Insulator-Metal Transition in *trans*-Polyacetylene

E. M. Conwell and S. Jeyadev
Webster Research Center, Xerox Corporation, Webster, New York 14580

(Received 20 November 1987)

Optical and energy-loss data suggest that the soliton lattice, which accounts for the low Pauli susceptibility χ^P at average doping concentrations $\langle y\rangle < 4\%$ to 6%, persists to higher $\langle y\rangle$. We have calculated the eigenvalues for a *trans*-polyacetylene chain with the electrons in soliton states for the geometry and y values appropriate to metallic Na-doped polyacetylene and the Coulomb potential of the ions and solitons on other chains included. We find that, allowing for chains $\simeq 100$ C-H units in length, we can account for χ^P in the metallic state.

PACS numbers: 71.30.+h, 71.20.Hk, 72.80.Le

The Pauli susceptibility of *trans*-polyacetylene, $(\mathrm{CH})_x$, rises steeply when the average doping $\langle y\rangle$ is increased beyond $\simeq 4\%$ to 6%,[1,2] the exact value depending on the dopant and on sample preparation. This suggests that the doping causes a transition from the semiconducting state, with a gap $\simeq 1.4$ eV, to a metallic state. In fact, conductivity close to that of copper has already been attained for carefully processed $(\mathrm{CH})_x$ with $\simeq 6\%$ iodine doping.[3] In the doping process donor (acceptor) impurities give up electrons (holes) to the polyacetylene chain, which then undergoes relaxation.[4] (We shall speak of electrons in what follows although the results apply to holes with obvious modifications.) A single electron added to the chain gives rise to a polaron, with spin, whereas a pair of electrons gives rise to a pair of solitons, each spinless because the extra electron is paired with a valence-band electron.[4] In the usual theory the soliton levels are centered at midgap, all filled, and separated by a substantial gap from valence and conduction bands.[4] Early attempts to account for the semiconductor-metal transition were based on disorder, specifically a highly disordered arrangement of the doping impurities causing the soliton states to spread throughout the gap.[5,6] Strong disorder was also suggested to cause a transition to an incommensurate Peierls state with a large density of states in the gap.[7] A serious difficulty with these suggestions is that structure studies by x-ray, neutron, and electron scattering establish that above very small doping levels, $\simeq 0.4\%$, the impurities, although concentrated in a second phase, are not disordered but form chains with constant or nearly constant spacing.[8,9] For Na doping, for example, there are several different ordered phases, each with three $(\mathrm{CH})_x$ chains per Na chain.[8,10,11] The ordered phase seen up to $\langle y\rangle \simeq 6\%$ has a spacing between ions of $5a$, a being the average distance between C-H units, thus corresponding to $y = 6.67\%$.[8,10] According to electrochemical evidence, the phase with next larger y has an ion spacing of $4a$,[10] corresponding to $y = 8.33\%$. The regular arrangement of the ions, plus the lack of spins, suggested the existence of a soliton lattice in the impurity-rich phase below $\langle y\rangle \simeq 6\%$.[2] The steep increase in Pauli susceptibility χ^P found above $\simeq 6\%$ doping led to the proposal of a phase transition from a soliton to a polaron lattice,[12] which, in addition to spins, would give metallic conductivity by virtue of the uppermost (polaron) band being half filled.[4] A strong argument against this suggestion is the fact that the three doping-induced infrared absorption lines attributed to solitons at low concentrations have been found to increase more or less linearly with ion concentration in K-doped $(\mathrm{CH})_x$ up to the maximum possible K doping of $\simeq 18\%$[13]; theoretical calculations have shown that these absorptions should be quite unobservable for a polaron lattice at such concentrations.[14] Further, electron energy-loss experiments on heavily Na-doped $(\mathrm{CH})_x$ show levels spread well across the gap,[15] whereas a polaron lattice would result in two narrow well-separated bands in the gap.

The energy-loss and infrared experiments suggest that the electrons given up by the ions go into regularly spaced solitons, specifically a soliton lattice, for *all* $\langle y\rangle > 0.4\%$.[16] In contrast to the usual theory,[16] however, the soliton states are not centered at midgap when we take into account the Coulomb potential of the ions. Not only does this attractive potential lower the soliton states but it pulls levels down from the bottom of the conduction band (and valence band), as shown by Bryant and Glick for a single donor ion,[17] tending to make a continuum of levels. To determine whether the Coulomb effects can account for metallic behavior above $\langle y\rangle \simeq 6\%$ ($y = 6.67\%$ in the ordered phase[8]), we have carried out calculations of the energy-level structure for a chain of Na-doped $(\mathrm{CH})_x$ with a soliton lattice for $y \geq 6.67\%$ taking into account the Coulomb potentials due to impurity ions and solitons on neighboring $(\mathrm{CH})_x$ chains. We find for $y = 6.67\%$ that for chains up to $\simeq 100$ C-H units in length, and appropriate boundary conditions, there is a relatively large gap between levels at the Fermi energy E_F, as well as between some pairs of deeper levels. For $y = 8.33\%$, the next ordered phase,[10] however, for chains > 100 sites long the large gaps are reduced and all level spacings are of the order of that between valence-band states. An example is shown in Fig. 1. Metallic behavior and Pauli susceptibility are therefore expected for the large chain lengths at these concentrations. The onset of this susceptibility as $\langle y\rangle$ increases should be sharp because, as will be discussed, χ^{P} increases rapidly with increasing doped chain length when y in the ordered phase goes beyond 6.67%.

To find the energy levels of the π electrons on the chains the Hamiltonian used was[17,18]

$$H=-\sum_{n=1}^{N-1}[t_0+\alpha(u_n-u_{n+1})][c_{n+1}^{\dagger}c_n+\mathrm{H.c.}]+\sum_{n=1}^{N}(V_n-V_0)c_n^{\dagger}c_n. \qquad (1)$$

Here u_n is the displacement of the nth lattice site, t_0 is the transfer integral when $u_n=0$ for all n, $\alpha=-\partial t/\partial u$, $c_n^{\dagger}$ and c_n are creation and annihilation operators for a π electron on the nth site, and N is the number of sites on the chain. The contribution to the Coulomb potential V_n at site n due to the ions is

$$V_n^{(I)}=-\sum_{i=1}^{N_I}\frac{e^2}{\epsilon_{\perp}[(n-n_i)a^2+(\epsilon_{\parallel}/\epsilon_{\perp})d^2]^{1/2}}, \qquad (2)$$

where e is the charge on the electron, $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the components of the dielectric tensor parallel and perpendicular to the chains, respectively, n_i is the site on the chain which the ion is opposite, a is the average distance between sites, d is the distance of the ion from the chain, and N_I is the number of ions. V_n was taken as the sum of (2) and similar terms for the contribution of the (negatively charged) solitons on neighboring chains. V_0 equals $N^{-1}\sum V_n$. The inclusion of V_0 in (1) shifts the energy scale of the eigenvalues so that their matrix remains traceless. The geometry used to determine V_n was essentially that of Ref. 11, which finds each $(\mathrm{CH})_x$ chain to lie along the side of an equilateral triangle with the ion column equidistant from the three chains. We took $d=2.4$ Å,[19] in close agreement with 2.26 Å found between Na^+ ions and graphite planes in intercalated graphite.[20] Outside its own triangle the largest Coulomb potentials experienced by a given chain will be due to another ion column at about the same distance as the one in its own triangle, and the solitons on second- and fourth-nearest-neighbor $(\mathrm{CH})_x$ chains.[11] In the absence of information about the distances to all these other chains, we assumed for the calculations two Na^+ ion columns at 2.4 Å from the chain and four $(\mathrm{CH})_x$ chains with centers at $2.4\sqrt{3}$ Å from the center of the $(\mathrm{CH})_x$ chain. The particular geometry assumed cannot be of prime importance because a similar rapid increase of χ^{P} occurs for other dopants[1] for which doped $(\mathrm{CH})_x$ has quite different geometry.[8,9] The contributions of more distant ions and $(\mathrm{CH})_x$ chains were neglected because they should be well screened. The presence of solitons on the chain was incorporated by our taking

$$u_n=-(-1)^n u_0\prod_{j=1}^{N_s}\tanh\left[\frac{n-jb}{l}\right], \qquad (3)$$

where u_0 is the displacement in the perfectly dimerized chain, N_s the number of solitons on the chain, l the half-length of a soliton, and b the spacing between soliton centers, a function of y. For three $(\mathrm{CH})_x$ chains per ion chain and an ion spacing of $5a$ ($y=6.67\%$), $b=15$ sites, while for an ion spacing of $4a$ ($y=8.33\%$), $b=12$ sites, and for $3a$ (11.1%), $b=9$ sites.

Calculations were carried out for two sets of dielectric constants: $\epsilon_{\parallel}=7.08$,[21] $\epsilon_{\perp}=1.77$,[21] and a more recent set $\epsilon_{\parallel}=11.5$,[22] $\epsilon_{\perp}=2.5$.[23] Only the results using the latter set are reported here, although both sets gave qualitatively similar results. Other numerical values used were $t_0=2.5$ eV, $\alpha=4.1$ eV/Å,[18] $a=1.22$ Å,[18] $u_0=0.0427$ Å (taken as the half-gap $\Delta=0.7$ eV divided by 4α), and $l=7$ sites.[18] Although it has been shown that l decreases to five sites in the presence of a single ion 2.4 Å from the chain,[18] it is to be expected that the presence of additional ions five or fewer sites away would counteract the shrinkage. The results of Fig. 1 are for $3N_s$ ions on the chain, corresponding to N_s solitons on each of the three chains surrounding the ion chain. We have also done calculations for $3N_s+2$ and for $3N_s+6$ ions in the chain, corresponding to shallower wells. The latter boundary condition is more appropriate when most of the sample is doped. Although these three different boundary conditions made for big differences in the energy levels for shorter chains, the differences in the states around E_{F} were not important for chains with $N>100$. We note that ordered chain lengths of several hundred sites would not be unreasonable. Molecular weights in typical undoped Shirakawa samples correspond to average chain lengths of $\simeq 1000$ sites.[24] Some of the defects that limit the coherent length,[9] such as random *cis* inclusions and gradual bends of the fibrils, need not hinder the diffusion of ions with accompanying polarons or solitons.

The eigenvalues of the Hamiltonian (1) were obtained for various chain lengths, corresponding to 2, 4, 6, etc.,

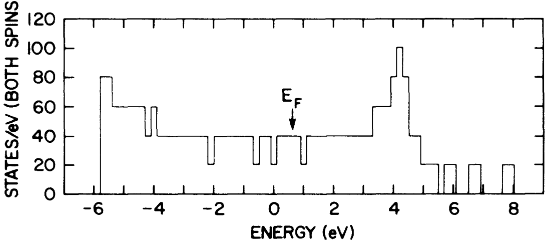

FIG. 1. Density of states vs energy calculated from the Hamiltonian (1) for a 132-site polyacetylene chain with ten solitons spaced twelve lattice sites apart. The Coulomb potential is due to 32 nearest-neighbor positive ions and 22 charged solitons plus polarons on neighboring chains.

solitons for $b=15$, $b=12$, and $b=9$. For the short chains, as indicated earlier, gaps of several tenths of an electronvolt remain between pairs of levels around E_F. At 6.67% doping, even for $N=134$, a gap of 0.2 to 0.3 eV remains. For the higher dopings, however, at this chain length all level spacings are close to the average spacing in what had been the valence and conduction bands. The results for $b=12$ with $N=132$ are shown in Fig. 1. Results for $b=9$ with $N=134$ (14 solitons) are very similar. For $b=12$ (8.33%), in the absence of the Coulomb potential the states would spread from -5.0 to 5.0 eV, with a gap of 1.68 eV. The average spacing between the soliton levels in the gap would be $\simeq 0.1$ eV, with the lowest and highest separated by 0.38 eV from the closest band edge. It is seen from Fig. 1 that the Coulomb potential, which corresponds to a well depth of 4.4 eV for the boundary condition chosen, causes the filling in of the gaps between the lowest and highest "soliton" levels and the closest band edges, with the result that all the states can now be considered to occupy a single band. It is clear from the wave functions that none of the states within 3 or 4 eV of E_F in this band are localized. However, the Coulomb potential does cause the lowest-energy states to be strongly localized. The strong concentration of the low-energy wave functions at the center of the chain is reflected in the highest-energy wave functions being more concentrated at the ends of the chain. This prevents the latter from taking advantage of the potential well, pushing up their energies. It is expected that this effect would be larger the higher the energy level, and that is indeed seen in Fig. 1 in the spread of states above the remains of the band-edge singularity at 4.2 eV.

The model just described leads to predictions in good agreement with many different kinds of experiment. In particular, it predicts a rapid increase in χ^P when b decreases below fifteen sites. We show below that, with the next stable phase corresponding to $b=12$,[10] the increase should match that observed experimentally.[2] χ^P arises from the (small) shift in occupation probabilities for electrons with spins parallel and antiparallel to the magnetic field. For the shortest doped chain length (two solitons) with twelve- or nine-site spacing, the energy interval 2Ω between the highest occupied and lowest empty level is large compared to kT and only these two levels contribute to χ^P, giving essentially $\chi^P \propto \exp(-\Omega/kT)$. As this doped chain length L_D increases, decreasing Ω, χ^P increases, exponentially at first, and then less rapidly. Significantly, for $L_D=84$ sites (6 solitons), and $b=12$ or less, Ω is down to $2.5kT$ and the calculated χ^P has attained about half the theoretical maximum. That maximum, calculated for $b=9$ or 12 and L_D a few hundred carbons, corresponds to a density of states at the Fermi energy $N(E_F)=0.14$ states/eV C atom. The calculated χ^P for $L_D=84$ sites corresponds to 0.06 states/(eV C atom). This value is close to that of 0.08 states/(eV C atom) deduced from the maximum χ^P observed by Moraes *et al.*[2] at $\simeq 8\%$ doping, suggesting that the average L_D in their samples is $\simeq 100$ sites. It is reasonable to identify the $\langle y \rangle$ value at which the rapid rise in χ^P begins, 0.055 or 0.056,[2] as the value for which the ion spacing begins to decrease from fifteen sites.[10] At $\langle y \rangle = 0.060$, where the average ion concentration has increased by $\simeq 7\%$ or 8%, χ^P has increased sharply to almost half of the maximum measured value.[2] The apparent saturation of χ^P observed[2] at $\langle y \rangle \simeq 8\%$ is additional evidence that the next stable phase corresponds to $b=12$. The 7% or 8% noted above corresponds to $\frac{1}{4}$ or $\frac{1}{3}$ of the 25% increase in y required to go from $b=15$ to $b=12$ throughout the sample. Given the rapid increase in χ^P with L_D and Ω remarked on earlier, $\frac{1}{4}$ of the sample in the next stable phase could easily contribute half of the maximum χ^P observed for that phase. Slower growth of χ^P beyond $\langle y \rangle = 0.060$ could be due to the decreasing rate of growth with increasing chain length. Also, some of the doping beyond $\langle y \rangle = 0.060$ might involve very short chains and disordered regions that contribute little to χ. It may be noted also that observation of sizable χ^P for very low $\langle y \rangle$, $<1\%$ for iodine-doped $(CH)_x$,[1] for example, can be accounted for by inhomogeneous doping, the surface regions being more heavily doped than the interior.[25]

In summary, we have shown that the metallic state of polyacetylene is achieved by (1) the donated electrons or holes being in soliton states and (2) the Coulomb potential of the doping ions and the solitons in other chains causing a redistribution of the states in energy. Calculations for a structure resembling that of Na-doped $(CH)_x$ lead to a continuum of levels for Na^+-ion concentrations of 8.33% or higher, supposed to be characteristic of the metallic phase, for chain lengths >100 sites. The insulator-metal transition, characterized by a rapid rise in χ^P, occurs as this length is achieved for a sizable percentage of the doped, ordered regions in the sample. In addition to accounting for the observation of doping-induced infrared absorption at concentrations above the "insulator-metal" transition, the addition of many states within the gap allows the model to account for the wide range of continuous optical absorption seen within the gap for $\langle y \rangle$ below the transition.[2]

We acknowledge useful discussions with Professor David Tanner.

---

[1] A. J. Epstein, R. W. Bigelow, H. Rommelmann, H. W. Gibson, R. J. Weagley, and A. Feldblum, Mol. Cryst. Liq. Cryst. **117**, 147 (1985).

[2] F. Moraes, J. Chen, T. C. Chung, and A. J. Heeger, Synth. Met. **11**, 271 (1985).

[3] N. Basescu, Z.-X. Liu, D. Moses, A. J. Heeger, H. Naarmann, and N. Theophilou, Nature (London) **327**, 403 (1987).

[4] See, for example, a review by E. M. Conwell, IEEE Trans.

Electr. Insul. **22**, 591 (1987).

[5] E. J. Mele and M. J. Rice, Phys. Rev. B **23**, 5397 (1981).

[6] W. P. Su, Solid State Commun. **42**, 497 (1983).

[7] X. Q. Yang, D. B. Tanner, M. J. Rice, H. W. Gibson, A. Feldblum, and A. J. Epstein, Solid State Commun. **61**, 335 (1987).

[8] R. H. Baughman, N. S. Murthy, G. G. Miller, L. W. Shacklette, and R. M. Metzger, J. Phys. (Paris), Colloq. **44**, C3-53 (1983); R. H. Baughman, L. W. Shacklette, N. S. Murthy, G. G. Miller, and R. L. Elsenbaumer, Mol. Cryst. Liq. Cryst. **118**, 253 (1985).

[9] J. P. Pouget, in *Electronic Properties of Polymers and Related Compounds,* edited by H. Kuzmany, M. Mehring, and S. Roth (Springer-Verlag, New York, 1985), p. 26.

[10] L. W. Shacklette and J. E. Toth, Phys. Rev. B **32**, 5892 (1985).

[11] M. Winokur, Y. B. Moon, A. J. Heeger, J. Barker, D. C. Bott, and H. Shirakawa, Phys. Rev. Lett. **58**, 2329 (1987).

[12] S. Kivelson and A. J. Heeger, Phys. Rev. Lett. **55**, 308 (1985).

[13] D. Tanner, G. Doll, K. Rao, M. H. Yang, P. C. Eklund, G. Arbuckle, and A. G. MacDiarmid, Bull. Am. Phys. Soc. **32**, 422 (1987).

[14] H.-Y. Choi and E. J. Mele, Phys. Rev. B **34**, 8750 (1986).

[15] J. Fink, N. Nücker, B. Scheerer, and A. vom Felde, to be published.

[16] Note that this soliton lattice is not described by either the usual theory for an amplitude soliton lattice [B. Horovitz, Phys. Rev. Lett. **46**, 742 (1981)] or a phase-amplitude soliton lattice [M. Grabowski, K. R. Subbaswamy, and B. Horovitz, Solid State Commun. **34**, 911 (1980)] because these theories neglect the effects of the ions. For example, in these theories the distance between solitons b is determined solely by the density N_s of solitons on the chain whereas, as will be discussed, b is actually determined by the ion spacing and is independent of N_s over wide ranges of concentration.

[17] G. W. Bryant and A. J. Glick, Phys. Rev. B **26**, 5855 (1982).

[18] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980).

[19] N. S. Murthy, L. W. Shacklette, and R. H. Baughman, Bull. Am. Phys. Soc. **31**, 232 (1986).

[20] A. Metrot, D. Guerard, D. Billaud, and A. Herold, Synth. Met. **1**, 363 (1980).

[21] G. Leising, R. Uitz, B. Ankele, W. Ottinger, and F. Stelzer, Mol. Cryst. Liq. Cryst. **117**, 327 (1985).

[22] C.-S. Neumann and R. von Baltz, Phys. Rev. B **35**, 9708 (1987).

[23] W. Ottinger, G. Leising, and H. Kahlert, Ref. 9, p. 63.

[24] M. A. Schen, F. E. Karasz, and J. C. W. Chien, Makromol. Chem., Rapid Commun. **5**, 217 (1984).

[25] A. J. Epstein, H. Rommelmann, M. A. Druy, A. J. Heeger, and A. G. MacDiarmid, Solid State Commun. **38**, 683 (1981), and references therein.