

THEORETICAL ASPECTS OF THE FIELD INDUCED SUPERCONDUCTIVITY IN POLYACENES AND C₆₀

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The electronic structure and the superconductivity in field-doped polyacenes are considered. Within a modified Thomas–Fermi approach for typical experimental values of the surface charge density the injected charge is confined to a monolayer. The electron–phonon coupling constant for internal modes λ_{intra} is estimated using the work of Devos and Lanoo (Ref. 4) and the density of states $N(0)$ estimated from a 2D tight-binding model derived from a full potential LDA band structure calculation for bulk anthracene. The empirical values of the Coulomb pseudopotentials are significantly enhanced. The strong Coulomb interaction is considered as a key quantity which determines the large differences in the critical temperatures achieved for n -doped polyacenes and C₆₀.

Recently field-induced superconductivity has been discovered for field effect transistors (FET) based on various aromatic organic systems.^{1,2} Although the details of that superconductivity are still unknown, a more or less standard electron-phonon (el-ph) mechanism is considered by the authors to be a likely candidate. Then due to the closely related physics of bulk electron n -doped A₃C₆₀ (A = K, Rb) the main contributions from high-frequency internal molecular optical phonons $\hbar\omega_{\text{ph}} \sim 100$ meV can be expected.³ There is a sizable corresponding el-ph coupling in aromatic molecules in general.⁴ Its strength $V_{\text{ph}} \approx 1800$ meV/ N_{π} increases with decreasing number of involved π -electrons N_{π} . Such a tendency is in line with the T_c values observed for short n -doped polyacenes which range from 2, 2.7, and 4 K for penta-, tetra-, and anthracene, respectively. However, details and the reason for the much higher fullerite T_c values up to 11 K and 52 (117) K for n - and h -doped

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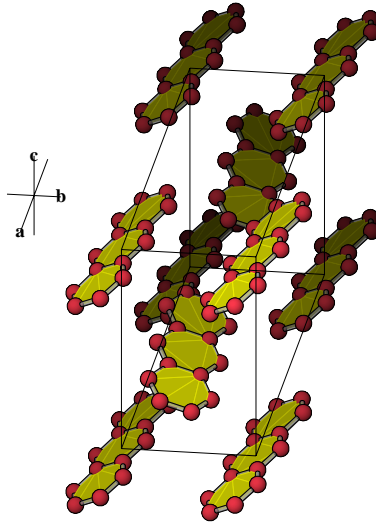


Fig. 1. Crystal Structure of anthracene. The charges injected in a FET move parallel to the surface within the bc -plane.

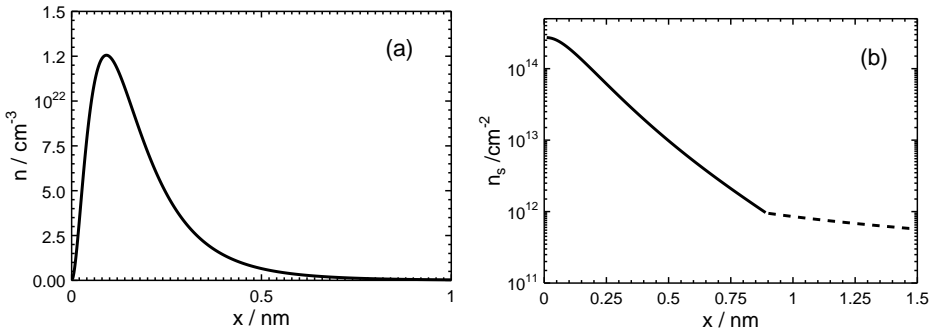


Fig. 2. Calculated concentration n (left panes (a)) and real charge density n_s (b) versus the distance to the oxide (b) within a fullerite based FET. In (b): full line — degenerate approximation with quantum confinement, dashed line — non-degenerate.

C_{60} , respectively, remains to be understood. In particular, the role of Coulomb interaction remains unclear. In Ref. 1 qualitative arguments have been that the field induced charge is accumulated approximately only within a *monolayer* at the surface of the organic semiconductor (for the C_{60} case). Since it is important to know whether the field-induced superconductivity does occur only in such an effectively 2D system, we check first that assumption quantitatively. Secondly, we report local density approximation (LDA) band structure calculations for the prototypical undoped bulk anthracene. From the calculated density of states (DOS) for the conduction and the valence bands the el-ph coupling constant λ is estimated using the results of Devos and Lanoo.⁴ Finally, from that λ and the measured T_c -values the

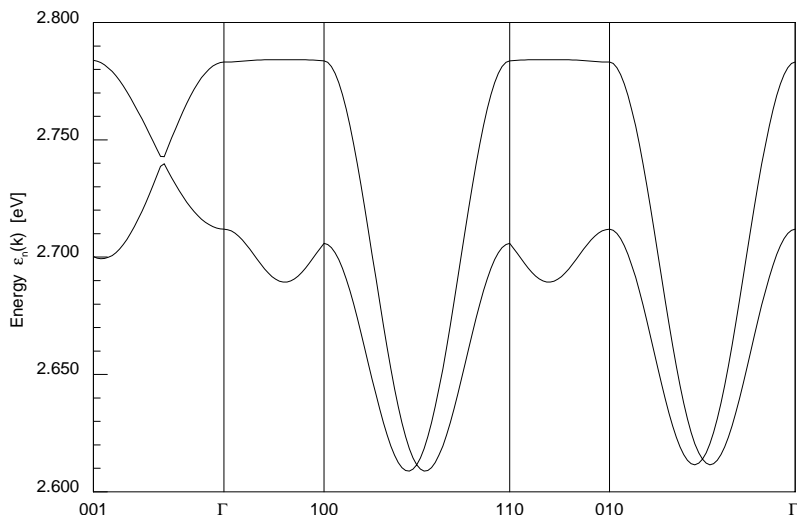


Fig. 3. The LDA-conduction band of bulk undoped anthracene.

value of the Coulomb pseudopotential μ^* is determined within the Eliashberg theory. In the FET-experiments the injected charge can be adjusted by the gate bias. Concentrations in excess of 10^{14} electrons/cm² can be accumulated at the surface of organic semiconductors. Such densities correspond to about one (three) electron(s) per polyacene (C₆₀) molecule, if one assumes that only the topmost molecular layer takes part in the conduction and the superconductivity (see Fig. 1). We calculated the concentration and the field profiles within a quasiclassical approximation for *n*-doped C₆₀. The undoped fullerite is modelled as an intrinsic semiconductor (gap 2 eV). Assuming for the effective density of states 1×10^{20} cm⁻³ the narrow bandwidth (large effective mass) is taken into account and a dielectric constant $\epsilon = 3$ is used. For E_F still in the gap, the carrier concentration is given by non-degenerate statistics and otherwise by Fermi statistics. Here we additionally take into account that the charge density of the inversion (accumulation) layer vanishes at the oxide interface due to the large potential barrier. This quantum mechanical confinement effect can be incorporated by using the modified Thomas–Fermi approximation.⁵ An example is shown in Fig. 2 for a total areal density¹ $n_s = 2.7 \times 10^{14}$ cm⁻² (corresponding to a surface electric field of 1.6×10^8 V/cm). Figure 2(a) shows the density as a function of the distance x to the oxide on a linear scale and Fig. 2(b) the areal density (from x to infinity). As expected the total induced charge is concentrated in a layer less than the C₆₀ diameter (0.7 nm) and the center of gravity is strongly shifted towards the interface. Our approach supposes the variation of the potential to be small over molecular dimension, therefore it is fully justified for fields up to 2×10^6 V/cm corresponding to $n_s = 3.3 \times 10^{12}$ cm⁻², where the system is already degenerated. For smaller distances the approximation formally does not work (but similar ones give even for metal surfaces with a strongly varying potential reasonable

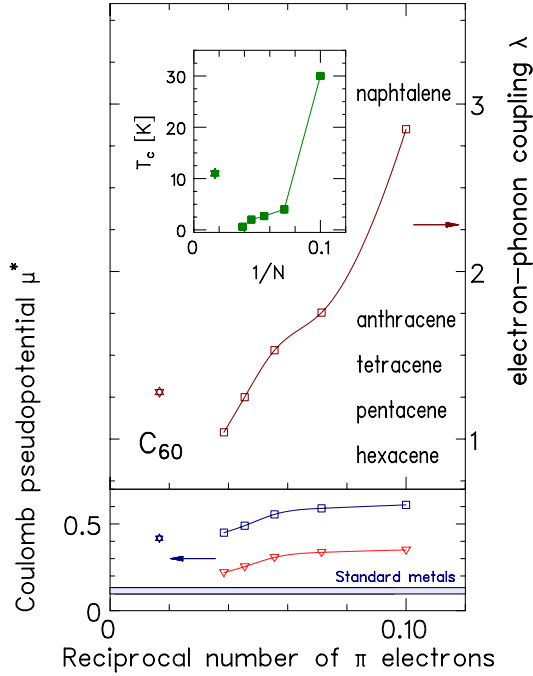
2D electron doped polyacenes and C_{60} 

Fig. 4. The empirical Coulomb pseudopotential for various polyacenes adopting $\hbar\omega_{ph} = 100$ meV.

results). Next we consider the LDA-electronic structure for 3D undoped anthracene. We calculated its electronic structure in the monoclinic spacegroup P21/c (No. 14) with the lattice constants $a = 11.172$ Å, $b = 6.0158$ Å, $c = 8.553$ Å, and the monoclinic angle $\beta = 124.596^\circ$ (see Fig. 1). Our calculations were performed using the FPLO scheme⁶ within the local density approximation (LDA). Details will be given elsewhere. Also for anthracene (as usual) the LDA underestimates the gap value: 2.6 eV compared with 4.1 eV (experiment). From Fig. 3 the anisotropic quasi-2D like nature of the conduction band can be deduced: a relatively strong dispersion along the b -axis, a reduced one along c , and a very weak one along the a -axis. The band width ~ 150 meV is extremely small compared with the expected value of the Hubbard repulsion $U \sim 1$ to 3 eV. From the noncosine shape of the dispersion along b the presence of strong frustrations can be derived. This might be important in explaining the metallic character at the half-filled situation where the maximal T_c is observed. The result of a simple Eliashberg analysis is shown in Fig. 4. Such an approach is supported by the direct measurement of at least the low-frequency part of the Eliashberg function $\alpha^2F(\omega)$ derived from the tunnel current reported for pentacene.⁷ The different T_c -values of polyacenes and C_{60} are strongly affected by the value of the Coulomb pseudopotential μ^* . In particular, anthracene shows

a significantly enhanced μ^* -value which is ascribed to reduced screening on small molecules and is considered as the main reason for the low T_c value despite the strong el-ph coupling. For the same DOS and an extrapolated nearly saturated μ^* -value as in anthracene, for the next smaller polyacene, naphthalene, a relatively high $T_c \sim 30$ K is predicted, whereas for hexacene with ~ 0.6 K it almost vanishes.

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