Ab initio theory of charge-carrier conduction in ultrapure organic crystals

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***Ab initio* theory of charge-carrier conduction in ultrapure organic crystals**

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We present an *ab initio* description of charge-carrier mobilities in organic molecular crystals of high purity. Our approach is based on Holstein's original concept of small-polaron bands but generalized with respect to the inclusion of nonlocal electron-phonon coupling. By means of an explicit expression for the mobilities as a function of temperature in combination with *ab initio* calculations of the material parameters, we demonstrate the predictive power of our theory by applying it to naphthalene. The results show a good qualitative agreement with experiment and provide insight into the difference between electron and hole mobilities as well as their peculiar algebraic and anisotropic temperature dependencies. © 2004 American Institute of Physics.

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Organic semiconductors are promising materials for low-cost and easy-to-process (opto)electronic devices.^{1–4} Besides π -conjugated polymers, an important material class is organic molecular crystals of high purity. Due to their high degree of structural order, such crystals are ideal candidates for the investigation of the *intrinsic* charge-carrier transport phenomena in organic solids. Thus, many interesting fundamental studies have been performed in recent years and new results emerge at a rapid pace.^{5–9} A particularly important topic and “still a great challenge for theoreticians”¹⁰ is the understanding of the charge-carrier mobilities in these crystals.

In comparison to covalently bonded inorganic semiconductors, organic molecular crystals exhibit weak intermolecular bonds and, hence, narrower electron bands and stronger electron-lattice interaction. As a result, the dressing of the charge carriers by phonon clouds, i.e., polaron formation, becomes quite important. Pioneering theoretical work in this area was done by Holstein,¹¹ who introduced the concept of small-polaron bands for a *local* (on-site) electron-phonon coupling. The main prediction of his theory is that the mobilities initially decrease with rising temperature T due to bandwidth narrowing but increase again for higher T due to phonon-assisted hopping. Two decades later, the interplay between metallic (bandlike) conduction and activated (hopping) transport in organic crystals was seen for the electrons in naphthalene but not for the holes.^{12–14} Later, Kenkre *et al.* were able to fit the measured electron mobilities reasonably well to Holstein's model, assuming directionally dependent local-coupling constants.¹⁵ Despite the success of such a *fitting* procedure, the lack of a first-principles description of charge-carrier mobilities in organic crystals has left several fundamental questions unanswered. This concerns, in particular, the different behavior of electrons and holes, the microscopic origin of the crystallographic anisotropy in the T dependence, and the influence of *nonlocal* (Peierls-type) couplings such as present in the Su-Schrieffer-Heeger model.^{16–18}

In this letter, we address the above-noted questions by presenting a first-principles approach to charge-carrier mo-

bilities in organic crystals. We consider a mixed Holstein-Peierls model for the interaction between electrons (holes) and phonons. In a tight-binding description, this corresponds to a Hamiltonian of the form $H = \sum_{mn} \varepsilon_{mn} a_m^\dagger a_n + \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} (b_{\mathbf{Q}}^\dagger b_{\mathbf{Q}} + \frac{1}{2}) + \sum_{mn\mathbf{Q}} \hbar \omega_{\mathbf{Q}} g_{\mathbf{Q}mn} a_m^\dagger a_n (b_{\mathbf{Q}}^\dagger + b_{-\mathbf{Q}})$. Here, the operators $a_m^{(\dagger)}$ and $b_{\mathbf{Q}}^{(\dagger)} := b_{\mathbf{Q}\lambda}^{(\dagger)}$ annihilate (create) an electron at equivalent lattice sites $\mathbf{R}$ with energy ε_{mn} and a phonon in the mode λ with wave vector $\mathbf{q}$ and frequency $\omega_{\lambda\mathbf{q}} := \omega_{\mathbf{Q}}$, respectively. The strength of the electron-lattice interaction is determined by the dimensionless quantities $g_{\mathbf{Q}mn}$ that describe both the *local* coupling to the on-site energies ε_{mn} (Holstein model) and the *nonlocal* coupling to the transfer integrals ε_{mn} ($m \neq n$, Peierls model).

In thermal equilibrium, the mobility μ_α in direction $\mathbf{e}_\alpha$ can be calculated by means of the Kubo formula for electrical conductivity. This basically amounts to evaluating a current-current correlation function where, in general, the current $\mathbf{j} := \mathbf{j}^{(I)} + \mathbf{j}^{(II)}$ is composed of a purely electronic term $\mathbf{j}^{(I)} = (e_0 / i\hbar) \sum_{mn} (\mathbf{R}_m - \mathbf{R}_n) \varepsilon_{mn} a_m^\dagger a_n$ and a phonon-assisted current $\mathbf{j}^{(II)} = (e_0 / i\hbar) \sum_{mn\mathbf{Q}} (\mathbf{R}_m - \mathbf{R}_n) \hbar \omega_{\mathbf{Q}} g_{\mathbf{Q}mn} (b_{\mathbf{Q}}^\dagger + b_{-\mathbf{Q}}) a_m^\dagger a_n$. We stress that the current $\mathbf{j}^{(II)}$ originates solely from the *nonlocal* electron-phonon coupling. In a recent article,¹⁹ we have performed an analytical evaluation of the Kubo formula using the method of canonical transformation which allowed us to incorporate the electron-phonon interaction in a nonperturbative manner, in accordance with the underlying physical picture of small-polaron bands. Here, we give only the results for the mobilities in the case of dispersionless optical phonons ($\omega_{\mathbf{Q}} \rightarrow \omega_\lambda$).

For the mobility $\mu_\alpha^{(I)}$ due to the current $\mathbf{j}^{(I)}$, we obtain

$$\mu_\alpha^{(I)} = \frac{e_0}{2k_B T \hbar^2} \sum_{n \neq m} (R_{am} - R_{an})^2 \int_{-\infty}^{+\infty} dt \times [\varepsilon_{mn} e^{-\sum_\lambda G_\lambda [1 + 2N_\lambda - \Phi_\lambda(t)]}]^2 e^{-\Gamma^2 t^2}, \quad (1)$$

where $N_\lambda = (e^{\hbar \omega_\lambda / k_B T} - 1)^{-1}$ denotes the phonon occupation number and Γ is a phenomenological broadening parameter that accounts for scattering processes beyond our model, e.g., due to defects. Those terms in the exponent of Eq. (1) that contain $\Phi_\lambda(t) = (1 + N_\lambda) e^{-i\omega_\lambda t} + N_\lambda e^{i\omega_\lambda t}$ describe *incoherent* scattering events involving actual changes in phonon

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FIG. 1. Calculated charge-carrier mobilities (in arbitrary units, see Refs. 22 and 23) vs temperature T for naphthalene crystals, as obtained from Eqs. (1) and (2). As a guide to the eye, several power laws $\mu_\alpha \propto T^{-\gamma}$ are also depicted.

numbers (hopping) whereas the remaining terms account for purely *coherent* scattering processes (bandwidth narrowing). While Eq. (1) is qualitatively similar to the Holstein-model mobilities obtained by Kenkre *et al.*,¹⁵ an important quantitative difference is that the exponent in our formula (1) is not only governed by the local coupling but by effective coupling constants $G_\lambda = (g_{\lambda mm})^2 + \frac{1}{2} \sum_{k \neq m} (g_{\lambda mk})^2$ that are composed of both the local and nonlocal ones.

In order to obtain the total mobilities μ_α within our Holstein–Peierls model, we have to include also the contributions from the phonon-assisted current $\mathbf{j}^{(II)}$. This results in an expression that is identical in form to Eq. (1) but with the replacement

$$(\varepsilon_{mn})^2 \rightarrow (\varepsilon_{mn} - \Delta_{mn})^2 + \frac{1}{2} \sum_{\lambda} (\hbar \omega_{\lambda} g_{\lambda mn})^2 \Phi_{\lambda}(t), \quad (2)$$

where $\Delta_{mn} = \frac{1}{2} \sum_{\lambda} \hbar \omega_{\lambda} [g_{\lambda mn} (g_{\lambda mm} + g_{\lambda nn}) + \frac{1}{2} \sum_{k \neq m, n} g_{\lambda mk} g_{\lambda kn}]$. An essential qualitatively new feature compared to Eq. (1) is that the total mobilities μ_α can account for an anisotropic T dependence due to the extra term containing $\Phi_{\lambda}(t)$ in Eq. (2), which describes additional phonon-assisted hopping processes that are absent in local-coupling theories and reflect an inherently transport-promoting effect solely caused by the nonlocal coupling.

We proceed by applying our mobility theory to naphthalene, which crystallizes in a monoclinic structure and exhibits a herringbone stacking with two equivalent molecules per unit cell. In order to obtain the material-specific parameters $\mathbf{R}_m$, ε_{mn} , $g_{\lambda mn}$, and ω_{λ} we use a three-step strategy described in more detail in Ref. 20.

First, we determine the equilibrium structure of the crystal by means of state-of-the-art DFT-LDA calculations using the *ab initio* total-energy and molecular dynamics program VASP.²¹ For the resulting geometry ($a=7.68$ Å, $b=5.76$ Å, $c=8.35$ Å, $\beta=125.7^\circ$), the intermolecular optical-phonon energies ($\hbar \omega_{\lambda}=10.7, 14.2, 17.4$ meV) and eigenvectors are obtained within the rigid-molecule approximation.²² Second, we obtain the values ε_{mn} from a fit of the ground-state *ab*

FIG. 2. Experimental charge-carrier mobilities vs temperature T for naphthalene crystals, as extracted from Ref. 14.

initio highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy bands to a tight-binding model, including the six most important transfer integrals. Third, the coupling constants $g_{\lambda mn}$ are obtained by rotating the molecules according to the phonon eigenvectors and fitting the resulting *ab initio* band structure to the Holstein–Peierls Hamiltonian. A compilation of all calculated material parameters can be found in Ref. 20. Finally, we have chosen a small line broadening of $\hbar \Gamma=0.1$ meV, corresponding to the case of ultrapure crystals.²³

In Fig. 1, we present the calculated electron and hole mobilities in naphthalene crystals as a function of temperature T for the a , b , and c' directions, with c' being perpendicular to the ab plane of the molecular layers. In Fig. 2, the corresponding experimental mobility data are replotted from the work of Karl.¹⁴

We make three important observations. First, the calculated hole mobilities are generally larger than the corresponding electron mobilities. Only at $T \approx 300$ K do we observe comparable in-plane mobilities for electrons and holes. This general trend is in good agreement with the experimental data, apart from the overestimated theoretical spread between electrons and holes for $\mu_{c'}$, which might be related to the difficulties of LDA in describing van der Waals bonds. We stress that the lower electron mobilities cannot be simply understood from the electronic transfer integrals but that they are mainly due to their stronger coupling to the phonons [$\text{LUMO: } \sum_{\lambda} G_{\lambda} = (1.52)^2$, $\text{HOMO: } \sum_{\lambda} G_{\lambda} = (0.92)^2$]. We note also that our *calculated* effective coupling constant of 1.52 for the LUMO is comparable in value to the directionally dependent *fitted* coupling values of 1.62, 1.83, and 1.88 obtained by Kenkre *et al.*¹⁵

Second, while the hole mobilities in the different directions decrease very similarly with T , the electron mobilities exhibit a pronounced anisotropic T dependence. In particular, we find a metallic (bandlike) behavior within the ab plane and a slightly activated (hopping) transport in the c' direction. Again, these findings from our *ab initio* calculations are in good agreement with the experiment, which shows such nearly T -independent mobility around $T \approx 150$ K exclusively

in the c' direction. As discussed earlier this pronounced anisotropy is solely due to the phonon-assisted currents $\mathbf{j}^{(\text{II})}$ and, in fact, the peculiar flatter seen for $\mu_{c'}$ is not obtained at all for $\mu_{c'}^{(\text{I})}$ alone. This clearly demonstrates that anisotropy effects in the T dependence can be explained in a natural way by the inclusion of nonlocal electron–phonon coupling, and do not require the use of additional concepts such as directionally dependent local couplings¹⁵ or correlated successive hops of strongly localized charge carriers.²⁴

Third, our calculated hole mobilities obey at elevated T the power law $\mu_{\alpha} \propto T^{-2.5}$. This agrees well with Karl's experiments where $\mu_{\alpha} \propto T^{-2.9}, T^{-2.5}, T^{-2.8}$. This peculiar power-law dependence, which has been poorly understood so far, can be straightforwardly understood from our theory. In the limit of small broadening $\hbar\Gamma$ and for $\mu_{\alpha} \approx \mu_{\alpha}^{(\text{I})}$ (here fulfilled for the holes), a spectral analysis of Eq. (1) shows that the dominant electron–phonon scattering processes are those that allow only energy exchange within each phonon mode but not between different modes, and the mobility can be expressed in terms of modified Bessel functions,

$$\mu_{\alpha}^{(\text{I})} \propto \frac{1}{\Gamma} \frac{1}{k_B T} (\Pi_{\lambda} e^{-2G_{\lambda}(1+2N_{\lambda})} I_0(z_{\lambda})),$$

where $z_{\lambda} = 4G_{\lambda} \sqrt{N_{\lambda}(1+N_{\lambda})}$. The limit of high T is obtained using $I_0(z_{\lambda} \rightarrow \infty) \approx e^{z_{\lambda}} / \sqrt{2\pi z_{\lambda}}$ and we find $\mu_{\alpha}^{(\text{I})} \propto T^{-1} (\prod_{\lambda=1}^3 T^{-0.5}) = T^{-2.5}$, which indicates that the exponent is actually a measure for the number of relevant phonon modes per molecule. For the electrons, the situation is more complicated due to a subtle interplay between the (here significant) contributions of $\mathbf{j}^{(\text{II})}$ and the larger coupling values. This prohibits an easy analytical evaluation but, by looking at our calculated in-plane electron mobilities in Fig. 1, we find at high T an approximate $T^{-1.5}$ dependence, again in close agreement with the experiment. The disagreement at low T between theory ($\mu_{\alpha} \propto T^{-1}$) and experiment ($\mu_{\alpha} \propto T^{-1.4}, T^{-1.5}, T^{-1.6}$) might be due to the neglect of acoustic phonons. Following our above discussion, they may be considered as effectively one dispersive phonon branch that could give rise to the missing factor $T^{-0.5}$.

In summary, we have presented a theoretical description of charge-carrier mobilities in ultrapure organic crystals based on a mixed Holstein–Peierls model. The predictive power of our theory has been demonstrated by *ab initio* studies for naphthalene crystals where our results show good qualitative agreement with experiment and provide microscopic insight into several hitherto poorly understood phenomena. Since our theory may also be applied to other

weakly bonded materials with strong electron–phonon coupling, it may become an important contribution to the understanding of the charge-carrier transport in these materials, too.

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²²In principle, our approach does also allow the inclusion of intramolecular phonons. However, due to their higher frequencies (Ref. 5), i.e., lower occupations, we expect them to have little influence on the T dependence of μ_{α} but their zero-point fluctuations can cause a considerable isotropic reduction of the overall values.

²³We have carefully checked that, for the T region of Fig. 1, smaller values of $\hbar\Gamma$ do not change the T dependence but lead only to a scaling $\propto 1/\Gamma$ of the mobilities.

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