2D bands and electron-phonon interactions in polyacene plastic transistors

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We present a simple tight-binding model for the two-dimensional energy bands of polyacene field-effect transistors and for the coupling of these bands to lattice vibrations of their host molecular crystal. We argue that the strongest electron-phonon interactions in these systems originate from the dependence of inter-molecule hopping amplitudes on collective molecular motion, and introduce a generalized Su-Schrieffer-Heeger model that accounts for all vibrations and is parameter-free once the band mass has been specified. We compute the electron-phonon spectral function $\alpha^2 F(\omega)$ as a function of two-dimensional hole density, and are able to explain the onset of superconductivity near 2D carrier density $n_{2D} \sim 10^{14}$ cm$^{-2}$, discovered in recent experiments by Schön et al. [1].

Recent studies [1,2] of high-mobility organic field-effect transistors by Battlogg and collaborators have demonstrated that their electronic properties can be tuned through an astonishing range, simply by adjusting the two-dimensional (2D) electron density $n_{2D}$ with a gate voltage. The high quality of these organic single crystals and of their interfaces with AlO$_3$ dielectrics opens up new possibilities for studying the physics of coherent band quasiparticle transport in organic semiconductors.

To date, however, the analysis of organic field-effect transistor electronic systems has been hampered by the absence of simple and reliable models for their electronic quasiparticles and for the interactions of these quasiparticles with each other and with vibrations of the host lattice. Indeed the discovery of coherent band quasiparticle properties and of the quantum Hall effect in these systems, which are usually thought of as being complex and relatively disordered, has been one of the major surprises that has emerged from recent materials quality advances.

The electronic properties of polyacene semiconductors are normally described by small polaron theory [3], which is quite successful at temperatures above $\approx$20 K. Small polaron theory starts from localized molecular orbitals and is therefore unable to describe the low-temperature band quasiparticle behavior seen in Battlogg et al.’s samples, which have room-temperature to low temperature resistance ratios $\sim 10^4$. Schubnikov-de Haas transport studies in these samples establish quasiparticle mean-free-paths in excess of 1000 lattice constants, demonstrating that the low-temperature regime can be described only by starting at the opposite limit and building a theory based on delocalized band electron states. Nevertheless, the interactions of quasiparticles with lattice vibrations remain strong, and are presumably responsible for superconductivity. In this Letter, we propose a simple tight-binding model for the quasiparticle bands that emerge from $\pi$-molecular orbitals and are filled with carriers by the field-effect, and for the interaction of these bands with the host crystal vibrational excitations. Our theory is parameter free once the band mass has been specified [3].

We find that over the entire wide range of studied densities, the quasiparticles of these systems lie within a single 2D band, bound to the crystal surface by the transistor’s electric field. We argue that the dominant electron-phonon interactions in polyacene crystals differ qualitatively from the deformation and Frohlich interactions of inorganic semiconductors [1] and from the intramolecule interactions that dominate in doped fullerene [5], being more similar instead to those of doped polycetylene [6] crystals. We describe these interactions using a Su-Schrieffer-Heeger model [6], detailed in the following paragraphs, generalized to account for the larger number of important rigid molecule motions. The lattice phonons, a mixture in general of translational and librational components, induce a change in the value of the hopping integral and hence couple [6] to the quasiparticle bands. We estimate the variation of hopping parameters with vibrational normal coordinates by assuming that they are proportional to the spatial overlap of Hückel-type LUMO and HOMO molecular orbitals, with the proportionality constant fixed by matching the measured equilibrium hopping parameter [7]. In this way, we have evaluated the carrier density dependence of $\alpha^2 F(\omega)$, the index of electron-phonon interactions that figures prominently in the theory of phonon-mediated superconductivity. We find peaks that match the spectrum extracted from recent tunneling experiments [8]. We also find that $\alpha^2 F(\omega)$ is large, due to a density-of-states peak, when the lowest energy 2D subband is close to half-filling. We propose this property as the explanation of the relatively sharp onset of superconductivity at a 2D carrier density of $\approx 10^{14}$ cm$^{-2}$ seen in experiments [1].

We focus in this study on anthracene which is monoclinic ($P2_1_1_{\alpha}$) with two basis molecules whose orientations are related by a gliding plane symmetry [5].
Huckel model intra-molecular hopping parameters have no linear dependence on low energy intra-molecular vibration normal coordinates, our model Hamiltonian includes only inter-molecular hopping parameters 3.

\[ H = H_t + H_{e-e} + H_{vib} + H_{ext} \]

where \( H_t \) is the LUMO or HOMO band Hamiltonian described by a nearest-neighbour hopping model, \( H_{e-e} \) describes Coulomb interaction between the electrons, \( H_{vib} \) is the free-phonon Hamiltonian, and \( H_{ext} \) describes the external electric field from the transistor’s gate.

We start by considering the field-induced energy bands obtained neglecting electron-phonon interactions. The key question we need to address is the number of 2D subbands that are occupied at a particular 2D density, \( n_{2D} \). As summarized in Fig. 1, we find that all carriers reside in a single subband up to much higher density in these transistors than in their inorganic counterparts, principally because of the relatively small dielectric constants (\( \epsilon \approx 3.5 \)) and the large effective in plane band mass \( (m_{\perp} = 1.5 m_e) \) and in spite of the rather large c-direction effective band mass \( m_z \approx 3 m_e \). Since the \( Al_2O_3 \) barrier is quite high (\( \approx 1.3 \text{ eV} \)), we take it to be infinite. Our conclusion is based partially on envelope-function density-functional calculations for which the local-density-approximation (LDA) can be used to estimate many-body effects in2 that favor a single subband. In our LDA calculations we find that the second subband is first populated at \( n_{2D} \approx 5 \times 10^{14} \text{ cm}^{-2} \), a density just larger than the highest achieved in experimental systems. However, as shown in the inset of Fig. 1, the wavefunctions in these calculations are already localized over \( \sim 1 - 2 \text{ nm} \) at densities well below this maximum value. We have therefore repeated these electronic structure calculations using our tight-binding model, and treating interactions in a Hartree approximation. With this approach we find that 99% of the charge density is in the first molecular layer at \( n_{2D} \approx 3 \times 10^{13} \text{ cm}^{-2} \), the density at which second subband occupation first occurs in this approximation. Since we believe that the experimental signatures of second subband occupation would be unambiguous and no anomalies in 2D density dependence have been reported, we conclude that a single 2D subband is occupied up to the highest densities and that the lowest subband is strongly localized in the top layer for \( n_{2D} \) larger than \( \approx 10^{13} \text{ cm}^{-2} \).

To model the electron-phonon interaction, we expand each \( a-b \) plane hopping parameter to first order in the twelve coordinates that describe rigid rotations and displacements of neighboring polyacene molecules:

\[ t = t_0 + \sum_{\mu} \sum_{m=1}^{6} t_{\mu,m} \hat{u}_{\mu,m} \]

where \( \hat{u}_{\mu,m} \) is the generalized displacement coordinate, \( \mu = 1,2 \) is the molecular basis index, \( m = 1,2,3 \) denote displacements of the molecular center of mass along \( \hat{x}, \hat{y} \) and \( \hat{z} \) directions, and \( m = 4,5,6 \) denote angular displacements around the 1,2,3 principal axes of each molecule. The electron-phonon interaction parameters \( \hat{t}_{\mu,m} = \partial t / \partial \hat{u}_{\mu,m} \) are calculated based on the assumption of proportionality between hopping integrals and overlap integrals between HOMO or LUMO orbitals on adjacent molecules. The values obtained using standard Huckel approximation 4 HOMO \( \pi \) orbitals (and hence appropriate to the hole systems on which we focus) are listed in Table I in units of \( t_0/a \) for \( m = 1,2,3 \) and \( t_0 \) for \( m = 4,5,6 \).

\[ \hat{t}_{\mu,m} \approx \hat{m}_{\mu,m} \]

\[ \hat{m}_{\mu,m} = \frac{\hbar}{2M_{\mu,m} N_{\omega}(Q)} \times \]

\[ \left[ \epsilon_{\mu,m}(Q,\nu) \hat{Q}_{\nu} e^{iQ \cdot R} + \epsilon_{\mu,m}^*(Q,\nu) \hat{Q}_{\nu} e^{-iQ \cdot R} \right] \]

FIG. 1. States per area with energy below the bottom of the second subband vs. 2D electron density for GaAs, Si, and polyacene field effect transistors from envelope-function LDA calculations. Second subband occupation occurs in the hatched area. The inset shows first and second sub-band wavefunctions obtained from envelope function LDA and tight-binding model Hartree-approximation calculations (bars) at \( n_{2D} = 3 \times 10^{13} \text{ cm}^{-2} \).
Here \( N \) is the total number of unit cells, \( \tilde{M}_{\mu m} \) is the molecular mass of the \( \mu \)th molecule for \( m = 1, 2, 3 \) and the molecular moment of inertia around the \( (m - 3) \)th principal axis \( I_{(m-3)}^\mu \) for \( m = 4, 5, 6 \). The phonon frequencies and polarization vectors are obtained by solving the standard secular equation

\[
\omega_i^2(q) \epsilon_m^i(q, \mu) = \sum_{\nu, n} D_{\mu m, \nu n}(q) \epsilon_n^i(q, \nu)
\]

These eigenmodes are in general a mixture of displacements and rotations \([13] \). We compute the dynamical matrix following the procedure outlined in Ref. \([14] \). The phonon density-of-states and dispersion curves that emerge from these calculations are shown in Fig. 2. The rigid-molecule density-of-states and dispersion curves that can be complemented if necessary by including coupling to important isolated molecular vibrations; it is however reasonably accurate for low-frequency vibrations of anthracene becoming less reliable for larger polyacenes.

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This picture implies a dependence of superconducting critical temperature on molecular lattice constant which contrasts with the case of doped fullerene superconductors. For the fullerenes, the important electron-phonon interactions are intramolecular so that the superconducting state begins to form relatively abruptly. At lower carrier densities, electron-electron interactions are dominated by repulsive Coulomb interactions, consistent with the occurrence of the fractional quantum Hall effect.

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FIG. 3. $\alpha^2 F(\omega)$ for $n_{2d} = 4.0 \times 10^{14}$ cm$^{-2}$ (solid line), $n_{2d} = 1.4 \times 10^{14}$ cm$^{-2}$ (dotted line), and $n_{2d} = 6.7 \times 10^{13}$ cm$^{-2}$ (dashed line).

The table lists electron-phonon interaction parameters.

| $\delta_1 = (a/2, b/2)$ | $\delta_1 = (a/2, b/2)$ | $\delta_2 = (-a/2, -b/2)$ |
|-------------------------|-------------------------|-------------------------|
| $t_{11} = 2.2706$       | $t_{14} = 1.4895$       | $t_{14} = -1.6095$      |
| $t_{12} = 3.3842$       | $t_{15} = 2.0318$       | $t_{15} = 1.8288$       |
| $t_{13} = 7.5308$       | $t_{16} = 1.0082$       | $t_{16} = 1.4658$       |

TABLE I. Electron-phonon interaction parameters. Note that interaction parameters for different near neighbors are different. All interaction parameters are related by symmetry to the nine values listed above. A complete list of hopping parameters for all near neighbors of the two molecules in the crystal’s primitive cell is available from the authors.