

# Transport in $\alpha$ -Sexithiophene Films

M. W. Wu and E. M. Conwell

*Center for Photoinduced Charge Transfer, Chemistry Department, University of Rochester,*

*Rochester, New York 14627, USA*

*and Xerox Corporation, Wilson Center for Technology, 114-22D, Webster, New York 14580,*

*USA\**

## Abstract

The field-effect mobility of hole polarons in  $\alpha$ -sexithiophene, measured in thin film transistors, was shown to be well fitted by Holstein's small polaron theory. Unfortunately, Holstein's formulation is based on an integral that does not converge. We show that the data are well fitted by a theory of polaron transport that was successful in accounting for mobility in molecular crystals of naphthalene.

The prospect of field-effect transistors, FETs, made of easily processible thin organic films has stimulated considerable research effort. The most successful devices to date have been made of oligomeric rather than polymeric material, an outstanding one being  $\alpha$ -sexithiophene,  $\alpha$ -6T.<sup>1,2</sup> From the device theory and operation it is possible to deduce a field-effect mobility,  $\mu_{FET}$ , for holes moving in the active part of the device, the  $\alpha$ -6T layer just above the gate dielectric. Recent measurements of mobility made in the space-charge limited current regime have been in good agreement with  $\mu_{FET}$  obtained in a long channel device,<sup>1</sup> indicating that the device measurements can be considered to represent the mobility reasonably well. For convenience of notation we will drop the subscript in referring to the device measurements.

The  $\alpha$ -6T films for the FETs are usually made by vacuum evaporation onto the gate dielectric, the latter frequently being  $\text{SiO}_2$  or  $\text{MgF}_2$ . This results in a polycrystalline film which is, however, well oriented in that the long axis of the  $\alpha$ -6T molecules stands almost perpendicular to the substrate.<sup>3,4</sup> The transport direction in the FETs, parallel to the substrate, is then essentially perpendicular to the molecular chains. Mobility as a function of temperature has been measured in  $\alpha$ -6T FETs by Horowitz *et al.*,<sup>5</sup> Waragai *et al.*<sup>6</sup> and Torsi *et al.*<sup>7</sup> In the two former cases the measurements were taken down to 100 and 77 K, respectively. Over this range mobility was seen to increase with increasing temperature. Waragai *et al.* attributed the transport to thermally activated hopping of polarons among the thiophene molecules. (Actually they used a derivative of  $\alpha$ -6T, dimethyl sexithiophene.) Horowitz *et al.* analyzed the data down to 150 K in terms of free carriers, specifically holes in the valence band, undergoing multiple thermal trapping and release involving shallow traps. Below 150 K they attributed the mobility to the free carriers hopping among deep traps. Such a model could never account for the increase in mobility with decreasing temperature found by Torsi *et al.* below  $\sim 50$  K.<sup>7</sup> (See Fig. 1.) The model would be appropriate for carriers moving in wide bands of the kind found in three-dimensional semiconductors such as silicon, but not for carriers moving in the narrow bands characteristic of a molecular crystal, or the polycrystalline array of molecular crystals that  $\alpha$ -6T samples generally consist of. For

these cases it is essential to include polaronic effects.

Torsi *et al.* showed that their data are well fitted by Holstein's small polaron theory based on his Molecular Crystal Model.<sup>8</sup> In this model the electron (or hole) wavefunction is limited to a single site. The electron or hole becomes a small polaron, still limited to a single site, due to its coupling to the vibrations of a diatomic molecule at the site. It is well known that an excess electron or hole on a conducting polymer or on a conjugated molecule such as naphthalene or  $\alpha$ -6T forms a polaron that is spread over a considerable number of sites,  $\sim 20$  if the conjugation length allows. Although Holstein's calculations are readily generalized to such a polaron, and to the vibrations being the usual acoustic and optical modes of a lattice,<sup>9</sup> they are fatally flawed by the fact that their essential result, the integral obtained for the probability of a polaron moving or hopping from site to site, does not converge.<sup>10,11</sup> Holstein obtains finite results for the high temperature (hopping) region and the low temperature (coherent motion) region by approximating the integral for each case with a leading term. Nevertheless, many of the ideas developed by Holstein and some predecessors form the basis for later theories of polaron transport.

A form of the theory that was successful in describing mobility over a wide range of temperatures for naphthalene crystals starts from a simple Hamiltonian used by many workers in this field:

$$H = \sum_m \epsilon_m a_m^\dagger a_m + \sum_{m,n} V_{m-n} a_m^\dagger a_n + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} (b_{\mathbf{q}}^\dagger b_{\mathbf{q}} + \frac{1}{2}) + N^{-1/2} \sum_{m,\mathbf{q}} \hbar\omega_{\mathbf{q}} g_{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{R}_m) (b_{\mathbf{q}} + b_{-\mathbf{q}}^\dagger) a_m^\dagger a_m, \quad (1)$$

where  $a_m^\dagger$  creates an electron with energy  $\epsilon_m$  at a site  $m$  in the crystal of  $N$  sites,  $b_{\mathbf{q}}$  creates a phonon with wave vector  $\mathbf{q}$  and frequency  $\omega_{\mathbf{q}}$ ,  $V_{m-n}$  is the intersite matrix element between sites  $m$  and  $n$ ,  $g_{\mathbf{q}}$  is the dimensionless electron-phonon coupling constant and  $\mathbf{R}_m$  is the lattice vector that locates site  $m$ . The Hamiltonian is transformed to the polaron picture by a unitary transformation,<sup>12</sup> resulting in

$$H = \sum_m \left\{ \epsilon_m - N^{-1} \sum_{\mathbf{q}} |g_{\mathbf{q}}|^2 \hbar\omega_{\mathbf{q}} \right\} A_m^\dagger A_m + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} (B_{\mathbf{q}}^\dagger B_{\mathbf{q}} + \frac{1}{2})$$

$$+ \sum_{n,m} V_{n-m} \theta_n^\dagger \theta_m A_n^\dagger A_m + N^{-1} \sum_{n,m,\mathbf{q}} |g_{\mathbf{q}}|^2 \hbar \omega_{\mathbf{q}} \exp[i\mathbf{q} \cdot (\mathbf{R}_n - \mathbf{R}_m)] A_n^\dagger A_m^\dagger A_n A_m, \quad (2)$$

$$\theta_m = \exp \left[ N^{-1/2} \sum_{\mathbf{q}} g_{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{R}_m) (B_{\mathbf{q}} - B_{-\mathbf{q}}^\dagger) \right], \quad (3)$$

where  $A_m$  creates a polaron at site  $m$  and  $B_{\mathbf{q}}^\dagger$  creates a phonon of wave vector  $\mathbf{q}$  that is associated with the motion of the ions about their displaced equilibrium positions.

The Hamiltonian (2), (3) was used in the calculation of polaron mobility in naphthalene by Kenkre *at al.*<sup>13</sup> The formulation of KADD includes disorder, the site energy  $\epsilon_m$  being taken as a randomly fluctuating quantity. The fluctuations can arise from crystal defects, which are surely present in these materials. It is usual to represent  $\epsilon_m$  by a Gaussian or Lorentzian distribution of width  $\hbar\alpha$ . The latter was chosen by KADD. It was specified that  $\alpha$  must be small compared to  $\omega_{\mathbf{q}}$ ; if  $\alpha$  were not small a different approach to the problem would be necessary.

As was done by Holstein and many others, KADD assumed that the hole interacts with only one phonon branch of mean energy  $\hbar\omega_0$  and width  $\hbar\Delta_i$  in the  $i$ th direction. The significance of this assumption will be discussed below. With these simplifications KADD obtained the mobility  $\mu_{ii}$  for field and current along the  $i$ th principal axis direction:

$$\begin{aligned} \mu_{ii} = & 2(ea_i^2)(k_B T)^{-1} |V_i/\hbar|^2 \exp[-2g_i^2 \coth(\frac{1}{2}\beta\hbar\omega_0)] \\ & \times \int_0^\infty dt e^{-\alpha t} I_0 \left\{ 2g_i^2 \operatorname{csch}(\frac{1}{2}\beta\hbar\omega_0) |J_0(\Delta_1 t) J_0(\Delta_2 t) J_0(\Delta_3 t)| [1 + J_1^2(\Delta_i t)/J_0^2(\Delta_i t)]^{1/2} \right\}. \quad (4) \end{aligned}$$

where  $\beta = 1/k_B T$ , the  $g_i$  are dimensionless electron-phonon coupling constants as defined in Eq. (1), the  $a_i$  are lattice constants and the  $V_i$  the nearest-neighbor transfer integrals along the  $i$ th direction. The bandwidth  $W$  is taken as usual as  $4V_i$ . It is seen that  $\mu_{ii}$  is similar to the result of Holstein's theory, but it converges due to the factor  $e^{-\alpha t}$ , representing disorder, in the integral.

It is clear that many phonon branches, not only one, have significant interaction with the current carrier, whether electron or hole. For example, when a carrier jumps onto or off a chain, the well known distortion that occurs involves a number of phonon frequencies and more than one phonon branch. This was calculated explicitly for the case of polyacetylene.<sup>14</sup>

A similar polaronic effect must occur when a hole jumps onto or off an  $\alpha$ -6T molecule. Of course the distortions are not large, but this represents a necessary energy expenditure that affects the hopping rate. A much bigger effect, however, can be caused by phonons that change the overlap of the molecules between which the polarons jump. For example, consider nearest neighbor hopping along that direction in an  $\alpha$ -6T crystallite perpendicular to the long axis of the molecules where nearest neighbors are tilted at opposite angles to the normal. Librations around an axis in this direction would greatly affect overlap of adjacent molecules and therefore the rate of polaron motion. This appears to be the situation in at least one of the structures attributed to  $\alpha$ -6T.<sup>15</sup> In such a case the libration would have by far the strongest effect on the hopping and the effect of the other phonons could be considered to be included in the value of  $g_i$ , which is determined by comparison with experiment in any case.

As has been shown by many authors, in the approximation that only one phonon branch interacts with the carriers the thermally averaged bandwidth for the  $i$ th direction is<sup>16</sup>

$$W_T = 4|V_i| \exp[-g_i^2 \coth(\beta\hbar\omega_0/2)] = 4|V_i| \exp[-g_i^2(m + 1/2)] , \quad (5)$$

where  $m = [\exp(\beta\hbar\omega_0) - 1]^{-1}$ , the number of phonons in the mode with frequency  $\omega_0$ . It is apparent that  $W_T$  decreases monotonically as the temperature increases from zero, rapidly when  $k_B T / \hbar\omega_0 > 1/2$ . Thus the mobility, which is proportional to  $W_T^2$ , decreases with temperature due to this factor, rapidly at high temperatures. A second factor depending on  $T$  is  $\text{csch}(\beta\hbar\omega_0/2)$  in the integrand. This factor is proportional to  $m$ , the phonon abundance. In the low temperature limit this factor makes the argument of  $I_0$  small and therefore the integral small. As  $T$  increases this factor increases and the integral increases, quite rapidly for  $k_B T > \hbar\omega_0$ . Crudely it can be thought that the integral represents the hopping probability. Thus as  $T$  increases from zero the librations play the dual role of decreasing the coherent or bandlike motion through the decrease in bandwidth and of increasing the hopping rate. How strong these effects are depends on  $g_i$ .

Before comparing these predictions with the data of Torsi *et al.* shown in Fig. 1, we note

that their mobility values do not show the effect of trapping; their measurements have been made for gate voltages past the threshold value required to obtain a carrier concentration large enough to fill the traps. Also they have shown that grain boundaries do not dominate the transport, at least above the minimum in  $\mu$  at  $\sim 45$  K. Increase in grain size by an order of magnitude did not improve the room temperature mobility.<sup>7</sup> From these facts Torsi *et al.* conclude that their FET mobility data represent intrinsic behavior of  $\alpha$ -6T. Comparing the data of Fig. 1 with the theory discussed above, we see above the temperature of the minimum,  $T_L$ , a region in which  $\mu$  increases rapidly with increasing  $T$ , consistent with hopping. Below  $T_L$  there is a region in which  $\mu$  decreases rapidly with increasing  $T$ , as expected for the coherent motion. The fact that  $\mu$  does not increase without limit with decreasing  $T$ , as predicted by Eq. (4), must be due to another process, perhaps boundary scattering, determining  $\mu$  in the low temperature limit.

To fit the data of Fig. 1 with Eq. (4) we took  $a_i = 0.38$  nm, the closest distance between adjacent molecules along the transport direction.<sup>7</sup> The widths of the phonon band, not known for  $\alpha$ -6T, were taken from a libration of similar frequency which determines the polaron transport in naphthalene,<sup>13</sup> specifically  $\hbar\Delta_1 = 0.70$  meV,  $\hbar\Delta_2 = 1.40$  meV and  $\hbar\Delta_3 = 0.24$  meV. In any case  $\mu_{ii}$  is not sensitive to the  $\Delta_i$  values. The quantities  $|V_i|$ ,  $g_i$ ,  $\hbar\omega_0$  and  $\alpha$  were treated as parameters. The fit shown in Fig. 1 was obtained for  $|V_i| = 14$  meV,  $g_i^2 = 11.5$ ,  $\hbar\omega_0 = 11.2$  meV and  $\alpha = 2 \times 10^{-5}$  ps<sup>-1</sup>. The first three parameters are quite close to those obtained by Torsi *et al.* using Holstein's results.

It is of interest to compare these results with those obtained by KADD in fitting Eq. (4) to the data for naphthalene. From 30 K, the lowest temperature for which there are data, to  $\sim 100$  K  $\mu$  for naphthalene decreases fairly rapidly with increasing  $T$ , although not as rapidly as for  $\alpha$ -6T. Above 100 K  $\mu$  continues to decrease with increasing  $T$  but the increase is much less rapid in two of the three directions shown. These results are consistent with Eq. (4) with a somewhat larger  $\hbar\omega_0$  but more importantly a smaller value of  $g_i$  as compared with  $\alpha$ -6T. Decreasing the electron-phonon coupling decreases both the rate of bandwidth decrease and the rate at which hopping grows with increasing  $T$ . The value of

$g_i^2$  for naphthalene, varying from 2.6 to 3.5 over the three directions, is small enough that the increase in the integral is not large enough to overcome the decrease in bandwidth and create a positive slope for mobility vs. temperature. Another contrasting feature of the naphthalene data is that the changes in slope of  $\mu$  vs.  $T$  are much more gradual. This is apparently a result of  $\alpha$ , the disorder parameter, being larger in naphthalene, 0.259 vs  $2 \times 10^{-5}$  ps $^{-1}$ . In fact, the later value for  $\alpha$  is surprisingly small. We speculate that this may be a result of the holes being confined to within 1 or 2 molecular layers of the interface<sup>2</sup> so that only a very small part of the  $\alpha$ -6T layer is sampled, that part being more ordered perhaps because of the proximity of the interface. Of course, it is not possible to be certain of the parameters because there may still be some differences between  $\mu_{FET}$  and the drift mobility, particularly below 45 K.

If higher mobility is the requirement for improved organic FET performance, it is clear from Eq. (4) that for molecular crystals desirable properties are lower electron-phonon coupling and lower frequency of the interacting phonons. There is a limit to how far one can go in this direction, however, because polaron theory is no longer valid if  $g^2\hbar\omega_0/W < 1$ . From what was said earlier, naphthalene is superior to  $\alpha$ -6T, its room temperature mobility ranging from 0.3 to 0.8 cm $^2$ /Vs in the different crystallographic directions.<sup>13</sup>

We acknowledge the support of the National Science Foundation under Science and Technology Center grant CHE912001.

## REFERENCES

\* Mailing address.

- <sup>1</sup> G. Horowitz, F. Garnier, A. Yassar, R. Hajlaoui, and F. Kouki, *Adv. Mater.* **8** (1996) 52.
- <sup>2</sup> A. Dodabalapur, L. Torsi, and H.E. Katz, *Science* **268** (1995) 270.
- <sup>3</sup> F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries, and P. Alnot, *J. Am. Chem. Soc.* **115** (1993) 8716.
- <sup>4</sup> A.J. Lovinger and L.J. Rothberg, *J. Mater. Sci.* **10** (1995) 2958.
- <sup>5</sup> G. Horowitz, R. Hajlaoui, and P. Delannoy, *J. Phys. III France* **5** (1995) 355.
- <sup>6</sup> K. Waragai, H. Akimichi, S. Hotta, and H. Kano, *Phys. Rev. B* **52** (1995) 1786.
- <sup>7</sup> L. Torsi, A. Dodabalapur, L.J. Rothberg, A.W.P. Fung, and H.E. Katz, *Science* **272** (1996) 1462.
- <sup>8</sup> T.Holstein, *Ann. Phys.* **8** (1959) 343.
- <sup>9</sup> E.M. Conwell, H.-Y. Choi, and S. Jeyadev, *Synth. Met.* **49-50** (1992) 359.
- <sup>10</sup> H.J. deWit, *Phillips Research Repts.* **23**, 449 (1968).
- <sup>11</sup> D. Emin, *Adv. Phys.* **24** (1975) 305.
- <sup>12</sup> This transformation has been used by many authors, among the earliest being S.I. Pekar, *Zh. Eksp. Teor. Fiz.* **20** (1950) 267, and K. Huang and A. Rhys, *Proc. R. Soc. A* **204** (1950) 406.
- <sup>13</sup> V.M. Kenkre, J.D. Anderson, D.H. Dunlap, and C.B. Duke, *Phys. Rev. Lett.* **62** (1989) 1165. This reference will be denoted KADD in what follows.
- <sup>14</sup> E.M. Conwell, H.-Y. Choi, and S. Jeyadev, *J. Phys. Chem.* **96** (1992) 2827.
- <sup>15</sup> G. Horowitz, B. Bachet, A. Yassar, P. Lang, F. Demanze, J.-L Fave, and F. Garnier,

Chem. Mater. **7** (1995) 1337.

<sup>16</sup> For discussion and references see J. Appel, “Polarons” in *Solid State Physics*, Vol. **21**, eds. F. Seitz, D. Turnbull and H. Ehrenreich, Academic Press, 1968.

## FIGURES

FIG. 1.  $\mu_{FET}$  vs.  $T$ . Squares give experimental data of Torsi *et al.*,<sup>7</sup> solid curve is the theoretical fit described in the text.