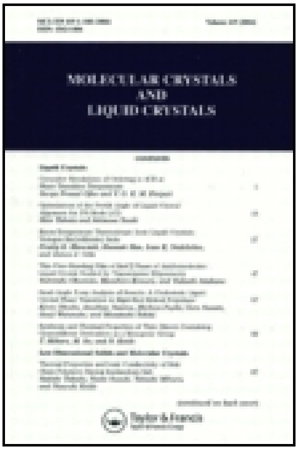

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THE ANALOGUE OF THE JAHN-TELLER THEOREM FOR EXTENDED CHAIN MOLECULES

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Abstract Vibronic instabilities in periodic chains with arbitrary repeat units and with partially filled bands are investigated systematically. It is shown that in each case nontotally-symmetric distortions exist, coupled linearly to the degenerate electronic states at E_F. Distortions of various geometries (LA, LO, TA, TO) can be involved and they may be twofold or fourfold degenerate themselves. Various symmetries can be broken and various types of kinks can appear; the translational period need not be enlarged.

Electron energy bands of Q1D molecular stacks and polymers containing several or many atoms in the translational repeat unit can form[1] various complex shapes, Figure 1. If, for a fixed stereochemical configuration, the Fermi level E_F falls within the highest occupied band, the electronic ground state is fourfold or eightfold degenerate. The resulting vibronic instabilities can be identified and characterized by the method introduced recently[1,2].

Let us denote by $|i\rangle$, $i=1,2,\dots,\deg(E_F)$, degenerate one-electron eigenstates at E_F ; by $\underline{Q}$ a small distortion, of period $2\pi/q$, from the initial polymer configuration ; by E_g the gap that opens at k_F, in the distorted configuration, and by $A_{ii'} \equiv \langle i|\underline{Q}\cdot(\frac{\partial V}{\partial \underline{Q}})_0|i'\rangle$ a linear vibronic coupling matrix element. The distortion $\underline{Q}$ is called allowed if $A_{ii'}(\underline{Q}) \neq 0$ for some i,i' and active if $E_g \propto Q$ for small Q.

Investigating all possible cases - as distinguished by the line group of the polymer, the band shape involved and the quantum numbers (quasi momentum, quasi angular momentum and mirror-plane

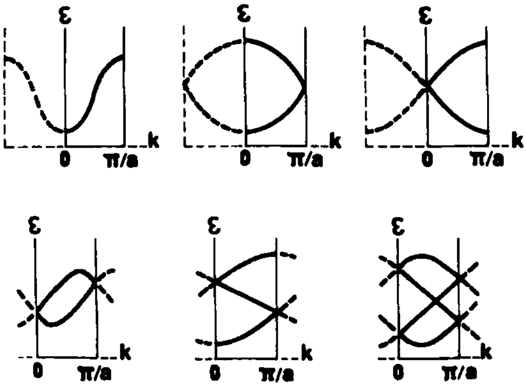


FIGURE 1 Some possible shapes of electron energy bands of polymers.

parities) of $|i\rangle$'s - I have proved that:

(1) in every case an active $\underline{Q}$ exists;

(2) $q \doteq 2k_F$ is neither sufficient nor necessary for a $\underline{Q}$ to be allowed;

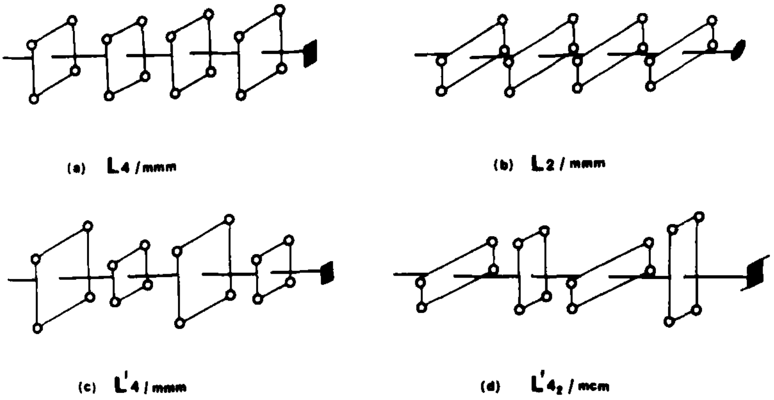
(3) an allowed $\underline{Q}$ need not be active;

(4) active $\underline{Q}$'s can be longitudinal or transversal, acoustic or optical, ferro- or antiferro-displacive or distortive;

(5) active $\underline{Q}$'s can be nondegenerate, twofold- or fourfold-degenerate themselves.

COMMENTS

Despite the analogy to the Peierls linear chain model[3], it is not a priori obvious that in every conceivable polymer configuration some $\underline{Q}$'s will survive all the symmetry restrictions; one has to run through all the line groups (symmetries of polymers), much like it was done for the point groups (symmetries of molecules) by Jahn and Teller[4]. In fact, in several recent quantum chemical studies[5] the undistorted metallic configuration was found to be the



(a) $L4/mmm$ (b) $L2/mmm$

(c) $L'4/mmm$ (d) $L'4_2/mcm$

FIGURE 2 Some possible types of symmetry breaking, (b)-(d), in a stack of square planar molecules (a) with a half-filled E band.

lowest-energy one for certain polymers, while for some others only higher-order instabilities were detected; it was concluded that "the Peierls theorem has to be qualified". However, from our conclusion (1) above it follows that *every metallic polymer is unstable*, against an *appropriate* periodic distortion. Indeed, $E_g(\underline{Q}) = 0$ can result from approximations that artificially increase symmetry of the Hamiltonian and/or from an improper choice of $\underline{Q}$. On the other hand, theorem (1) does not specify the magnitude of stabilizing distortion.

As for (2), for a distortion to be allowed, its quasi momentum, quasi angular momentum and parities must satisfy the corresponding conservation laws[1] and clearly $q \doteq 2k_F$ alone is not sufficient. Further, if E_F falls within an E band (i.e. a band twofold degenerate, in orbital space, throughout the Brillouin zone) some non-totally-symmetric fundamentals will be active, and for $k_F \neq 0$, $\pi/2a$, π/a one has: $q = 0 \neq 2k_F (\mathrm{mod}\ 2\pi/a)$.

Next, an allowed $\underline{Q}$ reduces the degeneracy at E_F but need not lift it completely. In some actual cases $\deg(E_F;\underline{Q}=0) = 8$ and $\deg(E_F;\underline{Q}\neq 0) = 4$, so that $E_g(\underline{Q}) = 0$ despite $A_{ii'} \neq 0$.

Vibronic instability can cause various types of symmetry breaking in polymers; in certain cases the translation period remains unaltered, Figure 2. Competition of CDW and SC instabilities under pressure and temperature variation will strongly depend on the geometry of the active mode.

As for (5), notice that the dimensionality of the order parameter determines the number of phase and amplitude modes in the distorted polymer. Let $Q^2 = \Sigma\, Q_i^2$ and $\theta = |Q_1Q_4 - Q_2Q_3|$; then $E_g \propto |Q^2 - 2\theta|^{1/2}$ for fourfold-degenerate active modes, while $E_g \propto Q$ for twofold-degenerate and nondegenerate ones. In the first two cases, free fluctuations of the distortion are possible, within the linear-coupling model. Higher-order couplings and interchain interaction can produce discrete deep minima, i.e. several degenerate ground-state configurations, connected through various (broken) symmetry elements (translations, reflections, rotations etc.) so that various types of interphase kinks can appear.

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