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Giovanni Bussi, Alice Ruini, Elisa Molinari, Marilia J. Caldas, Peter Puschnig, and Claudia Ambrosch-Draxl

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Interchain interaction and Davydov splitting in polythiophene crystals: An *ab initio* approach

Giovanni Bussi, Alice Ruini,^{a)} and Elisa Molinari

INFM-S³ and Dipartimento di Fisica, Università di Modena e Reggio Emilia, Via Campi 213/A, 41100 Modena, Italy

Marilia J. Caldas

Instituto de Física, Universidade de São Paulo, Cidade Universitária, 05508-900 São Paulo, Brazil and INFM, Italy

Peter Puschnig and Claudia Ambrosch-Draxl

Institute for Theoretical Physics, Karl-Franzens-University Graz, Universitätsplatz 5, A-8010 Graz, Austria

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The crystal-induced energy splitting of the lowest excitonic state in polymer crystals, the so-called Davydov splitting Δ , is calculated with a first-principles density-matrix scheme. We show that different crystalline arrangements lead to significant variations in Δ , from below to above the thermal energy $k_B T$ at room temperature, with relevant implications on the luminescence efficiency. This is one more piece of evidence supporting the fact that control of interchain interactions and solid-state packing is essential for the design of efficient optical devices. © 2002 American Institute of Physics. [DOI: 10.1063/1.1483905]

Among the molecular materials displaying a semiconducting behavior, poly- and oligothiophenes (PT and nT) were demonstrated to be suitable for several electronic and optoelectronic applications. nT -based films were successfully incorporated as active materials in field-effect transistors^{1,2} and light-emitting diodes² and were proven to show stimulated emission.³ A significant advantage lies in their versatility: for example, the emitted color of nT -based diodes can be easily modulated by chemical functionalization,^{4,5} which can affect both the emission properties of the single molecule, and the packing configuration in the films. The design of electro-optic devices with enhanced performance calls for a deeper understanding of the fundamental mechanisms governing device operation. While the optical properties of molecules or very small aggregates have been investigated extensively through quantum-chemistry approaches,^{6,7} much less is known on three-dimensional crystalline effects, which require the description of extended systems. In this case, the methods of theoretical solid-state physics give a significant contribution, as they are intrinsically suitable⁸⁻¹⁰ to take into account the periodicity of the structure, and can therefore investigate^{9,10} the very role played by intermolecular interactions.

Thiophene-based materials can be considered as prototype systems to investigate the issue of intermolecular coupling in organic crystals. Indeed, nT were widely studied by means of several experimental techniques, as they can be grown in thin films with high crystallinity and chemical purity. Some significant properties of nT crystals are experimentally well established: unsubstituted α - nT systems, with n from 4 to 16 (the number of thiophene units in a single molecule), usually crystallize in a herringbone structure, and there is overall agreement concerning the excitonic nature of

the lowest active state observed in the absorption spectrum.¹¹ Moreover, the optical properties of these systems are known to depend strongly on symmetry: due to the presence of non-equivalent molecules in the periodic cell, each excitonic molecular level is found to split in the solid in so-called Davydov components.¹² It is agreed that the lowest component is optically inactive (dark), leading to luminescence quenching in the zero-temperature limit. The size of this energy splitting (Davydov splitting, Δ) compared to the thermal energy $k_B T$ is a critical quantity for the efficiency of photoluminescence processes in nT -based systems. If $\Delta \gg k_B T$, excitations are expected to decay into the lowest available state, which leads to nonradiative emission; conversely, if the two lowest states (active and dark) are practically degenerate, the photoluminescence process is expected to maintain the same efficiency as for the isolated molecule. In spite of its crucial impact on the performance of optical devices, there is still an ongoing controversy about Δ , for which a wide range of values have been proposed.^{7,11,13-15} In this letter, we will examine this quantity by means of first-principles calculations for model solid-state systems, show that its magnitude compared to $k_B T$ is indeed highly sensitive to the crystalline arrangement, and discuss the implications for the interpretation of experimental data.

For $n=4$ and $n=6$ two different polymorphs have been identified,¹⁶ depending on the deposition temperature T , which are called, respectively, α - nT/HT (high temperature) and α - nT/LT (low temperature). Analysis of the structural data provided by diffraction experiments in Ref. 16 indicates that two different polymer crystals can be constructed, which reproduce essentially the same interchain geometry as the oligomer polymorphs, denoted henceforward as PT1 (HT) and PT2 (LT), respectively.⁹ In both cases, there are two chains per unit cell in herringbone structure, the main difference being a translation of the second chain relative to the first by half of a unit vector along the chain direction (z axis,

^{a)}Electronic mail: alice.ruini@unimo.it

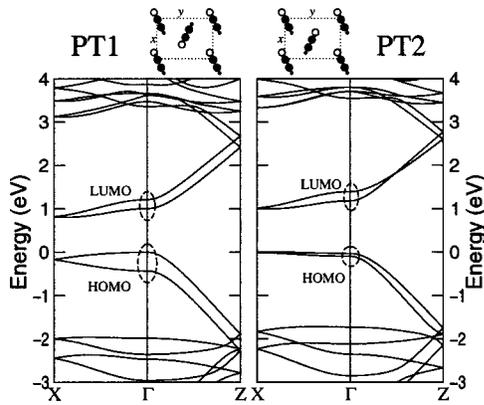


FIG. 1. Electronic band structure of PT1 (left-hand side) and PT2 (right-hand side); the pair of bands originating from HOMO is visibly more split in the first case. ΓZ corresponds to the chain direction while ΓX is perpendicular. The crystal geometry is depicted schematically as a projection of one thiophene layer on xy plane. ●, ○, • represent C, S, and H atomic positions, respectively.

see inset of Fig. 1). This leads to a different interchain configuration for the π -electrons in the *cis*-polyacetylenelike orbitals of PT. Previous theoretical work⁹ has shown that the highest occupied molecular orbital (HOMO) reflects this different environment in a higher interchain charge density for PT1 than for PT2.

To calculate the optical properties of the PT1 and PT2 crystals, we need to go beyond the mean-field (single-particle) study. We have implemented an *ab initio* density-matrix scheme where the correlated electron-hole spectrum is obtained from the interband polarizations $\langle d_v^\dagger c_\mu \rangle$, describing the creation of an electron in conduction state μ , with energy ϵ_μ^e , and a hole in valence state v , with energy ϵ_v^h (c_μ^\dagger and d_v^\dagger are the fermion creation operators; the labels $\mu = (c, \mathbf{k})$ and $v = (v, \mathbf{k})$ include both band index and wave vector). Following Ref. 17, the exciton states are obtained by direct diagonalization of the Schrödinger equation:

$$(\bar{\epsilon}_\mu^e - \bar{\epsilon}_v^h)A_{\mu\nu} + \sum_{\mu'v'} (2V_{\mu\nu',v\mu'} - W_{\mu\mu',vv'})A_{\mu'v'} = E_x A_{\mu\nu},$$

where W is the electron-hole screened direct Coulomb interaction and V is the unscreened exchange interaction, present only for singlet excitons; this is equivalent to the Bethe-Salpeter equation¹⁸ (obtained within the Green's function framework). The solution of the above equation yields the excitonic eigenenergies E_x and eigenstates \mathbf{A} , the expansion

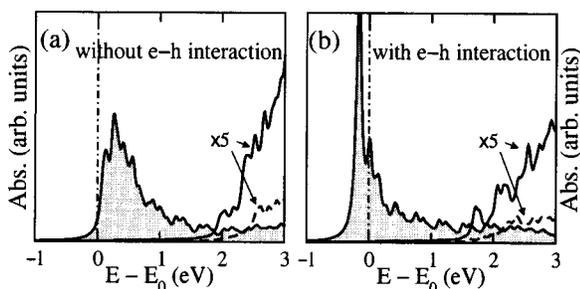


FIG. 2. Calculated absorption spectra (arbitrary units) of PT1 in three polarizations, relative to the quasiparticle band gap E_0 (x solid, y dashed, z solid shaded); the spectra in (a) and (b) are calculated without and with electron-hole interaction, respectively. The z polarization is dominant at low energy. The Gaussian broadening is 0.05 eV.

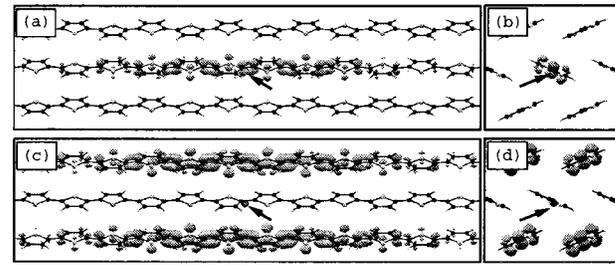


FIG. 3. Excitonic wave functions obtained by fixing the position of the hole (indicated by arrow); (a) and (b): lowest direct exciton wave function in (x,z) and (x,y) plane; (c) and (d) same for the lowest charge-transfer exciton.

coefficients for the real-space excitonic wave function $\Psi(\mathbf{r}_e, \mathbf{r}_h) = \sum_{\mu\nu} A_{\mu\nu} \psi_\mu(\mathbf{r}_e) \psi_\nu^*(\mathbf{r}_h)$. The calculation of noninteracting electron and hole quasiparticle energies $\bar{\epsilon}$ and wavefunctions ψ was accomplished by means of a first-principles approach within the density-functional theory and the local density approximation.^{19,20} we used a plane-waves basis set and *ab initio* pseudopotentials, with a rigid shift to the conduction band energies to account for the self-energy correction.²¹ The direct kernel W depends on the dielectric response of the medium, that we describe within the random-phase approximation through a static macroscopic dielectric tensor, to account for spatial anisotropy.²²

The single-particle electronic band structure (Fig. 1) is in excellent agreement with the previous all electron calculation of Ref. 9 for PT1 and PT2. The topmost pair of valence and the lowest pair of conduction bands originate, respectively, from the highest occupied band [highest occupied molecular orbital (HOMO)] and the lowest unoccupied band (LUMO) of a single thiophene chain: this “doubling” is due to the presence of two chains in the unit cell, and the splitting is the signature of the interchain interaction. We confirm that the coupling between non equivalent chains in PT1 is stronger than in PT2, particularly for the HOMO. We also note that, in ΓZ direction (chain direction) the bands have a strong dispersion, while the dispersion is smaller but not vanishing along ΓX (or ΓY).

In Fig. 2, we show the absorption spectrum for PT1 (plots for PT2 are quite similar) in three different polarizations, referred to the quasiparticle energy gap E_0 . The spectra are strongly polarized: at energies near the band gap only the component polarized in the chain direction (z) has a nonvanishing oscillator strength, while the perpendicular polarizations are active at higher energies. Electron-hole interaction crucially affects the spectrum, inducing an optically active state below the band gap. In addition, absorption just above band gap is strongly reduced.²³ Besides the optically active states depicted in Fig. 2, other transitions are also introduced below the single-particle gap, strikingly different in character. The lowest active exciton is “direct” (DE), that is, strictly confined to one chain, as is also its (inactive) Davydov partner; however, we find also charge-transfer excitons (CTE) with electron and hole on different chains, that are expected to be dark due to the low probability for radiative recombination. These CTE are ~ 0.2 eV below the single-particle gap, and always very close in energy to the active DE, particularly so for PT1. We show in Fig. 3 the excitonic wave functions for the active DE and the lowest CTE, where the spatial extension of the exciton and the large

TABLE I. Band splitting Δ_{HOMO} and Δ_{LUMO} (at the Γ point), and Davydov splitting Δ for the PT1 and PT2 crystal arrangements; all energies in eV.

	Δ_{HOMO}	Δ_{LUMO}	Δ
PT1	0.43	0.21	0.06
PT2	0.06	0.21	0.01

anisotropy of the system can also be appreciated.

We now focus our attention on the lowest direct excitons: for both crystal structures, the interchain interaction introduces the Davydov optically forbidden transition *below* the active state depicted in Fig. 2(b); even accounting for the differences expected between our infinite-chains model and nT crystals, this explains the low luminescence efficiency in the crystalline phase with respect to solutions. Results for Δ in both crystal arrangements are summarized in Table I, where they are also compared to single-particle band splittings for HOMO and LUMO; Δ_{HOMO} is larger in the first structure, due to the stronger interchain interaction, and accordingly Δ is found to be higher for PT1 than for PT2; however we observe that the single-particle values can be one order of magnitude larger than the final correlated splitting, and so no general rule can be inferred to obtain Davydov splittings directly from single-particle eigenvalues. It is interesting to note that in PT1 and in PT2 Δ is, respectively, above and below $k_B T$ at room temperature, which would lead to a crucial difference between the two crystal structures in luminescence efficiency at room temperature.²⁴ Currently reported experimental values for Δ for oligothiophene crystals are controversial, and range^{7,11,13–15} from 120 to 10 000 cm^{-1} . Due to the particular arrangement of the molecules in the crystal, both Davydov transitions can actually be seen in oligothiophene crystals: the extraordinary difficulty in measuring Δ arises (a) from a tilt of the long chain axis of the molecules relative to the interlayer axis, which mixes polarizations, and (b) from the “standing” configuration of the molecules on the substrate, which has special geometrical-optics effects on the polarized spectra.²⁵ Furthermore, vibronic couplings are very strong in the systems, and could mask the actual exciton transitions. Our results support the simplest interpretation of the spectra, leading to the smaller estimates^{11,13,25} of the splitting (on the range of 120 to 640 cm^{-1}).

In conclusion, we confirm that the detailed crystalline arrangement strongly affects the optical performances of PT- or nT -based materials, and, since relevant features such as the Davydov splittings can be quite subtle, it is important in this case that theoretical studies take into account the extended nature of the problem, and be performed with tools that have minimum dependence on empirical parameters.

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- ²¹We use a shift of 1.4 eV, taken from Ref. 8, very similar to the value for *trans*-polyacetylene from Ref. 18.
- ²²For the description of the first excitonic states, convergence was reached with the top four valence bands, the first four conduction bands and 320 \mathbf{k} points in the Brillouin zone, while we used a 45 Ry energy cutoff for the plane-wave expansion in the single-particle calculation.
- ²³Analysis of this effect in terms of density of excitations and oscillator strength shows that the former is virtually unchanged with respect to the joint density of single-particle states, while the latter is clearly quenched. This behavior is consistent with previous findings for other one-dimensional systems; e.g., see F. Rossi and E. Molinari, *Phys. Rev. Lett.* **76**, 3642 (1996); *Phys. Rev. B* **53**, 16462 (1996).
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