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Violation of the Peierls theorem in graphite chains

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Vibronic (or Peierls) instabilities in polyacene (PA), polyacenacene (PAA), and polyperylene (PP) are studied, combining tight-binding band-structure computations with rigorous line-group theoretical arguments. Contrary to the current belief, for each of these polymers a static distortion exists, opening a gap that is *linear with respect to the distortion amplitude,* at the Fermi level. On the other hand, their behavior departs significantly from that of the simple Peierls model. Novel types of symmetry breaking are identified; vibronically active modes are either transverse optical or longitudinal optical. In addition, PA and PAA are predicted to possess two inequivalent but equi-energetic distorted ground-state configurations each. Thus, these polymers can support interphase soliton kinks, which may be of novel (transverse) type. Experimental tests are suggested to check these predictions.

I. INTRODUCTION

In this paper I discuss whether the Peierls theorem is applicable to the quasi-one-dimensional (1D) graphite polymers polyacene (PA), polyacenacene (PAA), and polyperylene (PP) [see Figs. 1(a)—1(c)]. Electronic properties of these compounds are attracting great interest; the predicted features range from metallic conductivity combined with stability in air, to high-temperature superconductivity or ferromagnetic ordering.[1] The results of the first successful synthesis (of PP) are exciting indeed:[2] the material is perfectly ordered, highly conductive without any doping, and stable in air for months; furthermore, the conductivity is almost temperature independent, from 300 K down to 30 K. Finally, recent numerical results of several workers[3—7] imply that the Peierls theorem is *not* applicable to PA, PAA, and PP, contrary to the common belief that it should be valid for all metallic polymers and quasi-1D molecular stacks.

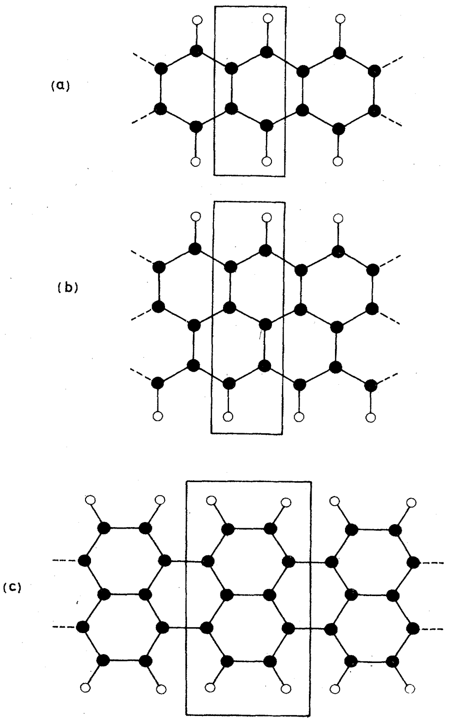

FIG. 1. Quasi-1D graphite polymers: (a) polyacene or $(C_4H_2)_x$, (b) polyacenacene or $(C_6H_2)_x$, and (c) polyperylene or $(C_{10}H_4)_x$.

Namely, it is easy to prove[8]—at least within a crude model that ignores electron-electron interactions, fluctations, interchain interactions, etc.—that, for every *simple metallic polymer* (i.e., a periodic chain of identical atoms, with the conduction band partially occupied) there exists a static distortion **Q** (of amplitude Q and of wavelength $\lambda=2\pi/q$) such that the following conditions apply:

(i) q is equivalent to $2k_F$.

(ii) **Q** breaks the symmetry of the chain.

(iii) **Q** opens a gap E_g at the Fermi level E_F.

(iv) $E_g \propto Q$ for small Q.

(v) The total electronic energy varies as $Q^2 \ln Q$.

(vi) The total adiabatic energy of the chain has a minimum for some $Q \neq 0$.

However, Yamabe *et al.*[3] calculated the total energy of PAA in various configurations and concluded that "in PAA the Peierls transition does not take place and one can expect the metallic behavior of this material." For PA, Brédas *et al.*[4] found the E_g values to be "either very low or identically zero." Baldo *et al.*[5] claimed that the ground-state PA is not Peierls distorted but rather antiferromagnetic. On the contrary, Tanaka *et al.*[9] found that PA should be distorted [along $\mathbf{Q}_3$, Fig. 3(b)]. Kertesz and Hoffmann[6] noticed that $E_g \propto Q^2$ in PA [for $\mathbf{Q}_2$ and $\mathbf{Q}_3$, Fig. 3(b)], $E_g \propto Q^3$ in PAA, etc., and concluded that their results "qualify Peierls theorem on intrinsic instability of one-dimensional systems." Indeed, they explicitly contradict condition (iv). However, Kivelson and Chapman[1] stated that $\mathbf{Q}_2$ and $\mathbf{Q}_3$ distortions probably do not occur at all in PA, being "superseded by one of the other analytically stronger instabilities" such as distortion along $\mathbf{Q}_1$ [Fig. 3(a)]. On the other hand, they found the total electronic energy to vary as $Q^{3/2}$, which contradicts condition (v).

As for PP, Tanaka *et al.*[7] found that in the ground state it should be distorted as shown in Fig. 8(a). However, this distortion preserves the symmetry of the chain, in contrast to condition (ii). Therefore, there is ample controversy to motivate a discussion on vibronic instabilities in PA, PAA, and PP, to which this paper is devoted.

II. THE METHOD

To begin with, PA, PAA, and PP are not simple polymers: their unit cells contain several atoms; there are intracell degrees of freedom, and the line-group symmetry is much lower. Let us list the following definitions: $\mathbf{R}^0=\{\mathbf{R}_1^0,\mathbf{R}_2^0,\ldots,\}$ denotes the initial (undistorted) configuration of the polymer considered; $\mathbf{R}$ denotes a distorted configuration; L is the line group of $\mathbf{R}^0$; $L^A=L+\theta L$ is the corresponding grey line group (θ is the time reversal); $|e\rangle, |e'\rangle$ are the degenerate one-electron eigenstates at E_F, belonging to a corepresentation D_e; $[D_e^2]$ is the symmetrized Kronecker square of D_e; $\hat{\mathbf{q}}_i$ are unit distortions forming a basis of D_Q; $\mathbf{Q}=\sum_i \lambda_i \hat{\mathbf{q}}_i$ is an arbitrary nontotally-symmetric static distortion; V is the effective one-electron potential;

$$\mathbf{W}(\mathbf{Q})=\langle \mathrm{e}\,|\,\mathbf{Q}\cdot(\partial \mathrm{V}/\partial \mathbf{Q})_0\,|\,\mathrm{e}'\rangle$$

is a matrix element of the linear vibronic coupling; $\mathbf{Q}$ is (linearly) *allowed* means that $W(\mathbf{Q})=0$ is not required by the symmetry of the polymer; $\mathbf{Q}$ is linearly vibronically active (LVA), which means that $E_g \propto Q$ for small Q.

In Ref. 10 it was shown that a variety of topologically inequivalent band shapes (e.g., single or double lines, semicrosses, semiloops, loops, butterflies, etc.) can be formed in complex polymers. By investigating all the possible cases, I have proved[11] the following:

Theorem 1. For every polymer with a partially filled conduction band there exists an LVA distortion.

For the three polymers under study, such LVA modes are explicitly identified below; the general proof is somewhat lengthy and it is presented elsewhere.[11]

The Peierls theorem thus can be generalized to complex polymers, to a certain extent. Important differences are found[11] also: in complex polymers the LVA modes can be transversal as well as longitudinal, optic as well as acoustic, ferro- or antiferro- distortive or displacive; they can even be fourfold-degenerate themselves. The condition (ii) (that q is equivalent to $2k_F$) is, in general, neither sufficient nor necessary. Finally, the counterexample to condition (v) given in Ref. 1 is valid, despite the fact that the model is highly idealized.

An efficient method for symmetry analysis of vibronic instabilities (including identification of the actual LVA modes, description and classification of interphase kinks, etc.) was presented recently.[10] Although systematic degeneracy was considered exclusively in Ref. 10, the same procedure is applicable to PA, PAA, and PP, which represent three distinct generic cases: a symmetry-required band crossing in PAA, an accidental symmetry-allowed crossing in PA, and a symmetry-forbidden (avoided) crossing in PP.

For maximal clarity, the present discussion is based on simple π-electron tight-binding Hamiltonians for PA, PAA and PP, quite analogous to the well-known Su, Schrieffer, and Heeger[12] model, except that here the electron-phonon interaction is taken into account by allowing both[1] the on-site energy α and the nearest-neighbor resonance energy (or transfer integral) β to vary upon distortion. Let i,i' label two neighboring atomic sites; then I suppose that

$$\alpha_i=\alpha_i^0+A_iQ,\quad \beta_{ii'}=\beta_{ii'}^0+B_{ii'}Q \tag{1}$$

for small Q. In fact, $B_{ii'}Q=B\Delta R_{ii'}$, where $\Delta R_{ii'}$ is the variation of length of the bond involved, induced by the distortion $\mathbf{Q}$. The typical values employed here are $\alpha=-11.4$ eV, $\beta=-2.5$ eV, $A=4$ eV/Å, and $B=4.5$ eV/Å; these estimates are based on *ab initio* Hartree-Fock calculations on small molecules.[13] It is shown below that in certain cases the values of A_i, rather than that of B, govern the gap opening and hence the strength of the vibronic instability.

Within this simple methodology I have calculated band structures for various configurations, regular and distorted, of the three polymers under study. In these computations, the symmetry-adaptation technique of Ref. 14 was utilized, rendering analytical solutions possible in most cases. In Figs. 2(a), 5(a), and 7(a) only the pairs of bands that are sufficient for a qualitative analysis (the highest occupied and the lowest unoccupied bands) are shown, for the regular PA, PAA, and PP, respectively. The relevant degenerate eigenstates at E_F are sketched also, in Figs. 2(b), 5(b), and 7(b), respectively. They are labeled by the following quantum numbers, in order of appearance:

(a) quasimomentum k, in units such that $-\pi<k\leq\pi$;
(b) the parity with respect to σ_v (the reflection in xz plane): A is even, B is odd;
(c) the quasi-angular-momentum of C_2 (the rotation for 180° about the z axis): 0 denotes even, 1 denotes odd;
(d) the parity with respect to σ_h (the reflection in xy plane): + denotes even, − denotes odd.

The conservation laws for these quantum numbers provide a simple alternative to the customary but much more sophisticated group-theoretical techniques.

To test the extent of the present analysis, I have investigated the effects of the second-neighbor, the third-neighbor, etc., interactions; the principal conclusions (given in Sec. VI) are not affected. More sophisticated band-structure computations[3,7,9,15] give similar band shapes again, in general; a detailed discussion is given below for each of the three polymers separately.

III. POLYACENE $(C_4H_2)_x$

The spatial symmetry of PA is described by the line group $L2/mmm$. There are four π-electron bands; the two relevant bands are sketched in Fig. 2(a). The degenerate one-electron states at E_F are $|\pi B\,0+\rangle$ and $|\pi B\,1+\rangle$, see Fig. 2(b). Thus $D_e=(\pi B\,0+)+(\pi B\,1+)$, and

$$[D_e^2]\sim 2(0A\,0+)+(0A\,1+) \tag{2}$$

where $(\pi B\,0+)$, $(\pi B\,1+)$, etc. denote the irreducible representations of $L\,2/mmm$.

Looking for the stabilizing distortion of PA, most investigators (Refs. 1, 4, 6, 9, and 15) followed common chemical intuition and examined $\mathbf{Q}_2$ and $\mathbf{Q}_3$ distortions shown in Fig. 3(b). However, it follows from (2) that $\mathbf{Q}_2$ and $\mathbf{Q}_3$ (and all their linear combinations) are linearly *forbidden.* Hence, none of them can cause E_g to vary with Q, and the $E_g \propto Q^2$ result of Kertesz and Hoffmann[6] is hardly surprising.

On the other hand, (2) also implies that *there exists* a nontrivial LVA mode in PA, namely, the $\mathbf{Q}_1$ mode of $(0A\,1+)$ symmetry [Fig. 3(a)]. (For simplicity, I am temporarily disregarding the hydrogen atoms.) In the present model $E_g=2AQ_1$ and if the upper (lower) carbon—carbon bonds are extended (contracted) for as small a distance as 0.02 Å, already $E_g \gtrsim 0.3$ eV. Hence, the Peierls theorem or, more precisely, its generalization, Theorem 1 of Sec. II, holds true for PA.

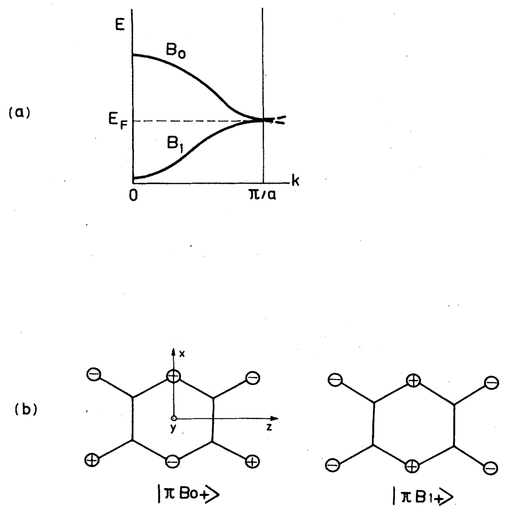

FIG. 2. (a) Highest occupied and the lowest unoccupied π-electron bands of polyacene (PA). The symmetry labels are defined in Sec. II. (b) Degenerate one-electron eigenstates at the Fermi level E_F.

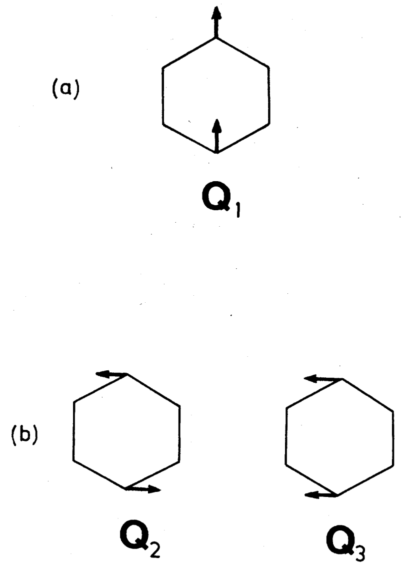

FIG. 3. (a) Linearly vibronically active distortion of PA. (b) Distortions of PA investigated in Refs. 4, 6, 9, and 15.

It is instructive to investigate further why the proper (i.e., symmetry-allowed) mode $\mathbf{Q}_1$ was ignored in the literature (except for Ref. 1). Notice first that $\mathbf{Q}_1$ opens a gap at E_F by affecting the values of α on the displaced carbon atoms. [$\mathbf{Q}_1$ also affects the values of β corresponding to the outer C—C bonds, but does not influence the energies of $|\pi B\,0+\rangle$ and $|\pi B\,1+\rangle$.] However, in the standard extended Hückel method (as utilized in Refs. 6 and 15) α is not allowed to vary, so that $A\equiv 0$ and $\mathbf{Q}_1$ is not active, *accidentally.* In fact, the Hückel Hamiltonian of PA possesses some additional dynamical symmetries. In particular, $\mathbf{Q}_1$-type distortions leave invariant the $k=\pi/a$ block of the π-electron Hückel matrix. The same is true for the sign flip of the π orbitals that contribute to $|\pi B\,0+\rangle$ and $|\pi B\,1+\rangle$, which, in fact, is the reason why these two states are degenerate. These artificial symmetries can be easily removed in practice. For the first one, it is sufficient to assume an appropriate nonzero value of A, or to utilize an iterative variant[16] of the extended Hückel method. The second artificial symmetry is lifted when the third-nearest-neighbor interactions are included; the result is that the B_0 band crosses the B_1 band inside the Brillouin zone (at $k_F \approx 0.85\pi/a$). In that case, there are *four* degenerate eigenstates at E_F, namely, $|k_F B\,0\rangle$, $|-k_F B\,0\rangle \equiv \theta\,|k_F B\,0\rangle$, $|k_F B\,1\rangle$, and $|-k_F B\,1\rangle \equiv \theta\,|k_F B\,1\rangle$. Now $D_e=(k_F E B\,0)+(k_F E B\,1)$ (E denotes[10] a two-dimensional representation) and hence

$$[D_e^2]\sim 2(0A\,0+)+(0A\,1+)+(0A\,1-)$$
$$+2(\kappa E A\,0)+(\kappa E A\,1)\ , \tag{3}$$

where

$$\kappa=2k_F(\mathrm{mod}\,2\pi/a)\simeq 0.3\pi/a\ .$$

The above result (3) deserves a few comments. First, notice that $(\kappa E A\,0)$ and $(\kappa E A\,1)$ modes grossly break the translational symmetry: $\lambda=2\pi\kappa \approx 6.7a$, which is incommensurate with a. Such distortions have not been investigated in PA yet; in principle, they could evolve into soliton lattices. Next, some fundamental modes (including

Q_1) remain active, although $q=0$ is *not equivalent to* $2k_F$ here, which contradicts statement (i). Finally, (3) implies that Q_3 [which belongs to $(0A0-)$] remains linearly forbidden, while Q_2 [of $(0A1-)$ symmetry] becomes *linearly allowed,* as soon as the third-nearest neighbors are taken into account. Thus $E_g \propto Q$ is true even for the Q_2 mode. This, by the way, explains why Q_2 stabilizes the chain more than Q_3. On the other hand, further-neighbor interactions are weak, and one expects a small stabilization energy ΔE and a small equilibrium distortion amplitude, as indeed found by Tanaka *et al.*[9] [They predict $\Delta E=0.025$ eV per one C_4H_2 unit and $\Delta R=R(\mathrm{C—C})-R(\mathrm{C{=}C})=0.033$ Å.]

As for the results of Brédas *et al.*[4], the distortions Q_2 and Q_3 they assumed are almost twice too large; indeed, one expects $E(Q\approx 2Q_{\min})\approx E(Q=0)$. Finally, Baldo *et al.*[5] assumed the undistorted configuration and found a SDW; however, if electron-phonon coupling is strong, as argued above, one does not expect[17] the SDW instability to dominate and the ground state should be Peierls distorted. [Notice that the relevant π bands of PA are very wide; joint width is 10—12 eV according to extended Hückel theory (EHT) studies[15] and as much as 25 eV according to self-consistent field (SCF) complete neglect of differential overlap results,[9] much larger than that of trans-polyacetylene. On the other hand, the CNDO calculations predict no crossing of $B0$ and $B1$ bands, but rather a pseudodegeneracy at $k_F=\pi/a$.]

Let me comment briefly now on the role played by the hydrogen atoms. Since the two atoms that form a C—H bond can move out of phase or in phase, Q1 splits in fact into two linearly allowed fundamental modes. The first of these two modes involves stretching of C—H bonds; it is infrared active and should give rise to an absorption band at ~ 3000 cm^{-1}. It is the second mode, in which each methine($=$CH—) unit moves as a whole, that is expected to soften within the present simple model. (Molecular chains with two competing modes have been studied recently by Lépine.[18] He concluded that a single phase transition should occur, in which certain linear combination of the two modes softens.) However, as seen from (3), the actual situation in PA could be more complex; several LVA modes can compete, including some totally symmetric ones, some other fundamental modes like Q_2, as well as some modes at $q=\kappa$.

To determine the actual ground state of PA, we undertake extensive geometry optimizations, utilizing both an iterative extended Hückel method and an *ab initio* SCF Hartree-Fock method.[13] At the same time an important suggestion of Kivelson and Chapman[1] that unusually strong instabilities could occur in PA will be tested on more realistic models of this polymer.

To conclude, let me stress why is it important whether the ground-state PA is distorted along Q_1, as suggested by the simple analysis presented above, or not. First, such a configuration is in variance with common chemical knowledge. Second, it represents a novel type of symmetry breaking, not yet studied in the physics of quasi-1D solids. In more detail, Q_1 breaks $(C_2\,|\,t)$, $(\sigma_v'\,|\,t)$, $(U\,|\,t)$, and $(U'\,|\,t)$, where $\sigma_v'=\sigma_v C_2$, $U=\sigma_h C_2$, $U=\sigma_h\sigma_v C_2$, and $t=0,\pm 1,\ldots$. The new, reduced line group is $L1/mm$, and the polymer is not centrosymmetric. Hence PA could possess high hyperpolarizability in addition to high polarizability, and hence it (or its shorter oligomers, or their derivatives) could be an efficient medium for second-harmonic generation in nonlinear-optic devices.

Finally, the Q_1-distorted PA resembles trans-polyacetylene in that each of them has two ground-state configurations of exactly the same energy (two equivalent vacua). An interphase kink (domain wall, soliton) between two such phases of PA is schematically represented in Fig. 4. Notice that this kink is "transverse" as opposed to the "longitudinal" kinks in trans-polyacetylene. Transverse kinks have not been studied yet, at least not in relation to metallic polymers.

Despite the difference mentioned above, interphase solitons could play in PA a role similar to the one they have in trans-polyacetylene. Thus one could expect localized midgap electron states as well as localized vibronic modes to appear in PA chains with kinks. These solitons could be charged by doping or photoexcitation in which case they should generate additional strong infrared absorption features; they could also play a role in charge transport processes. However, the excitation energy of a soliton should be much lower in PA than in trans-polyacetylene. The above remarks remain valid even if it turns out that the ground state of PA is distorted along Q_2 rather than along Q_1, since in either case there are two equi-energetic distorted ground-state configurations.

Finally, it should be noted that this polymer has not

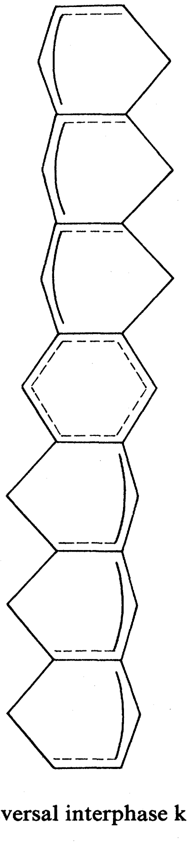

FIG. 4. Transversal interphase kink in polyacene.

been prepared yet. A successful synthesis of well-characterized, long-chain PA is a prerequisite for any definite conclusions.

IV. POLYACENACENE $(C_6H_2)_x$

The spatial symmetry of regular (i.e., aromatic) PAA [Fig. 1(b)] is $L2_1/mcm$. There are six π-electron bands; the highest occupied one and the lowest unoccupied one are of $B0$ and $B1$ symmetry, respectively. These two bands must cross[10] at $k_F=\pi/a$ and they form a "semi-loop" shape [Fig. 5(a)]. The degenerate one-electron states at E_F are $|\pi B0\rangle$ and $|\pi B1\rangle$, given by

$$\langle \mathbf{r}\,|\,\pi B0\rangle=(1/2N)\sum_t(-1)^t[\phi_H(t)-i\phi_L(t)]\ ,$$
$$\langle \mathbf{r}\,|\,\pi B1\rangle=(1/2N)\sum_t(-1)^t[\phi_H(t)+i\phi_L(t)]\ , \tag{4}$$

where $\phi_H(t)$ and $\phi_L(t)$ are the π orbitals of the highest and the lowest carbon atoms belonging to the tth unit cell, see Fig. 5(b). Since $D_e=(\pi EB)$ here, one has

$$[D_e^2]\sim(0A\,0+)+(0A\,1+)+(0A\,1-)\ . \tag{5}$$

Neglecting the hydrogen atoms, there are three linearly independent $(0A\,1+)$ modes, as well as three $(0A\,1-)$ modes. These modes are not uniquely determined by the symmetry of PAA. A convenient (orthonormal and symmetry-adapted) basis of $(0A\,1+)$ is formed by the zero-frequency mode **X** (i.e., translation along the x axis) together with two transverse-optical (TO) modes $\mathbf{Q}_1$ and $\mathbf{Q}_2$ [Fig. 6(a)]. For $(0A\,1-)$, a basis is formed by three longitudinal-optical (LO) modes $\mathbf{Q}_3$, $\mathbf{Q}_4$, and $\mathbf{Q}_5$ [Fig. 6(b)].

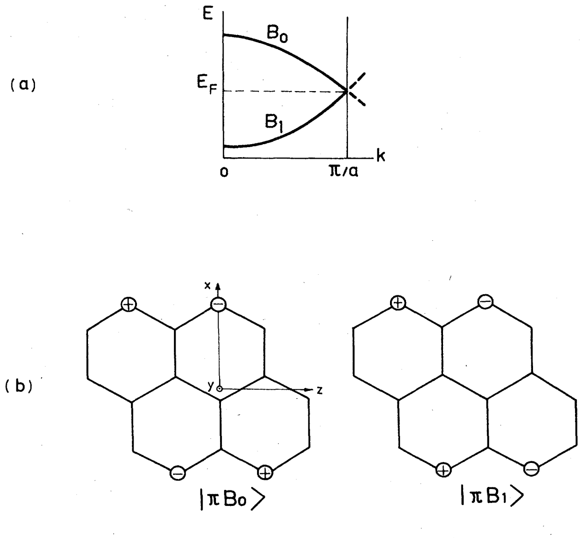

FIG. 5. (a) Highest occupied and the lowest unoccupied π-electron bands in polyacenacene (PAA). (b) Degenerate eigenstates at E_F; the lower-row π orbitals should be multiplied by i, see Eq. (9).

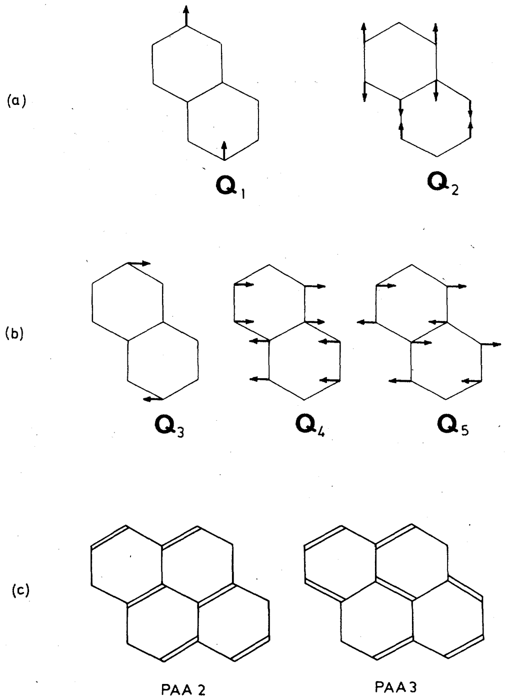

FIG. 6. (a) Linearly vibronically active distortions of PAA, of $(0A\,1+)$ symmetry. (b) Linearly allowed distortions of $(0A\,1-)$ symmetry. (c) Distorted configurations studied in Refs. 3 and 6.

Thus there are five nontrivial linearly allowed modes; however, not all of them are linearly active in the present model. Namely, within the second-order perturbation theory, none of the distortions $\mathbf{Q}_3$, $\mathbf{Q}_4$, $\mathbf{Q}_5$ lifts the degeneracy at the Fermi level; in fact, each of them opens a rather small gap $E_g\propto Q^3$. The same conclusion is reached if the second-nearest-neighbor interactions are included into consideration. Adding further interactions eventually lifts the artificial dynamical symmetry so that a first-order gap opens at E_F. For example, in the case of $\mathbf{Q}_3$, the fifth-neighbor interactions open a gap $E_g\propto Q_3$, which implies that there *is* a logarithmic instability in principle. However, these interactions are orders of magnitude smaller than β_0 and hence the predicted equilibrium distortion amplitudes, as well as the corresponding stabilization energies, must be rather small (and physically insignificant).

The above conclusions apply as well to the two distorted structures, PAA2 and PAA3 [Fig. 6(c)], studied in Refs. 3 and 6. In fact, these two distortions are neither mutually orthogonal, nor of well-defined symmetry species, but PAA2 roughly corresponds to (i.e. has a large projection along) $\mathbf{Q}_5$, and PAA3 to $\mathbf{Q}_4$. Utilizing the extended Hückel method and the second-neighbor approximation, Kertesz and Hoffmann[6] obtained $E_g\propto Q^3$ for both PAA2 and PAA3, in agreement with the above argument. As for the results of Yamabe *et al.*,[3] they employed the "standard" values $R(\mathrm{C{-}C})=1.46$ Å and $R(\mathrm{C{=}C})=1.34$ Å, thus assuming much too large distortions; indeed they found such PAA2 and PAA3 structures to be less stable than the aromatic structure (with all C$\equiv$C bonds 1.416 Å long).

On the other hand, there are two proper LVA modes in PAA, namely, $\mathbf{Q}_1$ and $\mathbf{Q}_2$ [Fig. 6(a)]. Distortion $\mathbf{Q}_1$ opens a gap $E_g = 2AQ_1$, which could be sizable (as in PA), since $A \simeq 4$ eV/Å. The same is true for $\mathbf{Q}_2$, and within the limitations of the present model the ground-state PAA is distorted along a linear combination of $\mathbf{Q}_1$ and $\mathbf{Q}_2$. More sophisticated geometry optimizations are in progress,[13] but certain conclusions are already apparent. Every $\mathbf{Q}=\lambda\mathbf{Q}_1+\mu\mathbf{Q}_2$ reduces the $L\,2_1/mcm$ line-group symmetry of the regular PAA onto $L\,1/mm$. In detail, the $(C_2\,|\,\frac{1}{2}+t)$ screw-axis symmetry is broken, together with $(\sigma_v'\,|\,\frac{1}{2}+t)$, $(C_i\,|\,\frac{1}{2}+t)$, and $(U'\,|\,\frac{1}{2}+t)$, where $\sigma_v'=\sigma_v C_2$, $C_i=\sigma_h C_2$, $U'=\sigma_h\sigma_v C_2$, and $t=0,\pm1,\ldots$. The distorted polymer is not centrosymmetric. There are two equivalent distorted ground-state configurations. The interphase kink is a transversal soliton.

Finally, the remarks given for PA at the end of Sec. III apply to PAA as well. The principal difference is that in PA the electronic degeneracy at E_F is accidental, and hence it need not appear in more realistic band-structure computations (although one does expect a pseudodegeneracy). In contrast, no such reservations apply to PAA, where the degeneracy is dictated by the line-group symmentry. In that sense, PAA is the main example in this paper; more discussion has been given to PA because its simple structure facilitates discussion of various concepts.

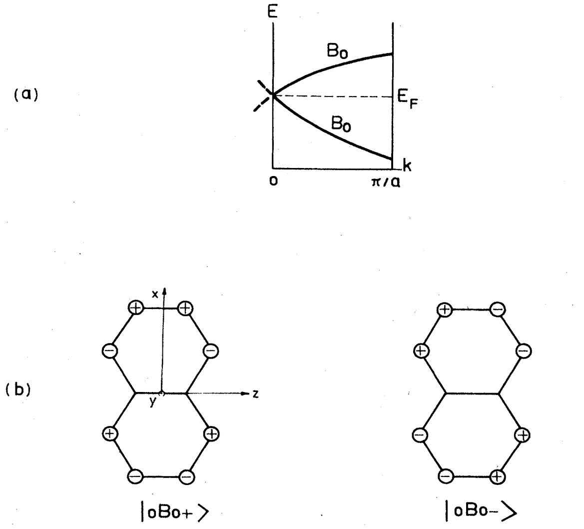

FIG. 7. (a) Highest occupied and the lowest unoccupied π-electron bands of polyperylene (PP). (b) Degenerate states at E_F.

V. POLYPERYLENE $(\mathrm{C_{10}H_4})_x$

The spatial symmetry of regular polyperylene (also called poly-perinaphtalene) [Fig. 1(c)] is $L\,2/mmm$. There are ten π-electron bands. Within the present model, the Fermi level is situated at the center of the Brillouin zone, and it falls exactly at an accidental crossing point of two $B0$ bands [Fig. 7(b)]. Such a crossing should be "avoided," i.e., it can be removed by a totally symmetric distortion, for example, by the $\mathbf{Q}_1$ distortion shown in Fig. 8(a). In fact, Yamabe *et al.*[3] found the lowest-energy configuration of PP to be distorted in just that way; they predict $R(\mathrm{C{-}C})=1.426$ Å, and $R(\mathrm{C{\equiv}C})=1.423$ Å, and $R(\mathrm{C{=}C})=1.356$ Å. This finding seems rather plausible: as far as the two degenerate states of Fig. 7(b) are concerned, the system is equivalent to two separate cis-polyacetylene chains, each one in its stable (i.e., cis-transoid) configuration. On the other hand, this result contradicts condition (ii) explicitly. However, notice that for $D_e=(0B0+)+(0B0-)$ one has

$$[D_e^2]\sim 2(0A0+)+(0A0-)\,, \tag{6}$$

so that some non-totally-symmetric $(0A0-)$ modes are linearly allowed as well. Neglecting the hydrogen atoms, there are five such modes in PP: one LA mode (Z mode, translation along the z axis), two LO modes [$\mathbf{Q}_2$ and $\mathbf{Q}_3$, Fig. 8(b)], and two TO modes [$\mathbf{Q}_4$ and $\mathbf{Q}_5$, Fig. 8(c)]. Each of these four LVA modes $\mathbf{Q}_2,\ldots,\mathbf{Q}_5$ breaks $(\sigma_h\,|\,t)$, $(C_i\,|\,t)$, $(U\,|\,t)$, and $(U'\,|\,t)$, where $C_i=\sigma_h C_2$, $U=\sigma_h\sigma_v$, and $U'=\sigma_h\sigma_v C_2$ and thus lowers the line-group symmetry onto $L\,2mm$. Such symmetry breaking

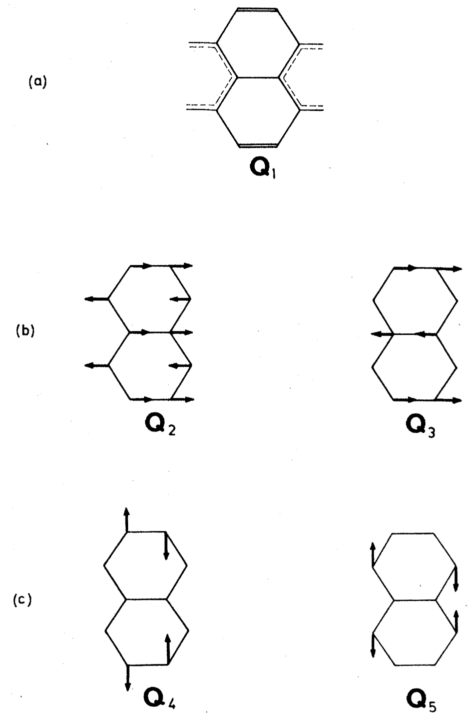

FIG. 8. (a) Distorted configuration of PP, which according to Ref. 7 is the ground-state structure of this polymer. (b) Longitudinal linearly vibronically allowed distortions of PP. (c) Allowed transverse distortions.

produces two equi-energetic ground-state configurations. The polymer supports solitons, either longitudinal (for $\mathbf{Q}_2$ and $\mathbf{Q}_3$) or transverse (for $\mathbf{Q}_4$ and $\mathbf{Q}_5$). In contrast, $\mathbf{Q}_1$ distortion produces a unique ground-state configuration, which does not support solitons, but rather bipolarons, like cis-polyacetylene. Again, further quantitative studies are needed to establish the ground state of PP with certainty, in particular, because none of the $(0A0-)$ distortions were investigated in Ref. 7. In view of the above dilemma, some experimental information on the structure of PP, such as x-ray, electron, or neutron diffraction data, would be rather welcome. Also, experiments that could provide some information on the in-gap excitations (such as photoinduced infrared absorption, or ESR spectroscopy combined with photoconductivity measurements, etc.) would help both to infer the nature of the ground state of PP and to understand the unusual electric conductivity results of Ref. 2.

To conclude, proper LVA modes do exist in the case of PP, and hence Theorem 1 is indeed valid for this polymer also, although eventually some totally-symmetric distortion may turn out to dominate. In this respect, PP differs from PA, in which totally-symmetric distortions are only rather weakly active, and from PAA where such distortions cannot open a gap at E_F at all, even if arbitrarily many neighbors are taken into account.

VI. CONCLUSIONS AND DISCUSSIONS

Attempting to resolve existing controversies about the validity of the Peierls theorem for quasi-1D graphite chains, in the present paper I have analyzed vibronic instabilities in PA, PAA, and PP. For each of these three polymers a non-totally-symmetric static distortion $\mathbf{Q}$ is identified, such that a gap E_g *linear* in the distortion amplitude Q opens at the Fermi level. On the other hand, substantial departures from the simple Peierls-model behavior are observed. Vibronically active modes are optical, and they can be transverse as well as longitudinal. Novel types of symmetry breaking can occur. The ground-state configurations may be noncentrosymmetric and need not conform to the common rules of thumb of organic chemistry, particularly in PAA in which a systematic degeneracy is found to occur at E_F.

In contrast to polyacetylene, in graphite polymers major vibronic effects can originate in variations of on-site electron energies caused by phonon-induced structure modifications. This coupling is included explicitly into the model Hamiltonians considered here, and in that they differ from the well-known Su, Schrieffer, and Heeger[12] model. However, as in trans-polyacetylene, degenerate states should occur in PA and PAA (and perhaps even in PP), and hence these polymers should support interphase soliton kinks. These solitons could be of a novel, transverse type, i.e., such that they interpolate between two distinct (but equi-energetic) transversally distorted phases.

From an experimental point of view, quasi-1D graphites (and other related polycyclic and ladder polymers) seem to be rather promising: these broadband, narrow-gap materials could combine good mechanical properties and chemical stability with high (i.e., semiconductive or even metallic) room-temperature conductivities. Optoelectronic applications are also conceivable. Hence, new syntheses, of well-characterized materials, would be of great interest. In addition, spectroscopic investigations could provide valuable information on the nature of the ground state and of low-energy excitations, and help understanding of the electric transport mechanisms in these materials.

Since, in general, it is not yet well understood how the stereochemical structure of a metallic polymer affects its vibronic instabilities, it might be worthwhile noting some observations based on the present study of graphite chains but with a more general scope. To begin with, the strength of vibronic coupling depends essentially on the geometries of the degenerate electron states $|e_1\rangle$, $|e_2\rangle, \ldots$, at the Fermi level, and of the LVA modes $\mathbf{Q}_1$, $\mathbf{Q}_2, \ldots$. Here one can distinguish whether the $|e_i\rangle$ states are "dense" (i.e., composed of atomic orbitals centered on neighboring atoms that form strong chemical bonds) or "sparse" (i.e., composed of orbitals that do not overlap significantly). Next, for every atomic orbital that belongs to some $|e_i\rangle$ one must check whether the active modes distort symmetrically or antisymmetrically the chemical bonds in which that atom participates. For examples, if the atom makes two bonds, one bond can be extended while the other one is contracted and vice versa, or else both bonds can be extended (contracted) simultaneously. In this sense, $\mathbf{Q}_1$ distortion of PA, $\mathbf{Q}_1$ distortion of PAA, and $\mathbf{Q}_2$ distortion of PP are all symmetric, while $\mathbf{Q}_2$ and $\mathbf{Q}_3$ modes of PA are antisymmetric, etc. Now, sparse electronic states [like, for example, $|\pi B 0\rangle$ and $|\pi B 1\rangle$ states of PAA, Fig. 5(b)] are not affected much by vibration modes in general; consequently, electron-phonon coupling is weak and the Peierls transition temperature is low in such a situation. The relative importance of on-site electron energy coupling of phonons increases in that case. However, this latter coupling can be rather weak also, if the "symmetric" distortions (that strongly affect α) are linearly forbidden by the symmetry of the $|e_i\rangle$ states. On the contrary, strong electron-phonon coupling is expected if the relevant $|e_i\rangle$ states are dense and if the active modes strongly distort the relevant chemical bonds. Extremely strong vibronic instabilities are possible[1] if, in addition, density-of-states (DOS) function peaks (or Van Hove singularities) occur at the Fermi level. This can happen because of accidental degeneracy at E_F, as illustrated in Fig. 2(a). Other combinations of band shapes that give rise to DOS peaks at E_F can also be specified, after Ref. 10.

Finally, it is fair to note that the above reasoning is based on crude models; yet, I believe that it contains some useful guidelines for experimentalists that search for new conducting polymers.

[1] S. Kivelson and O.L. Chapman, Phys. Rev. B **28**, 7236 (1983).

[2] M. Murakami and S. Yoshimura, Mol. Cryst. Liq. Cryst. (to be published).

[3] T. Yamabe, K. Tanaka, K. Ohzeki, and S. Yata, Solid State Commun. **44**, 823 (1982).

[4] J. L. Brédas, R. R. Chance, R. H. Baughman, and R. Silbey, J. Chem. Phys. **76**, 3673 (1982).

[5] M. Baldo, G. Piccito, R. Pucci, and R. Tomasello, Phys. Lett. **95A**, 201 (1983).

[6] M. Kertesz and R. Hoffmann, Solid State Commun. **47**, 97 (1983).

[7] K. Tanaka, K. Ueda, T. Koike, and T. Yamabe, Solid State Commun. **51**, 943 (1984).

[8] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, London, 1955), Chap. 5.

[9] K. Tanaka, K. Ozheki, S. Nankai, T. Yamabe, and H. Shirakawa, J. Phys. Chem. Solids **44**, 1069 (1983).

[10] I. Božović, Phys. Rev. B **29**, 6586 (1984).

[11] I. Božović, Mol. Cryst. Liq. Cryst.(to be published); I. Božović (unpublished).

[12] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980).

[13] J. Delhalle and I. Božović (unpublished).

[14] I. Božović and J. Delhalle, Phys. Rev. B **29**, 473 (1984).

[15] M. H. Whangbo, R. Hoffmann, and R. Woodward, Proc. R. Soc. London, Ser. A **366**, 23 (1979).

[16] R. Rein, N. Fukuda, H. Win, G. A. Clarke, and F. E. Harris, J. Chem. Phys. **45**, 4743 (1966).

[17] S. Kivelson and D. E. Heim, Phys. Rev. B **26**, 4278 (1982).

[18] Y. Lépine, Phys. Rev. B **28**, 2659 (1983).