the $\mu(T)$ dependence significantly, notably at lower temperatures when the apparent activation energy can become $< E_t$. Ultimately, $\mu(T)$ is controlled by the width of the distribution of trap levels. If it is narrower than that of the intrinsic DOS, the relaxation of charge carriers is diminished. As a result, the $\mu(T)$ dependence flattens and eventually the mobility in a trap-containing system can even exceed that of the undoped system.

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