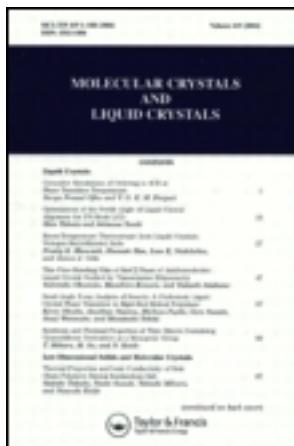


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ELECTRON CORRELATION VS PEIERLS DISTORTION IN POLYACETYLENE

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Abstract A selfconsistent numerical approach, which allows each (CH)-group in a finite polyacetylene chain to relax to its equilibrium position, is used to investigate the cross-over from the Peierls-gap to the electron-gap with increasing intrasite electron-electron interaction. The dependence of the crossover on the electron-phonon coupling constant is also examined.

The Peierls instability as a result of the electron-phonon interaction in a partially filled one-dimensional band¹ has been known for a long time. On the other hand, the effect of electron-electron interaction in quasi-one-dimensional systems, especially the short-range interaction has been extensively investigated for almost 20 years. The short range electron-electron interaction is most commonly approximated by the simple Hubbard model where only the intrasite Coulomb energy (the Hubbard U) is retained. Each of the Peierls distortion (a dimerization) and the intrasite electron correlation can create a gap in the single-particle energy spectrum. When both effects are present, it is important to find out the consequence of their interplay. This is one of the major interests in the recent studies on polyacetylene.

The early analysis of Ovchinnikov et al² reached a conclusion that the gap in a polyene chain is the electron-gap due to the Hubbard U instead of the Peierls-gap, which can not explain recent experimental data. The unrestricted Hartree-Fock calculation³ and the perturbation treatment⁴ on the Su-Schrieffer-Heeger (SSH)⁵ model show a transition from the Peierls-gap to the electron-gap with increasing Hubbard U. Dixit and Mazumdar⁶ have used a real space approach to find the enhancement of the Peierls distortion by U in the region $U/W < 1$, where W is the π -band width. The Monte Carlo study on a finite ring of 24 sites by Hirsch⁷ also demonstrates an initial enhancement of the Peierls distortion, followed by a gradual crossover from the Peierls gap to the electron-gap.

Except the Monte Carlo calculation, all the other treatments assume a frozen lattice constant when the electron-electron inter-

action (Hubbard U) is varied as a free parameter. While this additional degree of freedom is not important for a ring structure (i.e., periodic boundary condition), it does play a non-negligible role in reducing the total energy of the electron-phonon system if the configuration is an open chain (i.e., free-ends boundary condition). In real materials, the polyacetylene chains are open and of finite lengths. In this report we will investigate the ground state properties of an undoped polyacetylene with a selfconsistent numerical method which allows each (CH)-group in the finite open chain to relax to its equilibrium position.

We consider the SSH model with the electron correlation

$$H = - \sum_{i\sigma} \{ t_0 + \alpha(u_i - u_{i+1}) \} (c_{i+1,\sigma}^\dagger c_{i\sigma} + h.c.) + \frac{K}{2} \sum_i (u_i - u_{i+1} - C)^2 + \sum_i U n_{i\uparrow} n_{i\downarrow} \quad (1)$$

for a chain of N (CH)-groups and N electrons in the π -band. The values of the parameters are estimated⁵ as $K=21$ eV/Å², $t_0=2.5$ eV, $\alpha=4.1$ eV/Å, and C is determined from the condition that when $U=0$ and $u_i=0$ for all i , H gives the ground state energy of an undistorted chain. The electron correlation term is simplified with the broken-symmetry Hartree-Fock approximation by introducing the symmetry-breaking spin-order parameters $\{\lambda_i\}$ such that

$$\langle n_{i\uparrow} \rangle = (1 + \lambda_i)/2 ; \quad \langle n_{i\downarrow} \rangle = (1 - \lambda_i)/2 \quad \text{if } i \text{ is even,} \quad (2)$$

$$\langle n_{i\uparrow} \rangle = (1 - \lambda_i)/2 ; \quad \langle n_{i\downarrow} \rangle = (1 + \lambda_i)/2 \quad \text{if } i \text{ is odd.} \quad (3)$$

Within this approximation, we have

$$\sum_i n_{i\uparrow} n_{i\downarrow} = -\frac{N}{4} + \frac{1}{2} \sum_{i\sigma} n_{i\sigma} + \frac{1}{2} \sum_i (-1)^i \lambda_i (n_{i\downarrow} - n_{i\uparrow}) + \frac{1}{4} \sum_i \lambda_i^2 . \quad (4)$$

The ground state of H can be derived with a selfconsistent numerical method developed by us earlier.⁸ Assuming the initial values of the set of lattice displacements $\{u_i\}$ and set of order parameters $\{\lambda_i\}$, the exact electronic eigenstates of H are derived numerically. Then, knowing the electronic charge distribution, we find a new set of $\{u_i, \lambda_i\}$ by minimizing the total energy with respect to these parameters u_i and λ_i . By iteration the final self-consistent solution is obtained. If we define $v_i = \alpha(u_i - u_{i+1})$ and $\gamma = \alpha^2/K$ then we need to solve the following coupled equations

$$H(\sum_j c_{j\sigma}^\dagger B_{j\sigma}) = \epsilon_i (\sum_j c_{j\sigma}^\dagger B_{j\sigma}) \quad ; \sigma=\uparrow, \downarrow; i=1, 2, \dots, N \quad (5)$$

$$\lambda_i = \sum_{\ell \in F(\uparrow)} |B_{\ell i\uparrow}|^2 - \sum_{k \in F(\downarrow)} |B_{ki\downarrow}|^2 + 2X/U \quad ; \text{if } i \text{ is even,} \quad (6)$$

$$\lambda_i = \sum_{k \in F(\uparrow)} |B_{ki\downarrow}|^2 - \sum_{\ell \in F(\downarrow)} |B_{\ell i\uparrow}|^2 + 2X/U \quad ; \text{if } i \text{ is odd,} \quad (7)$$

$$v_i = \gamma \{ C' + \sum_{\sigma} \sum_{j \in F(\sigma)} (B_{i+1,j\sigma}^* B_{ij\sigma} + B_{ij\sigma}^* B_{i+1,j\sigma}) + Z \} , \quad (8)$$

where $C' = CK/\alpha$, $F(\sigma)$ is the set of all occupied σ -spin eigenstates of H , and

$$Z = \sum_{k\sigma} (t_0 + v_k) \sum_{j \in F(\sigma)} \partial (B_{k+1, j\sigma}^* B_{kj\sigma} + B_{kj\sigma}^* B_{k+1, j\sigma}) / \partial v_i , \quad (9)$$

$$X = \sum_{k\sigma} (t_0 + v_k) \sum_{j \in F(\sigma)} \partial (B_{k+1, j\sigma}^* B_{kj\sigma} + B_{kj\sigma}^* B_{k+1, j\sigma}) / \partial \lambda_i . \quad (10)$$

The forms of Z and X are very complicated. It is convenient to neglect the terms Z and X during the iteration process. The final selfconsistent solution is the same whether we neglect X and Z , because when the selfconsistence is reached we have $Z=X=0$ for the system under equilibrium. Of course, when Z and X are droped we need more iterations to achieve the same selfconsistent solution.

In our calculation we have used a straight chain (with free-ends boundary conditions) of 100 (CH)-groups so that the chain is sufficiently long to yield reliable result. The total gap Δ as a

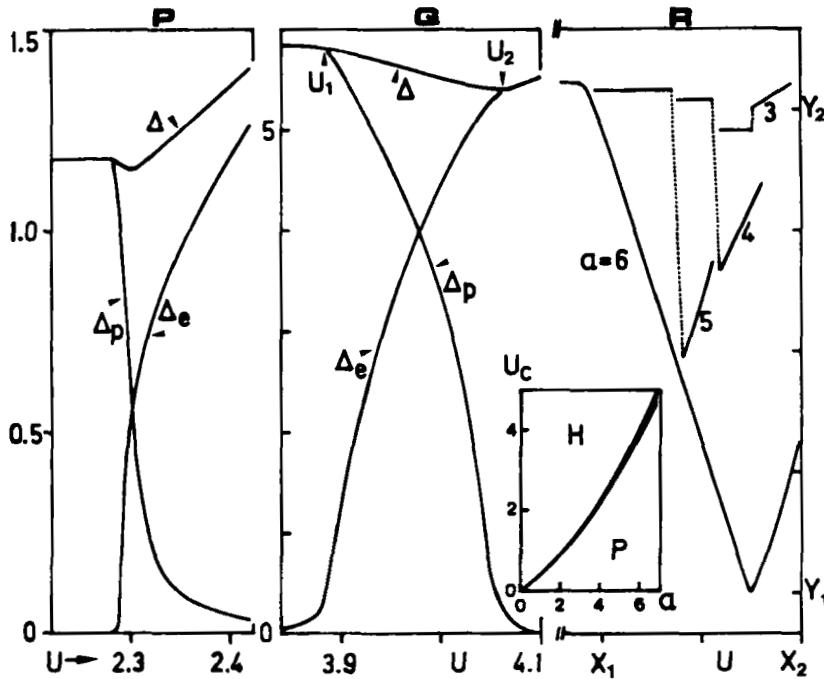


FIGURE 1 Total gap Δ , Peierls gap Δ_p and electron gap Δ_e as functions of U . Inset is the ground state phase diagram.

function of U in units of eV is shown in column P of Fig. 1. Using the so-obtained values of $\{u_i\}$ and setting $U=0$, we can recalculate

the eigenenergies spectrum of H and then derive the pure Peierls-gap Δ_p . On the other hand, we can set all $u_i=0$ to calculate the electronic gap Δ_e . Both Δ_p and Δ_e are also shown in column P of Fig. 1. The crossover from the Peierls-gap to the electronic-gap occurs around $U=2.3$ eV. Let us remind ourselves that the π -band width is about 10 eV. Since Δ_p and Δ_e are calculated in a decoupled manner, $\Delta_p + \Delta_e$ is slightly less than the total gap Δ . For the pure SSH model the dimerization order parameter ξ is linear in Δ_p . Therefore, the shape of ξ vs U is the same as Δ_p vs U . Furthermore, the analytical expression connecting Δ_e and the spin-order parameter λ can be easily derived. Hence, we will not show the functional dependence of λ on U in Fig. 1.

To study the effect of electron-phonon coupling strength α on the critical value of U (denoted by U_c) around which the crossover occurs, we have repeated the calculation for different values of α . In order to save the computer time, we have used a ring of 40 (CH)-group. For $\alpha=6$ the gaps Δ , Δ_p and Δ_e are plotted in column Q and their general structures are similar to those in column P. We notice that with increasing α the transition region (i.e. the mix-phase between U_1 and U_2) gets wider. The shape of Δ is shown in column R for various values of α with the axes specified as $(X_1, X_2; Y_1, Y_2) = (3.9, 4.1; 5.4, 5.8)$ for $\alpha=6$, $(2.95, 3.15; 2.7, 3.1)$ for $\alpha=5$, $(2.02, 2.22; 0.75, 1.15)$ for $\alpha=4$, and $(1.29, 1.49; -0.06, 0.34)$ for $\alpha=3$. The ground state phase diagram is illustrated by the inset, where H marks the antiferromagnetic phase (with pure electronic-gap) and P marks the dimerized phase (with pure Peierls-gap). Results in Fig. 1 agree qualitatively with those derived by other authors, except the curvature of the phase boundary. Our phase boundary is concave while the phase boundary obtained by Kivelson and Heim⁴ is convex. This difference is due to the fact that different values of the effective spring constant K are used in two calculations, as can be checked with Eq. (13) of Ref. 4.

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