Influence of traps on charge transport in organic semiconductors

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Abstract

The effect of extrinsic traps on the charge transport in organic semiconductors has been investigated. An analytical model describing hopping transport with traps is formulated on the basis of percolation theory. The results show that the presence of a trap distribution with energy offset and width different from that of the intrinsic density of states does not change the basic phenomenology of hopping transport, as revealed by the temperature dependence of the conductivity at high temperature. However the traps may significantly affect the transport at low temperature. The relation between trap concentration and conductivity is discussed. The model predictions are in good agreement with experimental results.
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1. Introduction

Over the past 10 years, the interest in organic semiconductors has increased dramatically. Devices such as organic light emitting diodes and organic field effect transistors have been realized [3,4]. In spite of these successful applications, the physical processes underlying the charge transport in organic semiconductors are not well understood. For example, a proper description of the effect of traps on charge transport is still a challenge. Extrinsic localized states differ from the majority of intrinsic hopping states in disordered media in that they require a substantially larger energy to release charge carrier to the intrinsic density of states (DOS). The Columb potential of trapped carriers will influence the charge transport [5]. Borsenberg studied the effect of traps on charge transport using computer simulation [1]. Arikipov has proposed a model for an effective transport energy for deep trap states. However, a direct proof for the existence such as energy in organic semiconductors is not known [8].

In this article we first derive an analytical expression for the trap-dependent conductivity based on the percolation theory. It is assumed that both intrinsic states and extrinsic traps are distributed with an exponential DOS of different widths, and that both distributions are occupied according to Fermi–Dirac statistics. Then we discuss the effect of traps on the conductivity of organic semiconductors. Finally we compare this model with experimental results.

2. Model theory

In organic semiconductors the transport of carriers is governed by hopping between localized states. The conductivity of such a system can be determined using percolation theory. The system is regarded as a random resistor network as proposed by Miller and Abrahams [9,11]. The current is flowing through bonds connecting the sites of such network. The conductance between the site i and j can be described as [12]

$$s_{ij} = \sigma_0 \exp\left(-2\alpha R_{ij} - \frac{|\epsilon_i - \epsilon_F| + |\epsilon_j - \epsilon_F| + |\epsilon_j - \epsilon_i|}{2k_B T}\right). \quad (1)$$

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Here, σ_0 is a prefactor, α^{-1} is the Bohr radius of the localized wave functions, R_{ij} denotes the distance between the sites i and j, and ϵ_i is the energy of carriers at site i. According to percolation theory [12,13], the critical conductance value s_c determines the conductivity of the system when the first infinite cluster occurs [11].

$$\sigma = \sigma_0 \exp(-s_c). \qquad (2)$$

In order to model the influence of traps in a simple manner, we assume a double exponential function for the DOS.

$$g(\epsilon) = \frac{N_t}{k_B T_0} \exp\left(\frac{\epsilon}{k_B T_0}\right)\theta(-\epsilon)$$
$$+ \frac{N_d}{k_B T_1} \exp\left(\frac{\epsilon - E_d}{k_B T_1}\right)\theta(E_d - \epsilon). \qquad (3)$$

Here N_t and N_d are the concentrations of intrinsic states and traps states, respectively, θ is the unit step function, T_0 and T_1 are parameters indicating the widths of the intrinsic and the trap state distributions, respectively, and E_d is Coulomb trap energy [14]. Vissenberg and Matters pointed out that they do not expect the results to be qualitatively different for a different choice of $g(\epsilon)$ [13], as long as $g(\epsilon)$ increases strongly with ϵ. Therefore, we assume that transport takes place in the tail of the exponential distribution. The equilibrium distribution of carriers, n, is determined by the Fermi–Dirac distribution as follows

$$n = \int \frac{d\epsilon\, g(\epsilon)}{1 + \exp\left(\frac{\epsilon - \epsilon_F}{k_B T}\right)}$$
$$= N_t \exp\left(\frac{\epsilon_F}{k_B T_0}\right)\frac{\pi T/T_0}{\sin \pi T/T_0}$$
$$+ N_d \exp\left(\frac{\epsilon_F - E_d}{k_B T_1}\right)\frac{\pi T/T_1}{\sin \pi T/T_1}. \qquad (4)$$

According to the classical percolation theory [12], at the onset of percolation, the critical number B_c can be written as

$$B_c = \frac{N_b}{N_s}, \qquad (5)$$

where $B_c = 2.8$ for a three-dimensional amorphous system. N_b and N_s are, respectively, the density of bonds and the density of sites in this percolation system, which can be calculated as follows [13,16]

$$N_b = \int d\mathbf{R}_{ij} d\epsilon_i d\epsilon_j\, g(\epsilon_i)g(\epsilon_j)\theta(s_c - s_{ij}) \qquad (6)$$

$$N_s = \int d\epsilon\, g(\epsilon)\theta(s_c k_B T - |\epsilon - \epsilon_F|). \qquad (7)$$

Here $\mathbf{R}_{ij}$ denotes the distance vector between sites i and j.

Substituting (4), (6) and (7) into (2), we obtain the expression

$$B_c = \frac{\pi N_t^2 \psi^3 \exp(2\eta) + \pi N_d^2 \xi^3 \exp(2\gamma) + \frac{\pi}{4}N_t N_d \exp(\eta + \gamma)(\psi^{-1} + \xi^{-1})^{-3}}{N_t \exp(\eta) + N_d \exp(\gamma)}$$
$$\qquad (8)$$

with

$$\eta = \frac{\epsilon_F + k_B T s_c}{k_B T_0}, \quad \gamma = \frac{\epsilon_F - E_d + k_B T s_c}{k_B T_1},$$
$$\psi = \frac{T_0}{2\alpha T}, \quad \xi = \frac{T_1}{2\alpha T}.$$

This equation is obtained under the following conditions:

- the site positions are random,
- the energy barrier for the critical hop is large,
- and the carrier concentration is very low.

The exponent s_c is obtained by a numerical solution of (8) and the conductivity can be calculated using (2). This model was initially proposed in [15], where a doping level E_d above the intrinsic level E_i was assumed. In the present work, we assume a trap level below the intrinsic level to study the effect of extrinsic traps on the conductivity of organic semiconductors.

3. Results and discussion

Figs. 1 and 2 illustrate the temperature dependence of the carrier conductivity for different trap concentrations. The parameters are $N_t = 10^{22}$ cm^{-3}, $E_d = -0.67$ eV, $T_0 = 800$ K, $T_1 = 400$ K, $\alpha = 5$ nm^{-1} and $\sigma_0 = 1 \times 10^4$ S/cm. Despite the effect of the traps, we can see an almost perfect Arrhenius-type temperature dependence in Fig. 1, with the slope affected by the trap concentration. Increasing the latter, the activation energy decreases. In Fig. 2, $\log \sigma$ versus T^{-2} is plotted. The deviation from a straight line occurs at higher temperature, where nearly all carriers occupy the intrinsic states, and the filled extrinsic trap states do not change the trap-free hopping relation $\log \sigma \propto T^{-2}$ [7]. However, at lower temperature, the carrier distribution will be pinned near the peak of trap DOS [6].

In Fig. 3 we compare the analytical model with experimental data reported in [1]. Parameters are the relative
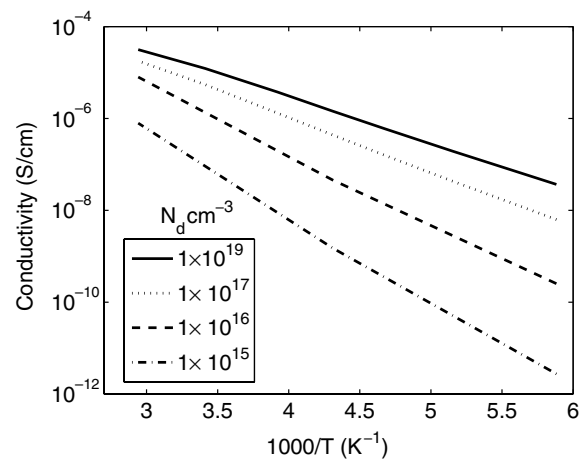

Fig. 1. Conductivity of an organic semiconductor versus T^{-1} for different trap concentrations.
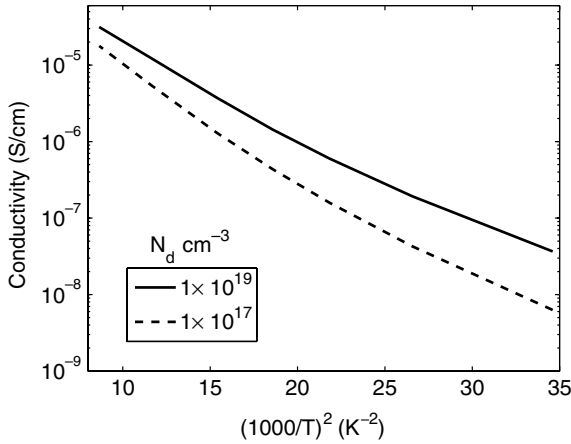
Fig. 2. Conductivity of an organic semiconductor versus T^{-2} for different trap concentrations.
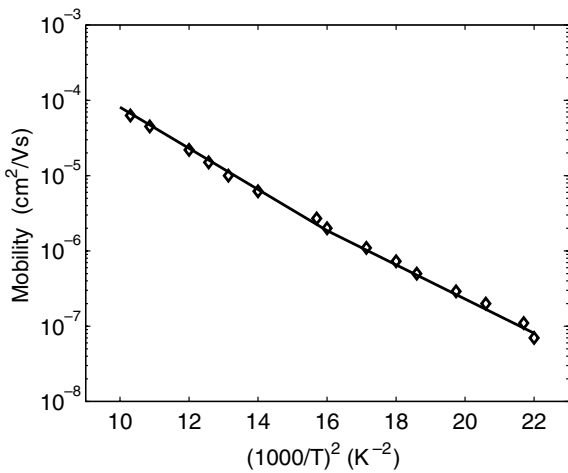

Fig. 4. Conductivity of an organic semiconductor versus the width of the trap distribution, T_1.

Fig. 3. Temperature dependence of the zero-field mobility for TTA doped with DAT. Symbols represent experimental data from [1].

Fig. 5. The dependence of the conductivity on the trap concentration.

trap concentration $c_t = N_d/N_t = 1 \times 10^{-2}$, $T_0 = 1200$ K, $T_1 = 400$ K, $E_d = -0.15$ eV, $\alpha = 6$ nm^{-1} and $\sigma_0 = 4.2784 \times 10^8$ S/m. The data are for TTA with doping DAT.

The relation between conductivity and T_1 is shown in Fig. 4. Parameters are $N_t = 1 \times 22$ cm^{-3}, $N_d = 1 \times 19$ cm^{-3}, $T_0 = 1200$ K, $T = 150$ K, $E_d = -0.5$ eV, $\alpha = 3$ nm^{-1} and $\sigma_0 = 100$ S/m. For the exponential trap DOS function of our model, the parameter T_1 is a characteristic temperature, where $k_B T_1$ represents the activation energy [17] and defines the width of the distribution [18]. Fig. 4 confirms that the conductivity decreases with T_1 almost linearly.

The relation between conductivity and trap concentration is shown in Fig. 5. The parameters are $N_t = 10^{22}$ cm^{-3}, $\alpha = 6$ nm^{-1}, $T_0 = 1000$ K, $T_1 = 500$ K, $E_d = -0.2$ eV, the temperature is $T = 400$ K and $\sigma_0 = 1 \times 10^4$ S/m.

At a critical trap concentration the conductivity has a minimum. This has been verified by experiments [19] and Monte Carlo simulation [2]. The minimum is due to the onset of inter-trap transfer that alleviates thermal detrapping of carriers, which is a necessary step for charge transport [2]. We can a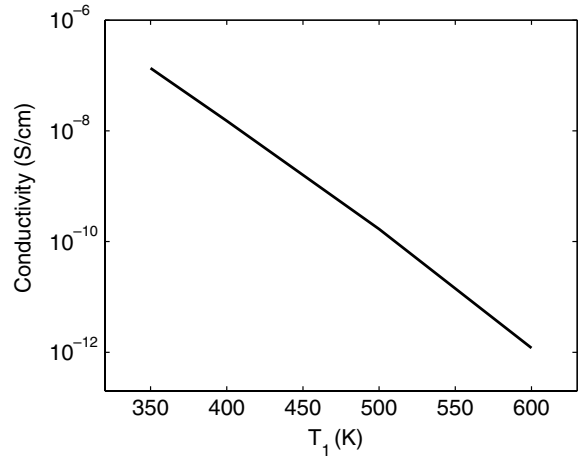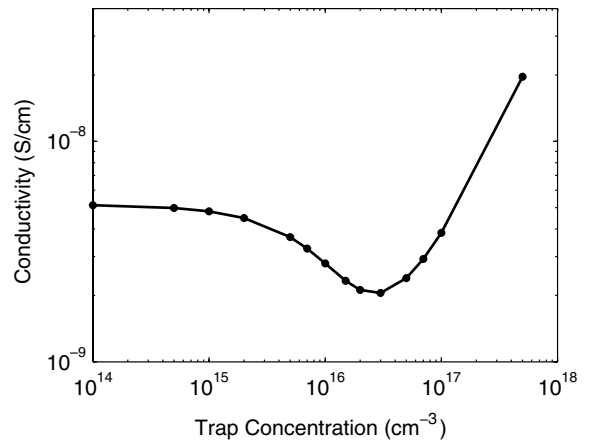lso see that a small trap concentration has virtually no effect on the conductivity. At higher trap concentration, however, the activation energy for the conductivity decreases. The traps themselves can serve as an effective hopping transport band, so the effect of traps on
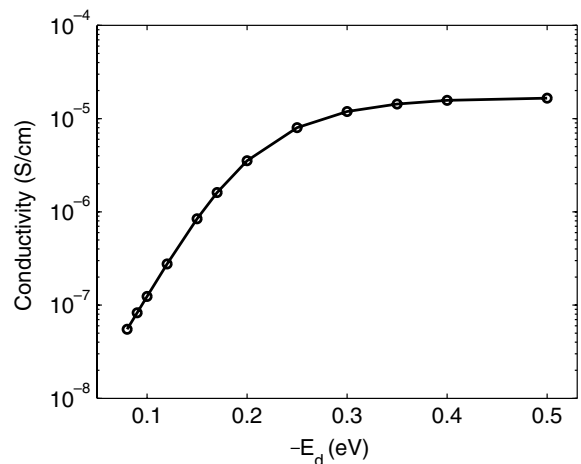

Fig. 6. The dependence of the conductivity on the Coulombic trap energy.

the charge conductivity is qualitatively similar to that caused by a high carrier concentration. It is interesting that such transition has also been observed in thermally stimulated luminescence (TSL) measurements [20].

The relation between the conductivity and the trap energy E_t is shown in Fig. 6. Parameters are $T_0 = 600$ K, $T_1 = 300$ K, $N_t = 1 \times 10^{22}$ cm^{-3}, $N_d = 1 \times 10^{19}$ cm^{-3}, $\alpha = 4$ nm^{-1}, $T = 200$ K and $\sigma_0 = 1 \times 10^4$ S/m. From Fig. 6 we can conclude that the conductivity increases approximately exponentially for $|E_d|$ below a certain critical value and saturates for larger $|E_d|$.

4. Conclusion

An analytical model to describe the effect of traps on the electrical conductivity in organic semiconductors has been derived. This model predicts an Arrhenius-type relationship $\log \sigma \propto T^{-1}$, which implies that the trap-free relationship $\log \sigma \propto T^{-2}$ is not satisfied for higher temperature. Moreover, a minimum of conductivity at low trap concentration, as observed by in experimental data, is also successfully described by this model.

Acknowledgement

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