Commensurability Effects and Modulated Structure in Polyanilines

Han-Yong Choi and E. J. Mele
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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We study a model for the protonated polyanilines in which the polarizability of the extended π electrons on the polymer promotes the ordering of the protonated sites in a series of commensurate composition waves on the polymer. The model predicts a succession of first-order transitions between locked commensurate structures for the protonated system, with the period of the structure determined by the electronic band filling. Several implications for the physical properties of the protonated polyanilines are suggested.

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A number of the ground-state and excited-state properties of conjugated polymers can be understood within a continuum theory for the coupled electron-phonon system in the polymer. In most of the systems studied to date the underlying electronic bandwidth is relatively large which leads to a large coherence length for density fluctuations in the valence electron sea. As a consequence, fields describing the propagating electrons and the associated lattice polarization are well described as slowly varying functions of position on the polymer; theories based on this physical observation have been developed to describe broken-symmetry ground states, and various localized charged and neutral structural excitations exhibited in a broad class of conjugated systems.[1]

The physical properties of a new class of conjugated polymers, the polyanilines, are beginning to be explored experimentally. Typical structures for the polymer are sketched in Fig. 1. The polymer consists of a series of C_6H_4 rings which are interconnected by nitrogen (N) sites. The electronic structure of the polymer can be modified by the adsorption of protons at the N sites,[2] interacting with the N lone-pair orbitals. We note that the modification of the electronic properties of the polyanilines by this procedure differs in an important way from the more familiar charge-transfer doping of the more conventional conjugated polymers, and consequently, the physics of the doped polyanilines is likely to be more interesting. The properties of the "doped" polyanilines depend on two independent parameters, namely the electronic band filling (f_e) and the fraction of the available sites which are protonated (f_p). We define $f_e = n_e - 6n_{\mathrm{N}}$ and $f_p = n_e/n_N$, where n_e, n_p, and n_{N} are the numbers of electrons, protons, and nitrogens, respectively, so that $f_e = (f_p - 1)/2$ denotes a compensated structure. The variation of the proton content introduces qualitatively new physics. The adsorbed protons may occupy only discrete N sites on the polymer, so that only periodic configurations with period equal to a multiple of inter-N spacing are possible. Commensurability effects between the resulting composition wave on the discrete N lattice and the Fermi wave vector of the π-electron sea dominate the physics of this system. The polymer can exhibit an array of periodic ground-state structures, as a function of f_e and f_p, as the system evolves through a series of locked "commensurate" structures. Similar phenomena have been encountered in the study of competing interactions in other contexts in condensed-matter physics[3]; in this Letter we will construct a simple model to describe these phenomena in the polyanilines, and extract some of the important structural implications.

A typical starting material used in the doping studies, emeraldine base (EB), is shown schematically in Fig. 1(b). In EB, half the available N sites are hydrogenated, so that the excess electron concentration is compensated by the excess protons on the structure. In this structure the hydrogenated sites order in a partially segregated structure with two adjacent occupied sites followed by two empty ones. The conductivity of the polymer is varied by treatment of EB with an acidic solution

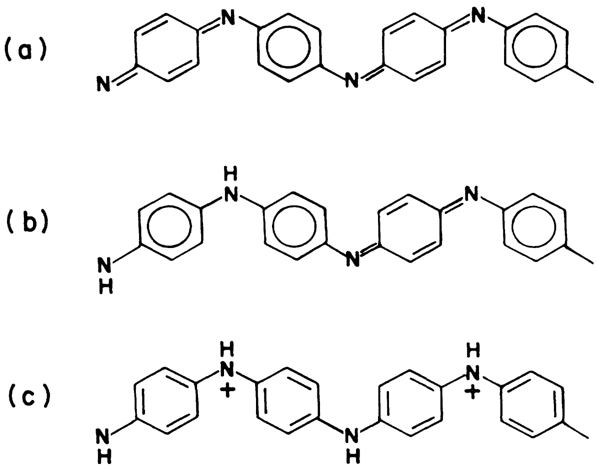

FIG. 1. Three reference structures for polyaniline: (a) the completely oxidized polyaniline base, (b) the partially reduced emeraldine base, (c) a model for the high-density protonated structure.

in which a fraction of the N sites are protonated, and a proposed "polaron" lattice[4] for the highly doped state is represented in Fig. 1(c). To date, analyses of the doped polymers have focused on the response of the bond-alternation pattern on the backbone to the modulated potential provided by the proton-adsorption pattern. We focus instead on the patterns in which the protonated sites order on the backbone.

The low-temperature equilibrium "proton" adsorption pattern is determined by the electronic band filling. Adsorption of a proton on an N site produces a shift of the "on-site" energy for π electrons propagating across the N site, and the energy of the system is optimized when the proton sites order so that the resulting modulated site-diagonal potential (Δ) produces a (low-order) gap at the Fermi energy in the π-electron spectrum. The argument is complicated slightly by the presence of bond relaxation on the polymer, which modulates the nearest-neighbor off-diagonal terms in the electronic Hamiltonian, and can also contribute to the gap at the Fermi energy. Therefore, there are two factors which contribute to open a gap at the Fermi energy. For the parameter values which are appropriate for polyanilines, the site-diagonal potential dominates the bond-relaxation term. But for different parameter values (small Δ and large electron-phonon coupling), it is possible that bond relaxation dominates the Δ term.

This simple model allows us to interpret the interactions leading to the partially segregated EB structure. Consider a reduced electronic Hamiltonian in which the C_6 rings mediate a hopping amplitude between nearest-neighbor N sites. For the neutral EB structure, the effective π band is $\frac{3}{4}$ full, i.e., $f_e = \frac{3}{4}$, and consequently the system is especially stable for ordered protonated configurations with period 4. If we denote an occupied (empty) site by a spin up (down), these configurations correspond to the period-4 structures $\uparrow\downarrow\downarrow\downarrow$, $\uparrow\uparrow\downarrow\downarrow$, and $\uparrow\uparrow\uparrow\downarrow$, i.e., the $f_p = \frac{1}{2}$ system seeks the partially segregated $\uparrow\uparrow\downarrow\downarrow$ structure. More generally, if we monitor the total energy as a function of f_p for fixed f_e, we can expect a discontinuity in slope at the points at which f_p becomes commensurate with f_e. A partial map of stable phases with $f_e > 0.5$ is given in Fig. 2. Among these, the phases found in the dense region which represent the long-period structure would be particularly difficult to synthesize in a strictly periodic form. The stable period-4 phases listed above occur along the ordinate $f_e = 0.75$; the terminal phases $f_p = 0$ and $f_p = 1$ correspond to the empty and saturated N lattices, respectively.

We wish to transform the data presented in Fig. 2 into a low-temperature phase diagram for the system as a function of the experimentally controllable chemical potentials for electrons, μ_e, and protons, μ_p. To describe the energetics of this system, we construct a Su-Schrieffer-Heeger-type Hamiltonian[5] for the coupled electron-phonon system:

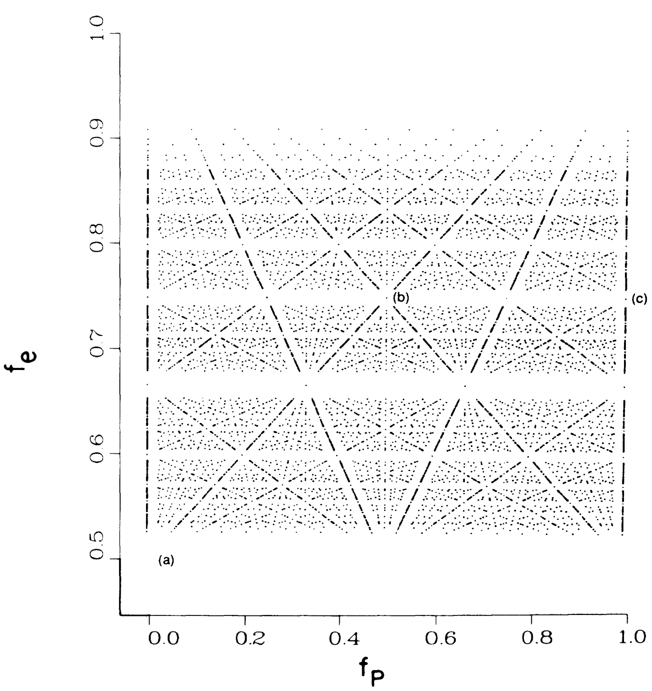

FIG. 2. Stable phases in f_e-f_p plane. Dots correspond to the pure phases of finite period. (a)-(c) refer to the structures (a)-(c) in Fig. 1, respectively.

$$H = -\textstyle\sum_n t_n (C_n^\dagger C_{n+1} + C_{n+1}^\dagger C_n) - \Delta \textstyle\sum_n C_n^\dagger C_n S_n + (K/2) \textstyle\sum_n (U_n - U_{n+1})^2,$$

where $t_n = t_0 - \alpha(U_n - U_{n+1})$ is the nearest-neighbor hopping amplitude (between C-C, or C-N), $C_n^\dagger$ (C_n) is the creation (annihilation) operator of electrons at the nth site; S_n can take the value either 1 or 0, where $S_n = 1$ means the occupied site and $S_n = 0$ the unoccupied site. Δ represents the shift of the diagonal self-energy of an occupied site due to the proton adsorption. These parameters were adjusted by fits to the quantum chemical calculations.[6] We take $t_0 = 3.5$ eV, $\alpha = 6.5$ eV/Å, $K = 45$ eV/Å^2, and $\Delta = 1.0$ eV. We integrate out the electron propagation through the ring structure and find that the effective hopping amplitude between nearest N sites is $t_{\text{eff}} \approx t_0/2$.[7] The diagonal self-energy Δ is not changed by the elimination of the ring structure and neither is the spring constant K in the lowest-order approximation. α_{eff} is chosen to produce the same gap size at the Fermi energy and is taken as $\alpha_{\text{eff}} \approx \alpha$.[8] By diagonalizing the electronic part of the Hamiltonian for various f_e and f_p, we seek the structural configurations satisfying the following self-consistency relation:

$$y_n = -\frac{\alpha}{K} \sum_k{}' [\chi_k(n)^\dagger \chi_k(n+1) + \chi_k(n+1)^\dagger \chi_k(n)],$$

where $\chi_k(n)$ is the eigenfunction of the electronic part of the Hamiltonian and the prime on the sum means that it runs up to the Fermi level. The total energy is given by

$$E_{\mathrm{tot}}(f_e,f_p) = 2\sum_k{}' E_k + (K/2)\sum_n y_n^2,$$

where $y_n = U_n - U_{n+1}$; the factor of 2 comes from the electron-spin degeneracy. From these calculations we extract an energy "surface" as a function of the f_e and f_p at the points plotted in Fig. 2. For selected structures, we solved the full Hamiltonian including the ring structure and obtained very similar results.

We make the following general observations about this energy surface. At fixed f_p, the energy is a convex function of f_e. This implies that for fixed f_p the electronic chemical potential produces a single unique phase, although for low-order commensurate band fillings, a phase can be stable over a finite range of electronic potential. This is quite similar to the familiar situation for charge-transfer doping of simple conjugated polymers like polyacetylene, where the range of stability corresponds to the critical energy for the creation of a discommensuration of a low-order periodic configuration. However, at fixed f_e we find that the energy of the phases of finite period is a nonconvex function of f_p. This implies first-order phase boundaries separating neighboring stable phases, and phase coexistence between adjacent phases. This behavior is particularly striking across the open regions of the phase map in Fig. 2 which correspond to low-order commensurate electronic densities. We make these arguments more quantitative by applying a Maxwell construction to the calculated energy surface, and extracting critical values of μ_e and μ_p which isolate various ordered configurations of the polymer; the results are presented in Fig. 3. For comparison, two trivial limits of the model are presented in the insets. In the upper right-hand panel we consider the situation where $\Delta=0$; this leads to a critical potential for proton insertion ($\mu_p=0$) which is independent of the electronic chemical potential. For the case where $t=0$, the structural modulation is also trivial in the sense that the empty and saturated phases fill up the phase diagram with all other phases degenerate along the transition line. When t and Δ are comparable, the degeneracy between the modulated structures is lifted, leading to a rich array of possible stable structures. For our system, with $\Delta/t_0 = 1/3.5$, we obtain the more intricate phase diagram presented in the central panel.[9] The shaded regions contain higher-order periodic structures which we have not included. The upper half of this diagram is relevant to the experimental work on polyaniline. The dashed curve which winds through the upper region denotes the configurations which are exactly compensated, i.e., the number of excess electrons equals the number of adsorbed protons. Deviations from the dashed line then denote charged (doped) configurations. First-order phase boundaries separate adjacent stable phases.

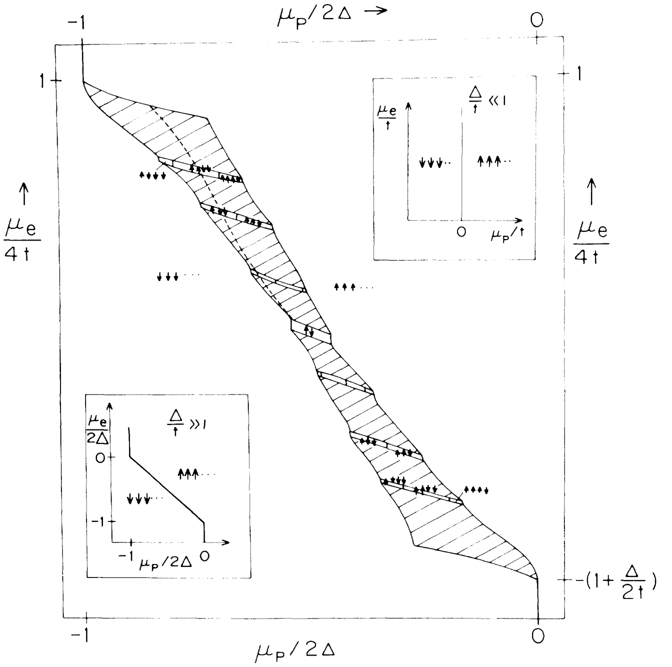

FIG. 3. Phase diagram in μ_e-μ_p plane. Vertical lines between adjacent stable phases denote the first-order phase boundaries. Pure phases up to period 5 are shown and the shaded region corresponds to longer-period phases. Similar plots for two limit cases are drawn for comparison.

It is useful to note that the interactions which stabilize the intermediate modulated structures inevitably produce insulating materials with a gap separating the occupied and unoccupied electronic states. However, the limiting empty and saturated lattices ↓↓↓↓... and ↑↑↑↑... have a uniform site-diagonal potential on the N sites. A small gap is produced by the residual bond relaxation; however, this is a very small gap (about 0.05 eV) which is unlikely to survive three-dimensional interactions neglected in our model Hamiltonian. Thus, for all practical purposes, we should regard the terminal states as degenerate quasi one-dimensional metals.

EB is found as the ↑↑↓↓ period-4 structure in the upper half of the phase diagram. We believe that the doping procedure most commonly employed, in which the EB structure is equilibrated in an acidic solution, can best be modeled by a trajectory in this diagram which holds f_e fixed, and varies μ_p. This directs the system through the intermediate ↑↑↑↓ phase[10] before a final first-order transition to the saturated ↑↑↑↑ emeraldine salt structure. The most obvious experimental implication of this doping mechanism is the phase coexistence of normal and metallic regions, leading to a Pauli susceptibility which scales linearly with proton concentration above a critical proton potential. This is in qualitative agreement with the reported onset of Pauli susceptibility in the doped materials, although the experiments also reveal a nonmonotonic evolution of Curie spins at lower dopant densities (with the maximum signal around $f_p = 0.8$.[11,12] Although a plausible explanation would be unpaired spins at interfaces between coexisting ↑↑↓↓ and ↑↑↑↓ structures, we have been unable to identify a center which should be associated with a localized spin at such an interface. More suggestive are recent measurements which have begun the doping procedure from a starting state which is hydrogen rich relative to the EB configuration ($f_e = \frac{7}{8}$ and $f_p = \frac{3}{4}$).[13] Protonation from this state produces a new high-spin state as the proton content is increased. We suspect that the variation in this doping schedule is forcing the system through one of the "dense" regions of Fig. 2, containing many neighboring competing phases. The formation of defects containing isolated spins is likely in these congested regions of the phase diagram. It has been suggested that the physical properties of the protonated polyanilines must be understood in terms of the degree of oxidation and the degree of protonation[2]; the phase diagrams presented above should be useful for systematizing these data.

More detailed consideration of the electronic structure in the doped states of this system may well point to characteristic features in the optical and infrared spectra which will allow their identification. Also important is the extension of this theory to finite temperature. As the temperature increases, the stability region of each phase shrinks down and the higher-order modulated phases become unfavorable against the disordered state. In this case it might be possible that the ↑↑↓↓ phase goes directly to the ↑↑↑↑ phase without passing through the intermediate ↑↑↑↓ phase as f_p is increased.[12]

In summary, it appears that a number of the physical properties of the doped polyanilines may be interpreted in terms of a theoretical model in which lattice commensurability effects are playing a fundamental role. We provide a simple theory which predicts a series of structural modulations due to the commensurability effects. It will be very interesting to further explore the extent to which this sort of model can be applied to study other physical properties of the polyanilines.

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[7] Simple calculation shows that $t_{\text{eff}} = t_0\{t_0(E+t_0)/[2t_0^2 - E(E+t_0)]\}$, so that for $E_{\text{F}} \approx 0$, $t_{\text{eff}} \approx t_0/2$.

[8] We checked the reliability of the reduced Hamiltonian by comparing the energy surface with that of the full Hamiltonian along the $f_e = \frac{3}{4}$ line which passes EB and emeraldine salt. They show the same behavior, that is, the slope of the energy is discontinuous when f_e is commensurate with f_p for both cases.

[9] The calculation with $\alpha = 0$ shows almost the same phase diagram.

[10] The observation of this phase would give key experimental support to the present theory. The structure of this intermediate phase would be the EB structure with a proton attached at every fourth (unoccupied) N site, as denoted by (↑↑↑↓).

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