

First-Order Transition to a Metallic State in Polyacetylene: A Strong-Coupling Polaronic Metal

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We present a theory of the first-order transition to the metallic state in polyacetylene in terms of a crossover from a lattice of charged solitons to a regular array of polaronlike distortions. The polaronic metal is shown to have a strong indirect attractive interaction, $U^* \simeq -2\Delta/3$, between electrons in the half-filled, narrow, polaron subband within the Peierls energy gap ($E_g = 2\Delta$).

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The discovery¹ that the onset of metallic behavior in *trans*-(CH)_x takes place as a first-order phase transition suggests that the metallic state at high dopant concentrations is both novel and of fundamental interest. This first-order transition is inconsistent with a description² in terms of a "dirty" metal which would arise from a disorder-induced gradual evolution of finite density of states in the Peierls gap. Moreover, there is considerable evidence that structural distortions persist into the metallic regime; specifically, the doping-induced infrared modes remain³ even at the highest dopant concentrations. Since these modes are the signature of structural distortions which form around injected charges, the infrared data imply that the metallic state is not a uniform-bond-length polyene. Rather, it is a dimerized structure with a high density of localized structural distortions.

In this Letter we present a theory of the first-order phase transition in terms of a crossover from a lattice of charged solitons to a novel metallic state consisting of a regular array of polaronlike distortions, with electrons delocalized in the partially filled polaron subbands within the Peierls gap. We find a critical concentration and a jump in the density of states at the transition in agreement with the experimentally measured values. Moreover, since the existence and shape of the polaron structural distortion are sensitive to the local occupancy, the polaronic metal has a strong electron-phonon coupling and a correspondingly strong indirect attractive interaction between electrons.

Important parameters for *trans*-(CH)_x are the intersite transfer integral t_0 (the π -electron bandwidth is $4t_0$) and the Peierls energy gap, $E_g = 2\Delta$. In *trans*-(CH)_x $t_0 \simeq 2.5$ – 3.0 eV and $\Delta \simeq 0.8$ eV. The ground state and nonlinear excitations of *trans*-(CH)_x have been successfully described in terms of the Su, Schrieffer, and Heeger (SSH)⁴ model [or its continuum Takayami, Lin Liu, and Maki (TLM)⁵ version]. We will use interchangeably expressions derived from the SSH and TLM models. Since the interesting physics occurs over lengths of order the electronic coherence length $\xi_0 = a(2t_0/\Delta) \simeq 6a - 7a$, where a is the projection of the carbon-carbon distance along the chain axis, the differences between the two are not significant.

The ground state of *trans*-(CH)_x is a Peierls distorted state of commensurability 2 (dimerized), and hence is twofold degenerate. The relative charged excitations involve large-scale distortions of the lattice. They are the spinless topological kinks, solitons, and the topologically trivial polarons,⁶ with creation energies $E_s = (2/\pi)\Delta$ and $E_p = \sqrt{2}(2/\pi)\Delta$, respectively. Since $E_p > E_s$, the SSH model predicts that upon doping or photoexcitation charge will be stored in soliton-antisoliton pairs. This has been verified through a variety of experimental studies⁷ which demonstrate charge storage in nonmagnetic midgap states. However, the energy difference between the two configurations is relatively small, $E_p - E_s = (\sqrt{2} - 1)(2/\pi)\Delta \simeq 0.2$ eV. Thus, at finite dopant concentrations (y), this energy difference is reduced through delocalization of electrons in the gap states into subbands. This causes a crossover of the energies, at a critical dopant concentration y_c from a nonmetallic soliton lattice ($y < y_c$) to a metallic polaron lattice ($y > y_c$).

The essential physics of this transition is contained in the band diagram sketched in Fig. 1. Figure 1(a) is appropriate to a lattice of charged (n -type) solitons; the midgap band is symmetric about the gap center and all states in this subband are filled. As a result, the energy per soliton remains unchanged, $E_s(y) = (2/\pi)\Delta$ plus corrections (discussed below) of order $\Delta \exp(-2R/\xi_0)$ where $R = a/y$ is the mean separation between solitons. For an array of polarons [sketched in Fig. 1(b)], the upper subband in the gap is half-filled. Consequently, the energy per polaron decreases as the density of polarons increases; $E_p = \sqrt{2}(2/\pi)\Delta - (1/\pi)W_p(y)$, plus corrections of order $\Delta \exp(-2R/\sqrt{2}\xi_0)$, where W_p is the polaron bandwidth. These simple observations suggest a transition to a polaronic metal at a concentration sufficiently large that

$$W(y_c) = \pi(E_p - E_s) = 2\Delta(\sqrt{2} - 1). \quad (1)$$

An expression for the polaron bandwidth at small y [exact to leading order in the overlap factor, $\exp(-R/\sqrt{2}\xi_0)$] is obtained by calculating the off-diagonal matrix elements of the TLM Hamiltonian between unperturbed states on each polaron and computing the band structure in the tight-binding approxi-

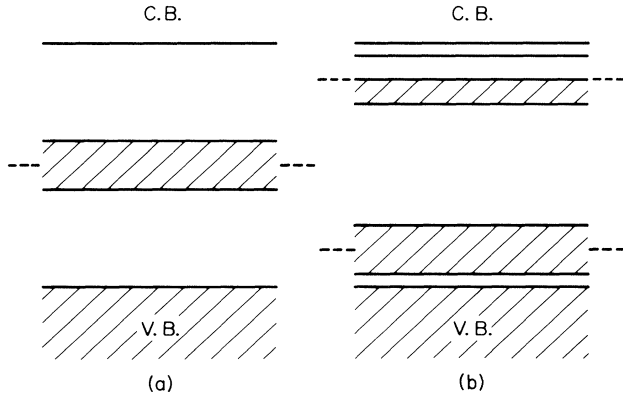


FIG. 1. (a) Band diagram for a soliton lattice; the midgap band is full (n -type doping). (b) Band diagram for a polaron lattice; the upper polaron band is half-full (n -type doping).

mation. The result is

$$W_p(y) = 4\sqrt{2}\Delta \exp(-R/\sqrt{2}\xi_0) \quad (2)$$

plus terms of order $\exp(-\sqrt{2}R/\xi_0)$.

Using Eqs. (1) and (2) we obtain $y_c = 0.053$ (a mean separation between polarons of $R_c = 19a$) and $W_p(y_c) = 0.66$ eV. This value for y_c is in excellent agreement with the measured value.¹ At the transition, the density of states at the Fermi energy in the half-filled polaron band is given by

$$\rho_c = 4/\pi [W_p(y_c)R_c]^{-1} = A\rho_0, \quad (3)$$

where $\rho_0 = [\pi t_0 a]^{-1}$ is the density of states of the uniform-bond-length polyene and

$$A = \{\sqrt{2}(\sqrt{2}-1)\ln[2\sqrt{2}/(2\sqrt{2}-1)]\}^{-1} = 0.89.$$

Therefore, at the transition, the density of states is approximately 2 states/eV-polaron or 0.11 state/eV-C, in excellent agreement with that obtained from the magnitude of the Pauli susceptibility.¹

Although the electron-electron interactions, electron-dopant-ion interactions, and intersoliton (or interpolaron) repulsive energies must also be included, we argue that the *net* effect of these contributions to the energy difference between the soliton and polaron lattices is small. The energy of the soliton lattice⁸ has been analyzed; within the single-chain approximation

exact solutions are available which demonstrate that the intersoliton repulsive energies are of order $\Delta \exp(-2R/\xi_0)$. Similarly for a lattice of polarons, the repulsive energy⁹ is of order $\Delta \exp(-\sqrt{2}R/\xi_0)$. There is also an overall shift in the average energy of the electronic subband in the gap and a slight change in the polaron shape, both of which produce effects of this same order.¹⁰ Thus, because of the larger spatial extent of the polaron, the intersite repulsive terms slightly favor the soliton lattice. This has been confirmed by numerical calculations on the SSH model which show that these repulsive energies begin to be important at concentrations defined by Eq. (1) and that they favor the soliton lattice at this concentration by an amount $\approx 0.07\Delta$. Thus the first-order transition does not occur within the strict SSH model. However, since the energy difference between the soliton and polaron lattices is so small for y near y_c , even weak interactions which are not included in SSH will drive the transition. In particular, Coulomb interactions tend to favor the polaron lattice: Electron-electron repulsion favors the more delocalized charge distribution in the polaron (width $\approx \sqrt{2}\xi_0$) over the soliton (width $\approx \xi_0$). By roughly the same factor, the binding energy of the soliton to a dopant ion is larger than that of the polaron. The polaron lattice is further stabilized by correlation effects within the polaron band.¹¹ The observation that the net repulsive energy and the net Coulomb energy are both small and tend to cancel (in the energy balance) rationalizes the excellent agreement of the simple expressions [Eqs. (1), (2), and (3)] with the experimental results.

We conclude that the metallic state is a polaronic metal with a half-filled polaron subband within the Peierls gap. Since the energy of the electronic bound states in the gap is sensitive to the shape of the polaron structural distortion, the polaronic metal has a particularly large electron-phonon coupling. In addition, since the polaron band is relatively narrow, electron-electron interactions (both direct and indirect) can produce large correlation effects *within the polaron subband*. To describe the physics of this novel metallic state we consider an effective Hamiltonian for the half-filled electronic subband and the coupling of these electrons to the shape of the local lattice distortion

$$H = -t_p(y) \sum_{\mathbf{R},s} [C_{\mathbf{R},s}^\dagger C_{\mathbf{R},s} + \text{H.c.}] - t_\perp(y) \sum_{\mathbf{R},s,1_\perp} [C_{\mathbf{R},s}^\dagger C_{\mathbf{R}+1_\perp,s} + \text{H.c.}] + U_p \sum_{\mathbf{R}} (C_{\mathbf{R}\uparrow}^\dagger C_{\mathbf{R}\uparrow} - \frac{1}{2})(C_{\mathbf{R}\downarrow}^\dagger C_{\mathbf{R}\downarrow} - \frac{1}{2}) + \sum_{\mathbf{R},s} \epsilon(x_{\mathbf{R}}) (C_{\mathbf{R},s}^\dagger C_{\mathbf{R},s} - \frac{1}{2}) + \sum_{\mathbf{R}} E_p + \sum_{\mathbf{R}} \Phi(x_{\mathbf{R}}) + \frac{1}{2} \sum_{\mathbf{R}} M^*(x_{\mathbf{R}}) \dot{x}_{\mathbf{R}}^2, \quad (4)$$

where $C_{\mathbf{R},s}^\dagger$ creates an electron of spin s on the polaron at impurity site \mathbf{R} , $t_p(y) = \frac{1}{4} W_p(y)$ is the hopping matrix element for electrons between nearest-neighbor polaron sites on the same $(\text{CH})_x$ chain, and $t_\perp(y)$ is the transverse hopping matrix element between polaron sites on neighbor chains. The magnitude of t_\perp can be estimated by including the coupling, t_3 , between π orbitals on adjacent $(\text{CH})_x$ chains which gives rise to a finite transverse π

bandwidth; t_3 has been estimated previously¹² to be about 0.1 eV. So long as the separation between polarons on adjacent chains, $|1_\perp|$, is less than about $\sqrt{2}\xi_0$, $t_1 \approx t_3$. Since there are four nearest-neighbor chains, we expect $|1_\perp| \approx R_c/4 < \sqrt{2}\xi_0$. Therefore, $t_p(y_c)$ and t_\perp are comparable and the polaron subband is three dimensional. U_p is the repulsive energy between two electrons on the same polaron, with the lattice configuration frozen. To estimate U_p , we include an on-site Hubbard interaction U in the SSH model. In this case^{10,13}

$$U_p = (2\sqrt{2}a/3\xi_0)U = U_s/\sqrt{2}, \quad (5)$$

$$\Phi_{(x)} = (4\Delta/\pi) \left\{ [\cos^{-1}[K(x)\xi_0] - \pi/4] \operatorname{sech}[K(x)x] + \tanh K(x) - 1/\sqrt{2} \right\} \approx \frac{1}{2}(\Delta/\xi_0^2)(x - \bar{x})^2, \quad (6b)$$

where $\bar{x} = \sqrt{2}\xi_0 \ln(\sqrt{2} + 1)$ is the equilibrium polaron width, $K(x)$ is defined implicitly by $K(x)\xi_0 = \tanh[K(x)x]$,

$$\epsilon_1 = \frac{1}{2}[\sqrt{2} - \ln(\sqrt{2} + 1)] = 0.94,$$

and

$$\Phi_2 = (\sqrt{2}/\pi)[\sqrt{2} - \ln(\sqrt{2} + 1)]^{-2} = 1.59.$$

The effective mass of the lattice mode is $M^*(x)$.

There exists an indirect attractive interaction between electrons in the polaron subband, mediated by the exchange of virtual phonons. In the linearized approximation

$$U^* = -[\epsilon'(x)]^2/\Phi''(x) = -(\sqrt{2}\pi/8)\Delta \quad (7)$$

and hence is greater than the polaron bandwidth. The combined effect of the Coulomb and electron-phonon terms is a net effective interaction between electrons

$$U_{\text{eff}} = U_p - U^*, \quad (8)$$

which could, in principle, be positive or negative. Using the experimental value¹⁴ for $U_s \approx 0.9$ eV, Eqs. (5) and (8) yield $U_{\text{eff}} \approx 0.2$ eV.

Although the underlying electronic structure of $\text{trans}(\text{CH})_x$ is quasi one dimensional, the excitation spectrum within the polaron subband described by Eq. (4) is that of a three-dimensional narrow-band metal. Charge fluctuations occur at a rate $\approx W_p/h$, so long as this is fast compared to the optical photon frequency the equilibrium lattice configuration is sensitive only to the expectation value of the charge. We distinguish three possible regimes of parameter space. When $0 < U_{\text{eff}} < \frac{1}{2}W_p$, the polaron lattice is stable and has the $4k_F$ periodicity characteristic of a Peierls system with repulsive interactions.¹⁵ When $U > W_p$ and the polaron band is sufficiently one dimensional, we expect a Peierls distortion of the polaron lattice to produce a $2k_F$ component to the overall periodicity and a gap at the subband Fermi energy. In the strong-coupling limit, this state would look like a bipolaron

where U_s is twice the difference in energy between a charged and a neutral soliton. The remaining terms in the Hamiltonian describe the interaction between the metallic electrons and an optical phonon which consists of a single localized lattice mode per polaron, the polaron width mode, which is parametrized by the collective coordinate x_R . With this approximation^{6b}

$$\epsilon(x) = \Delta \{ \operatorname{sech}[K(x)x] - 1/\sqrt{2} \} \\ \approx -\epsilon_1(\Delta/\xi_0)(x - \bar{x}) \quad (6a)$$

and

bound to every other dopant ion. When $U^* > U_p$, and the polaron band is quite three dimensional, there is the possibility of superconductivity. In all three cases, the effects of disorder can be quite severe, since the polaron band is relatively narrow.

For polyacetylene, the good agreement of the Pauli susceptibility with the value obtained from the theory without interactions suggests that U_{eff} is small. The absence of superconductivity implies that either $U_{\text{eff}} > 0$ or that the disorder is too large in the samples studied to date.

The results presented in this Letter are readily generalized to the case in which the ground-state degeneracy of the polymer is weakly lifted. Since the energy difference between confined soliton pairs (bipolarons) and polarons is less than (but comparable to) that between solitons and polarons, the crossover between the two occurs at a dopant concentration comparable to y_c for $\text{trans}(\text{CH})_x$. We therefore anticipate that at high dopant concentrations polyheterocycles such as polythiophene, polypyrrole, etc., may be polaronic metals. This is particularly interesting, for these systems offer the possibility of controlling the magnitude of U_p to some degree by changing the structure of the monomer. A specific example is the addition of a polarizable aromatic ring to the thiophene monomer to make isothianaphthene.¹⁶ The smaller energy gap of polyisothianaphthene (about one-half that of the parent polythiophene) may be at least partially due to a reduction of the effective Coulomb interaction.¹⁷

In conclusion, the abrupt onset of the Pauli susceptibility in doped $\text{trans}(\text{CH})_x$ is shown to be consistent with a first-order transition from a soliton lattice to a polaronic metal. The critical concentration and the magnitude of the density of states in the polaron subband are found to be in agreement with the experimental values. The strong, indirect, attractive interaction between electrons in the narrow polaron subband suggests the possibility of superconductivity in conducting polymers provided the direct Coulomb interac-

tion can be reduced through the use of appropriate monomers and provided the materials can be improved to minimize disorder.

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