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Extended states in finite one-dimensional, disordered, highly doped, *trans*-polyacetylene chains

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In this work we calculate the density of states for long finite one-dimensional *trans*-polyacetylene chains with a disordered distribution of solitonlike defects. The theoretical model adopted is a combination of the negative-factor-counting technique and Austin method 1 calculations. Our results show the presence of extended (conducting) states at the Fermi level that could explain the semiconductor-metal transition for highly doped *trans*-polyacetylene, in accord with the experimentally observed infrared-active vibrational modes.

Polyacetylene is the most studied conducting polymer. In spite of the extraordinary amount of theoretical and experimental work on this system, there are many aspects of its electronic behavior that are not well understood. One of these questions is the nature of the metallic regime for highly doped *trans*-polyacetylene (*trans*-PA).

Highly doped *trans*-PA has some properties of a common metal: high electrical conductivity, finite Pauli susceptibility, metal-like thermopower, and infrared absorption. However, the conductivity does not follow the T^{-1} law and the presence of localized infrared active vibrational (IRAV) modes indicates that doped *trans*-PA is not a simple metal.[1]

The most accepted models on the electronic structure of doped *trans*-PA have assumed a periodic distribution of conformational defects like solitons and polarons,[2,3] in connection with a periodic array of dopants. However, the assumption of an ordered distribution of solitons or polarons (solitonic or polaronic lattice) seems incompatible with some experimental data.[4–7]

The solitonic lattice implies the closing of the Peierls energy gap with the suppression of bond alternation. However, as has been pointed out by Kim and Heeger,[8] the existence of enhanced IRAV modes, which are red shifted with respect to the corresponding Raman ones, requires either the existence of localized phonons associated with the coupling of nonuniform charge distributions to the lattice, or the uniform phase motion of an incommensurate charge density wave to the symmetric Raman modes. Among these, only the polaronic lattice would appear consistent with the experimental data for susceptibility and electrical conductivity. However, for the polaronic lattice the intensities of the IRAV modes are weaker by many orders of magnitude in comparison with experimental data.[8]

In what concerns the distributions of dopants, samples doped with heavy alkali metals have presented dopant distributions which are incommensurate with respect to the chains for dopant concentrations greater than 0.125.[4] Doping processes with Li and Na (Refs. 5 and 6) could lead to a disordered array of dopants; as to doping with I_2, the ions are arranged in columns parallel to the chains, but there is evidence that the distance between them is not constant.[7]

If the models based upon periodicity are not fully consistent with experimental observations, theoretical works based on disordered distribution of conformational defects found in the literature are not able to reproduce important features of doped *trans*-PA. In some models the metallic regime with suppression of bond alternation is attained only at very high dopant concentration.[9,10]

The main theoretical objections against models based on disordered one-dimensional chains arise from Anderson localization theory; the slightest disorder introduced in perfect one-dimensional lattice renders all states localized.[11] Thus, *a priori,* a disordered system cannot explain the metallic properties of highly doped *trans*-PA. However, Galvao *et al.*[12] have performed a series of molecular orbital calculations on linear disordered one-dimension polyaniline chains and have concluded that the semiconductor-metal transition arises from the movement of the Fermi level towards conducting (extended) states located inside the valence band (*p*-type metal). The precise origin of these states has been explained by Wu and Phillips,[13] based on the random-dimer model proposed by Dunlap, Wu, and Phillips.[14] Their random-dimer model states that if two site energies are assigned at random to pairs of lattice sites, then $N^{1/2}$ of the electronic states will be extended at a particular energy in the band. This model explains the semiconductor-metal transition in polyanilines as well as the experimentally observed dc conductivity.

In this work molecular orbital calculations on long finite disordered *trans*-PA chains are performed in order to investigate the evolution of the density of states (DOS) as a function of the doping concentration. The main purpose of the present calculation is to investigate the role of disorder on the electronic structure of highly doped *trans*-PA and whether it could explain the metallic regime. In what follows the model calculation adopted and the results obtained are presented.

Since for planar conjugated systems the optical, electrical, and magnetic properties are dominated by π electrons, the *trans*-PA chain is treated as a π-electron system described by one orbital per site ($2p_z$) and in the first-neighbors approximation where the tight-binding Hamiltonian matrix elements are obtained from the extended Hückel theory with Clementi's parametrization.[15]

The geometrical data used in this work were adapted from fully Austin method 1 (AM1) (Ref. 16) calculations of neutral polyene chains with 22 and 21 carbon atoms. The former is a completely dimerized chain and the latter contains a soliton-like defect in its center. AM1 results show that the difference between single and double bonds is 0.097 Å in the perfectly dimerized chain and the soliton-like defect has a half-width of about three bondlengths.

The chains are built using two basic cells: One of them is a segment of a dimerized chain containing 10 carbon atoms and the other is a segment with 9 carbon atoms with a soliton-like defect in its center. In order to study disorder effects, a random distribution of the defect cell controlled by the compositional percentage of defect and defectless cells is assumed. For all calculations, the minimum distance between two defect centers in the chains is 10 bondlengths. As the defect half-width takes three bondlengths, there are at least four bondlengths between two defect edges, with the same bond alternation of the dimerized chain. The concentration of dopants y is calculated as the number of defect cells divided by the total number of carbon atoms in the chain. The relation between y and the actual concentration in the samples would be made using the existing structural models.[5]

The density of states of ordered and disordered *trans*-PA chains are obtained using the negative-factor-counting technique,[17] a powerful method to treat aperiodic polymeric systems. The eigenvectors associated to eigenvalues of interest were obtained using the inverse iteration method.[18] This technique allows the access to the wave function pattern and length localization.

The evolution of the DOS pattern as a function of the doping level should be able to explain some aspects of the complex behavior of doped *trans*-PA. When the doping level increases the conductivity increases, the system undergoes a semiconductor-to-metal transition, and the intensities of localized IRAV modes grow linearly. The transition is not well understood and the increase of the intensities of IRAV modes are not compatible with the expected picture of a metal to which the bondlengths are uniform.

The calculated DOS of a 3000-carbon-atom chain with a disordered distribution of defects in the present model is shown in Fig. 1 for y ranging from 0.0 to 0.072. The arrow indicates the position in energy of the highest occupied level in Fig. 1(a) and in Figs. 1(b)–1(d) the evolution of this level can be followed. A defect band is built up by increasing the number of defects and band tailing and antiresonance effects are clearly seen. The closure of the gap is the most important feature observed; this fact does not occur for an ordered distribution of defects.[19]

For the calculations above, in the highly doped regime the defects keep the same distortion pattern of the isolated defect and therefore the increase of the intensities of IRAV modes is possible. The finite value of the DOS at the Fermi level is a necessary but not a sufficient condition to ensure a semiconductor-to-metal transition since these states could be localized. An investigation on the extension of these states is necessary and is presented below.

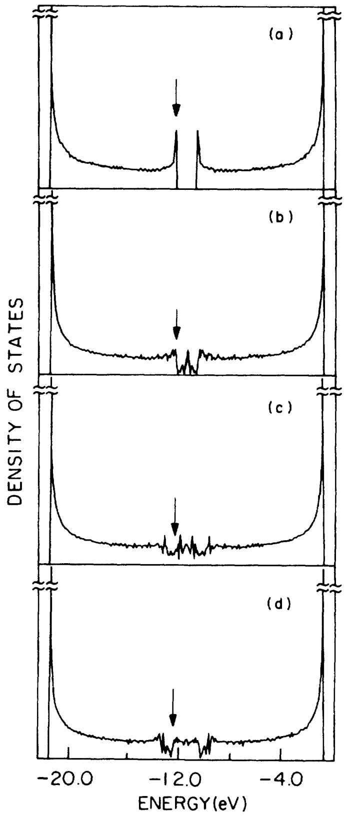

FIG. 1. The DOS of a 3000-carbon-atom chain with a disordered distribution of defects for defect concentrations $y=0.0$ (a), $y=0.021$ (b), $y=0.054$ (c), and $y=0.072$ (d). The arrow indicates the highest occupied energy level position in (a); for comparison it is also shown in (b)–(d).

The extensions of the wave functions are inferred from the plot of the square of the coefficients of the expansion of the eigenfunctions in the $2p_z$ basis versus the carbon-atom positions for chains with 200 atoms (Figs. 2 and 3). The wave-function patterns of states close to Fermi level as a function of doping are calculated for ascending values of y (Fig. 2). For the low y regime the states are localized but delocalization increases with the number of defects. This behavior is not expected for a disordered distribution of defects and is observed for all the defect states near the Fermi level.

The model can be improved to stress the effects of doping on the DOS and wave-function patterns. In order to simulate charge transfer from dopants to the chain and the movement of the Fermi level position with doping, the α parameter (diagonal Hamiltonian element) of the central carbon atom of the soliton cell is modified to $\alpha+\delta$. The p-type doping process pushes down the defect band and accelerates the overlap of the defect and the valence band. The wave functions of the defect levels close to the Fermi level become more delocalized for nonzero δ values (Fig. 3). The results shown for the wave-function patterns and the finite values obtained to the DOS indicate that a semiconductor-to-metal transition is possible to doped PA.

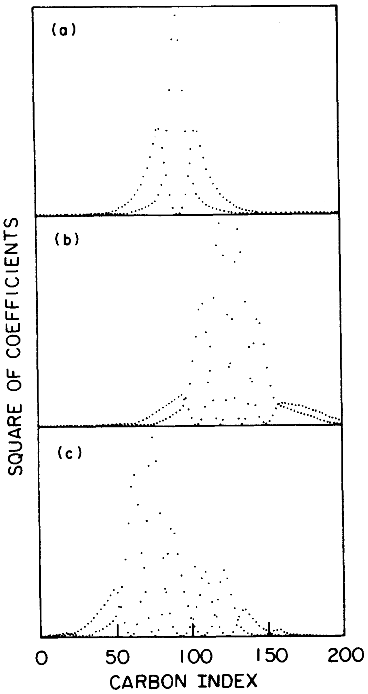

FIG. 2. Plot of the square of the coefficients of the expansion of the eigenfunctions in the $2p_z$ basis vs the carbon-atom positions to states near the Fermi level for $y=0.031$ (a), $y=0.049$ (b), and $y=0.054$ (c).

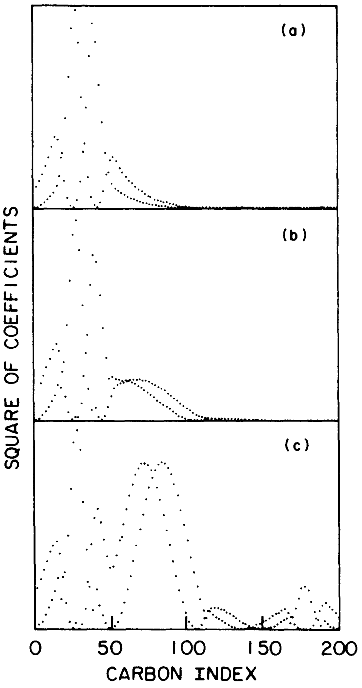

FIG. 3. Plot of the square of the coefficients of the expansion of the eigenfunctions in the $2p_z$ basis vs the carbon-atom positions to states near the Fermi level for $y=0.041$ with $|\delta|$ equal to 0.0 eV (a), 1.0 eV (b), and 2.0 eV (c).

The above results suggest that the origin of metallic regime of highly doped *trans*-PA could have the same physical basis as in the polyaniline case, i.e., disorder: The semiconductor-metal transition arises from the movement of the Fermi level toward the conducting states.

In spite of the crudeness of the model, it seems to be able to reproduce qualitatively the main features of the electronic behavior, as the semiconductor-metal transition compatible with the presence of IRAV modes with structural disorder suggested by experimental data. If the results for polyaniline and *trans*-PA could be generalized to other conducting polymers, disorder would have a more important role than hitherto supposed.[20]

In summary, the calculated DOS for a disordered distribution of soliton-like defects shows a finite value at Fermi energy and delocalized wave functions for highly doped *trans*-PA.[21] The persistence of the distortion patterns for the defects even at high doping are possible within the model presented here.

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