

Analysis of possible field-induced superconductivity in anthracene, other polyacenes, and C₆₀

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*We consider electronic structure and superconductivity aspects in field-doped polyacenes (PA) and C₆₀. 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_{int} is estimated using the work of Devos et al. (Phys. Rev. B **58**, 8236 (1998)) and the density of states estimated from a 2D-one-band model derived from a full potential LDA band structure calculation for bulk anthracene. The large differences in the reported T_c -values for PA and C₆₀ are ascribed to enhanced empirical Coulomb pseudopotentials μ^* for PA.*

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Recently field-induced superconductivity (FISC) has been reported for field effect transistors (FET) based on various organic systems.¹⁻³ Unfortunately, its very existence and the possibility to produce the necessary extremely high electric fields in FETs have not been verified so far by other groups.⁴ Anyhow, an electron-phonon (el-ph) mechanism is considered to be a likely candidate^{1,2}, although, details of the FISC are still unknown. 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 $\hbar\omega_{ph} \sim 100$ meV could be expected.⁵ There is a sizable corresponding el-ph coupling in aromatic molecules in general.⁶ Its strength increases with decreasing number of π -electrons N_π , in line with the T_c values (2, 2.7, and 4 K) reported for n -doped penta-, tetra-, and anthracene, respectively). Anyhow, with respect to PA the reason for the much higher $T_c \approx 11$ (18 - 26) K, 52 (80 - 114) K for n - and h -doped C₆₀, respectively, (values in brackets for

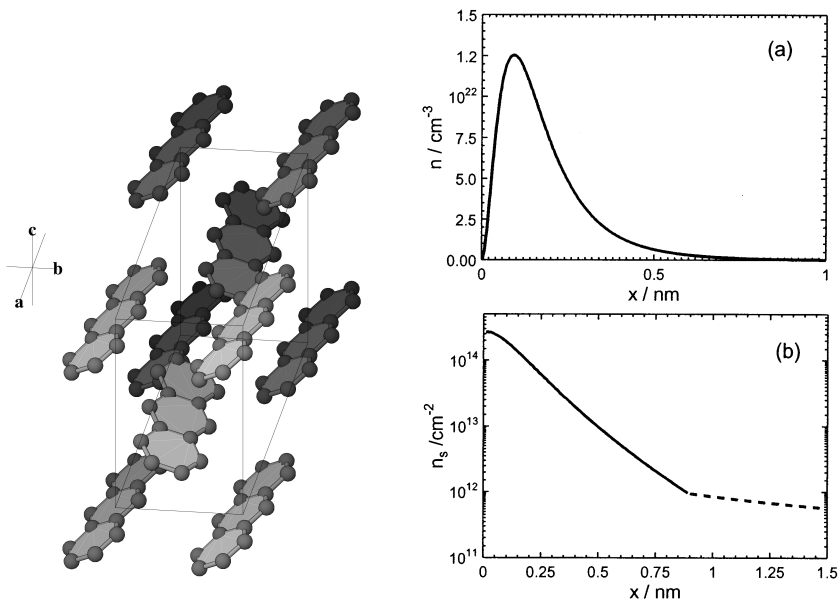


Fig. 1. (Left panel) Crystal structure of anthracene. The FI charges in a FET move \parallel to the surface within the *bc*-plane. (Right panel) Calculated volume density n (a) and area charge density n_s (b) vs. distance x to the oxide within a FET. In (b): full line - degenerate statistics approximation with quantum confinement, dashed line - nondegenerate statistics.

haloforms $\text{CHCl}(\text{Br})_3$ intercalated⁷, additional coupling to internal modes of these haloforms has been proposed⁸) and the role of Coulomb interaction remain to be understood. According to qualitative arguments¹ the FI charge is accumulated \approx only within a *monolayer* at the surface of the organic semiconductor. Since it is important to know whether the FISC is confined to such an effective 2D subsystem, we check first that assumption. Secondly, we report local density approximation (LDA) band structure calculations for the prototypical undoped bulk anthracene. Consequences for novel many-body physics and possible FISC are briefly discussed.

In the FET the injected charge can be adjusted by the gate bias. Concentrations $n_s > 10^{14}$ electrons/ cm^2 can be accumulated at the surface of organic semiconductors. Such densities correspond to about one (three) electron(s) per PA (C_{60}) molecule, if one assumes that only the topmost molecular layer takes part in the conduction and in the FISC (see Fig.

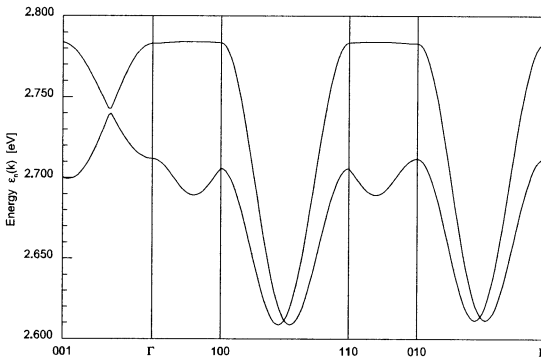


Fig. 2. The LDA-conduction band of bulk undoped anthracene. Notice its anisotropic quasi-2D like nature: a strong unusual dispersion along the b -axis, a reduced one along c , and a very weak one along the a -axis.

1). We calculated the concentration and the field profiles within a quasi-classical approximation for n -doped C_{60} . The undoped C_{60} is treated as an intrinsic semiconductor (gap 2eV). Assuming for the effective density of states $1 \times 10^{20} \text{ cm}^{-3}$ the narrow band width (large effective mass) is taken into account⁹ and a dielectric constant $\epsilon = 3 - 4$ is used.¹⁰ 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 practically vanishes at the oxide interface due to the large potential barrier caused by the big oxide gap $\sim 8 - 10$ eV. This quantum confinement effect can be incorporated by using the modified Thomas-Fermi approximation.¹¹ An example is shown in Fig. 1 for a total area density¹ $n_s = 2.7 \times 10^{14} \text{ cm}^{-2}$ (corresponding to a surface electric field of $1.6 \times 10^8 \text{ V/cm}$). Fig. 1a shows the density as a function of the distance x to the oxide on a linear scale and Fig. 1b the area density (from x to infinity). The total FI charge is concentrated in a layer *less* than the C_{60} diameter (0.7nm) 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 valid for fields up to $2 \times 10^6 \text{ V/cm}$ corresponding to $n_s = 3.3 \times 10^{12} \text{ cm}^{-2}$, 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 results). Note that within a microscopic approach Wehrli et al.¹² came to the same conclusion: the FI charge is indeed confined to one C_{60} layer, only. However, the questions of the detrimental role of fluctuations should be addressed since they might destroy any FISC in a truly 2D-system

(see e.g. the lack of superconductivity in an isolated CuO_2 bilayer¹³).

Next, we consider within the LDA-FPLO scheme¹⁴ the electronic structure for 3D undoped anthracene. We calculated its band 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). Also for anthracene the LDA underestimates as usual the gap value: 2.6 eV vs. 4.1 eV (exp.). The band width ~ 150 meV (see Fig. 2) is rather small compared with the expected value of the Hubbard $U \sim 2$ to 3 eV (≈ 1.6 eV for C_{60} ¹⁵ which gives a lower bound for the less screened smaller PA molecules). Then, formally, the injected charge carriers in the FI effective 2D PA surface band at half-filling would be even stronger correlated than those in undoped cuprates. So, an antiferromagnetic (afm) Mott-Hubbard insulator might be expected at $T = 0$. However, from the non-cos shape (i.e. beyond the n.n. tight-binding picture) of the dispersion along b the presence of strong "frustrations" (for a corresponding afm $S=1/2$ Heisenberg-model) can be derived. This might be important in explaining the metallicity at half-filling where the maximal T_c is observed. To illustrate this point, we consider a 1D example (see Fig. 3) where the optical gap derived from the optical conductivity (calculated using standard Lanczos and continued fraction methodes) is shown. For strong t_2 the Mott-Hubbard (charge) gap could be strongly reduced and/or a spin gap¹⁶, helpful for FISC, might occur.

A phenomenological Eliashberg analysis has been considered by us in Ref. 17. Such an approach would be supported by the direct measurement of the Eliashberg function $\alpha^2 F(\omega)$ derived from the tunnel current

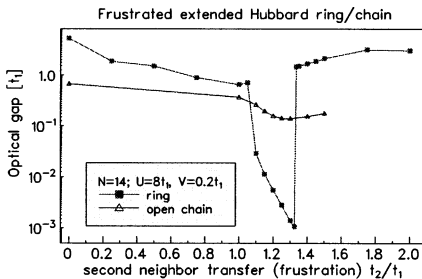


Fig. 3. Optical gap vs. second neighbor transfer integral t_2 (in units of the nearest neighbor transfer integral t_1) for strongly correlated chains with $N = 14$ sites and weak intersite Coulomb interaction V at half filling.

such as reported for pentacene³. From the calculated density of states (DOS) for the conduction band the el-ph coupling constant $\lambda = N(0)V_{ph} \approx N(0)1800\text{meV}/N_{\pi} \approx 1.76$ was estimated using V_{ph} of Ref. 6. Finally, from λ and the reported T_c the value of the Coulomb pseudopotential $\mu^* \approx 0.59$ was determined within Eliashberg theory. The reported different T_c -values of PA and C₆₀ are affected by the value of the Coulomb pseudopotential μ^* . In particular, anthracene shows an enhanced μ^* -value which is ascribed to reduced screening on its small molecules. This is considered as the main reason for the low T_c despite the strong el-ph coupling. Adopting the same DOS and an extrapolated nearly saturated value $\mu^* \approx 0.61$ like in anthracene, for naphthalene (the next shorter PA) even $T_c \sim 30$ K would be expected, while with $\mu^* \approx 0.45$ for the longer hexacene $T_c \sim 0.6$ K should almost vanish.

To summarize, the charge carriers induced by very strong electric fields $\sim 10^8$ V/cm in PA and C₆₀ are confined to one monolayer. In the case of PA they should be described by nontrivial 2D tight-binding models with possible new many-body effects. We believe that these results remain valid independently of the reliability of the reported data¹⁻³. On the contrary, our FISC analysis does rest on them. Hence, any confirmation, modification, or even refutation at all by other experimental groups would be highly desirable.

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