

SOLITONS, DISORDER AND CHARGE CONDUCTION IN NEARLY METALLIC POLYACETYLENE

A. J. EPSTEIN, R. W. BIGELOW, A. FELDBLUM and H. W. GIBSON

Xerox Webster Research Center - W114, Webster, NY 14580 (U.S.A.)

D. M. HOFFMAN*

Department of Physics, Ohio State University, Columbus, OH 43210 (U.S.A.)

D. B. TANNER

Department of Physics, University of Florida, Gainesville, FL 32611 (U.S.A.)

Abstract

Polyacetylene doped in the range one to five per cent has been shown to have low susceptibility yet high conductivity. A coordinated study of the structural, optical, magnetic and transport properties of polyacetylene doped with iodine to these nearly metallic levels shows that essentially all charges go into soliton-like states. The measurements are in quantitative agreement with charge transport via variable range hopping among soliton-like levels. A parallel conduction mechanism of thermal activation of charge carriers to 'high mobility' extended band states is proposed, and may dominate in less disordered samples.

1. Introduction

The transformation of polyacetylene, $(CH)_x$, from a semiconductor to a metal-like material upon doping with donors or acceptors has been under intense study for the past several years [1, 2]. The soliton model [3, 4] has been very successful in explaining many of the transport, spectroscopic and magnetic properties of polyacetylene, especially in the lightly doped regime [5 - 12]. The nearly metallic region of one to five per cent doping ($0.01 \leq y \leq 0.05$) is of particular interest. Here, the magnetic susceptibility of samples carefully doped with iodine [8], perchlorate [13], arsenic pentafluoride [9] or sodium [14] is substantially lower than that of metallic polyacetylene ($y \geq 0.06$) yet the conductivity (σ) is 'nearly metallic' ($10^2 \geq \sigma \geq 10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$). This result has led to a variety of suggestions for the

*Present address: Department of Physics, University of Kentucky, Lexington, KY 40506, U.S.A.

charge conduction mechanism in this regime, including: variable range hopping [15] among soliton-like centers [16], collective transport by mobile spinless charged solitons [14] and interchain hopping of bipolarons [17]. In this paper we demonstrate the important central role of charged solitons using iodine-doped polyacetylene as the model. We show how, under some conditions, disorder will dominate and charge conduction will be via variable range hopping. Finally, we introduce a parallel conduction path to account for variations from sample to sample and dopant to dopant: thermal activation of charge carriers to 'high mobility' extended states.

2. Experimental methods

Free standing polyacetylene films were prepared by the Shirakawa technique [18]. The films were $\sim 90\%$ crystalline [19] and were composed of ~ 500 Å diameter fibrils [20]. The samples were doped with iodine using the 'slow doping' technique [8, 9]. Room-temperature reflectance measurements [21] were made between 20 and 20 000 cm^{-1} and Kramers-Kronig analysis gave the frequency(ω)-dependent conductivity, $\sigma(\omega)$. The temperature(T)-dependent magnetic susceptibility (χ) was measured from 4 to 320 K with a calibrated [8] Faraday technique. The temperature-dependent thermopower $S(T)$ and the four-probe $\sigma(T)$ were measured from 10 to 300 K with an apparatus that allows these quantities to be determined in the same run.

3. Optical properties

The $\sigma(\omega)$ for $y = 0.033$, 0.042 and 0.048 are shown in Fig. 1 for frequencies up to 6000 cm^{-1} . Extension to 20 000 cm^{-1} for $y = 0.042$ shows that neither the interband transition at $\sim 12\,000$ cm^{-1} nor the strong midgap absorption observed [7] at ~ 6000 cm^{-1} is present. Instead, a single intense peak at 3000 - 3500 cm^{-1} is found. The far-infrared conductivity obtained is in good agreement with the measured d.c. conductivity. The broad maximum in $\sigma(\omega)$ at 900 cm^{-1} and the narrow peak at 1370 cm^{-1} have been associated with charged solitons created by chemical doping [5, 6]. The oscillator strength of these features (calculated after subtraction of the low-energy tail of the ~ 3000 cm^{-1} absorption) is plotted *versus* doping concentration in the inset in Fig. 1. The straight lines are extensions of the strengths of these absorptions at low doping levels [5, 22], $y < 0.01$. Because the strength per dopant molecule is unchanged up to $y = 0.048$, we conclude that doping proceeds through the formation of charged solitons even for doping levels approaching five per cent. This value is twice the critical concentration measured [23] for the divergence of the dielectric constant ($y_c = 0.022$) in similarly iodine-doped samples. This dielectric divergence may then correspond to the formation of a soliton lattice [24] or Anderson transition [25] at y_c .

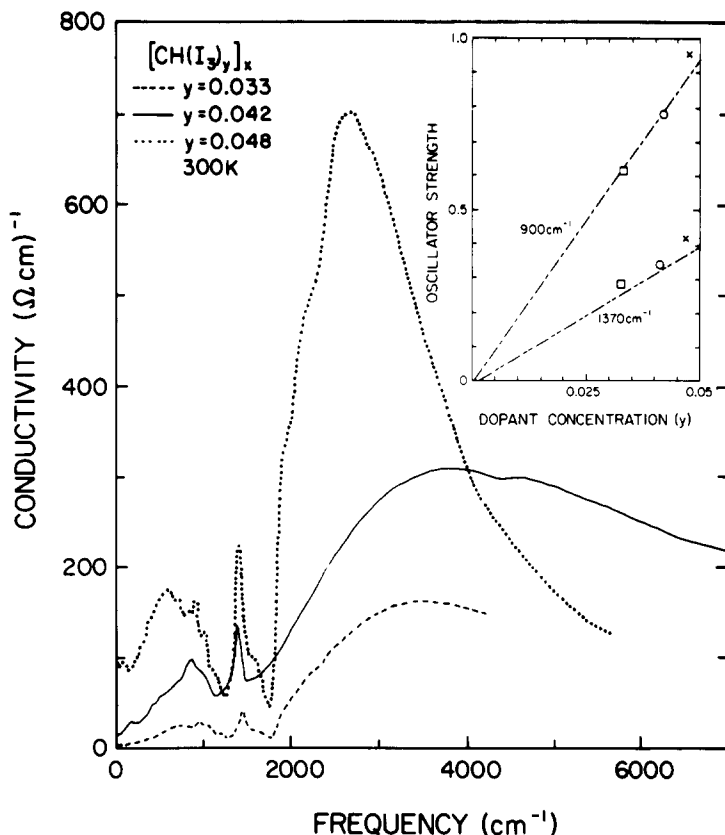


Fig. 1. Conductivity *versus* frequency for $[\text{CH}(\text{I}_3)_y]_x$ (from reflectance data). Inset: the oscillator strength *vs.* y of the 900 and 1370 cm^{-1} peaks. The solid lines are extrapolations of the earlier results [22] for $y < 0.01$.

The broad mode centered at 900 cm^{-1} for lightly doped samples has been identified as the 'pinned' mode of the charged soliton bound to a charged impurity [6, 26]. Examination of Fig. 1 shows that for these iodine-doped samples, the pinned mode remains at 900 cm^{-1} up to $y = 0.042$, but shifts to $\sim 700 \text{ cm}^{-1}$ for $y = 0.048$. This supports the idea that the charged solitons remain pinned to the dopant position and do not diffuse independently of the dopant. At low frequencies the room temperature optical conductivity equals the measured d.c. conductivity, in agreement with the prediction of variable range hopping [27].

4. Magnetic properties

The $\chi(T)$ is a sum of χ^{Curie} and $\chi^{\text{Pauli}} = 2\mu_B^2 N(E_F)$, where μ_B is the Bohr magneton and $N(E_F)$ the density of states at the Fermi level. Note that $(\text{CH})_x$ with zero band gap would have [8, 9, 28] $N(E_F) \sim 0.16 - 0.20 \text{ states/eV C}$

TABLE 1

Summary of results for $[\text{CH}(\text{I}_3)_y]_x$

| Starting (CH) _x | y | $N(E_F)$ (states/eV C) | $\sigma(295 \text{ K})$ ($\Omega^{-1} \text{ cm}^{-1}$) | T_0 (10^5 K) | α^{-1} (\AA) | σ_H ($\Omega^{-1} \text{ cm}^{-1}$) |
|-------------------------------|-------|---------------------------|--------------------------------------------------------------|-------------------------------|-----------------------------------|-------------------------------------------------|
| <i>trans</i> | 0.017 | 0.014 | 2.5 | 19 | 5.2 | 1.9 |
| <i>cis</i> | 0.033 | 0.045 | 8 | 29 | 3.1 | 9.1 |
| <i>trans</i> | 0.042 | 0.027 | 20 | 3.8 | 7.1 | 3.1 |
| <i>cis</i> | 0.048 | 0.069 | 50 | 4.6 | 4.9 | 12 |

atom, while Table 1 shows that $N(E_F)$ for the two initially *trans*-doped samples is much smaller, nearly as low as that reported earlier [8, 9] for low-susceptibility, slowly doped samples. Though small, the measured $N(E_F)$ is much larger than that of an uncompensated amorphous semiconductor [29] such as amorphous Si. The finite $N(E_F)$ is in accord with the phase disordering of the $(\text{CH})_x$ Peierls insulator due to the aperiodic location of the dopants, where $N(E_F)$ is non-zero due to states being pulled out of the valence and soliton bands by the I_3 disorder [28]. These states should retain soliton-like character. Figure 2(a) is a schematic diagram of the resulting electronic structure of the iodine-doped nearly metallic polyacetylene.

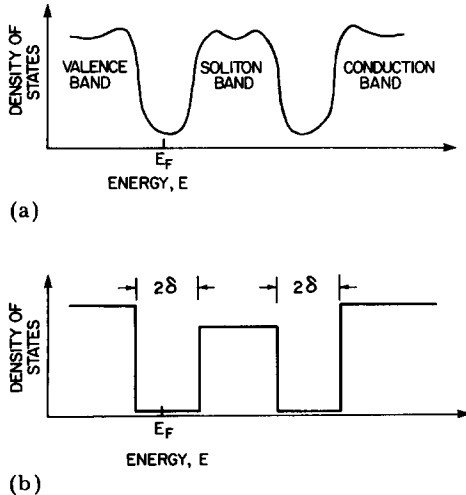


Fig. 2. Schematic electronic structure for doped polyacetylene. The Fermi energy is shown for acceptor doping. (a) Disorder strong; (b) disorder weak. 2δ is the energy gap between the valence (conduction) band and the soliton band.

5. Structural disorder

X-ray diffraction measurements [30] of *cis*-(CH)_x slowly doped to $y = 0.033$ and $y = 0.048$ show the same pattern as those for *trans*-(CH)_x slowly

doped to $y = 0.017$ and $y = 0.042$. This result is in agreement with earlier optical [22] and transport [31] studies which indicated that the doping of *cis*-(CH)_x resulted in doped *trans*-(CH)_x. For all iodine doping levels studied [30], about one-third of the sample volume remains undoped, probably in the centers of the fibrils. Three broad X-ray reflections are found for [CH(I₃)]_x for interplanar spacings of 7.9 Å, 4.1 Å and 2.9 Å, in agreement with a model [31] of intercalation between polyacetylene planes. The transverse coherence length for the doped (CH)_x is 20 ± 5 Å.

The coherence observed in the X-ray structural studies suggests that a side view of the iodine-doped (CH)_x system is as schematically shown in Fig. 3. The actual extent of the disorder, and hence the magnitude of $N(E_F)$, is expected to be a sensitive function of initial polyacetylene state (*cis-trans* content, crystallinity, fibril diameter, crosslinking, etc.), doping conditions (vapor pressure, soliton concentration or electrochemical potential, temperature, etc.) and dopant (dopant size, shape, reactivity, etc.). For example, $\chi[N(E_F)]$ of the doped initially *cis*-(CH)_x films, while smaller than the zero bandgap value, is generally larger than that of *trans*-(CH)_x doped to approximately the same concentration [16, 33]. This may be due to increased disorder in the doped *cis* because of the large structural charges that accompany doping-induced isomerization, leading to a higher $N(E_F)$. In comparison, doping in *trans* is an intercalation process [32] that may introduce less disorder and hence lower $N(E_F)$ [34].

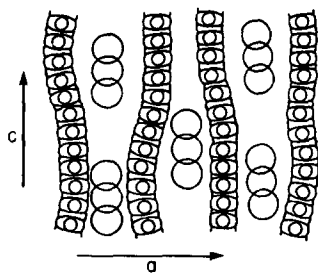


Fig. 3. Schematic view of the *ac* plane of [CH(I₃)_y]_x. The X-ray data show only a 20 ± 5 Å coherence length perpendicular to the chain axis [30].

6. Transport properties

Because $N(E_F)$ is below the metallic value yet very high for a semiconductor, we have analyzed $\sigma(T)$ within the variable-range hopping (VRH) model [29]. This model gives

$$\sigma(T) = (0.39[N(E_F)/\alpha k_B T]^{1/2} \nu_0 e^2) \exp[-(T_0/T)^{1/4}], \quad (1)$$

where $T_0 = 16\alpha^3/k_B N(E_F)$, α^{-1} is the decay length of a localized state, and ν_0 is a hopping attempt frequency. The fit of $\sigma(T)$ by the functional form $T^{-1/2} \exp[-(T_0/T)^{1/4}]$ is shown as a solid line for each sample in Fig. 4, with

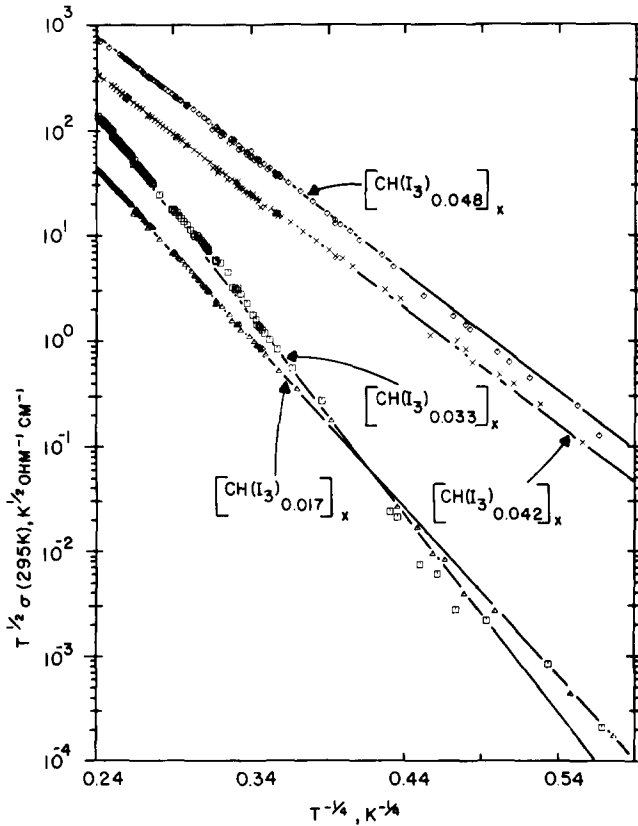


Fig. 4. $T^{1/2}\sigma(T)/\sigma(295\text{ K})$ vs. $T^{-1/4}$ slow-doped $[\text{CH}(\text{I}_3)_y]_x$. The solid lines are from theoretical fits described in the text (eqn. (1)).

the one adjustable parameter, T_0 , given in Table 1. Fits with other behaviors, e.g., $\exp[-(T_0/T)^m]$ with m other than $1/4$, were not as good. Using the measured values of $N(E_F)$ from χ and T_0 from σ , we calculate $\alpha^{-1} \approx 5\text{ \AA}$, varying slightly from sample to sample (see Table 1). Then, assuming that [35] $\nu_0 = \nu_{\text{ph}} \exp(2\alpha R)$, where R is the separation between hopping sites and ν_{ph} is an optical phonon frequency ($\sim 3.6 \times 10^{13}\text{ s}^{-1}$), the conductivities calculated from eqn. (1) (σ_H in Table 1) are in good agreement with experiment. The decay length α^{-1} evaluated for these samples is consistent with the effective dimensionally averaged decay length of a non-interacting soliton [10, 36], $\xi = (\xi_{\perp}^2 \xi_{\parallel})^{1/3} = 3.6\text{ \AA}$. This picture is also consistent with $N(E_F)$ being non-zero due to states being pulled out of the valence and soliton bands by the I_3 disorder [28]. These states should retain a large soliton-like character.

The temperature-dependent thermopower is an independent probe of the specific charge transport mechanism. For example, for VRH [29]

$$S^{\text{VRH}}(T) = 1/2(k_B/e)k_B(T_0T)^{1/2}(N^{-1}dN/d\epsilon) \quad (2)$$

while for a metal [29],

$$S^m(T) = (2\pi^2/3)(k_B/e)k_B T(N^{-1} dN/d\epsilon). \quad (3)$$

The $S(T)$ was measured on the same samples during the $\sigma(T)$ study [16, 37]. The best fit [16, 37] for $y < 0.04$ was with eqn. (2) with $N^{-1} dN/d\epsilon \sim 0.4 \text{ eV}^{-1}$, in agreement with variable range hopping. For the most highly doped samples, $S(T)$ becomes more nearly linear in T , reflecting the nearly delocalized behavior consistent with the larger α^{-1} .

7. Discussion

Although the disordered Peierls insulator with variable range hopping among soliton-like states is appropriate for these samples doped with I_3^- in the range $0.01 \lesssim y \lesssim 0.05$, other samples of iodine-doped $(\text{CH})_x$ [38], ClO_4^- -doped $(\text{CH})_x$ [13] and Na-doped $(\text{CH})_x$ [14] in the same concentration range have Pauli susceptibilities (and hence $N(E_F)$) too small for the straightforward application of the VRH model. This result has led to the suggestion of the importance of collective transport by mobile spinless charged solitons [14] and interchain hopping of bipolarons [17].

We present here an alternative approach to understanding the charge conduction in these small $N(E_F)$ samples: thermal activation of charge carriers to 'high mobility' extended states [39]. As discussed above and illustrated in Fig. 2(a), the phase disordering of the Peierls insulator by the random dopant potentials and reduced crystallinity lead to a finite density of states in the gaps between the valence and conduction bands and the soliton band. The edges of the valence, soliton (condensate) and conduction bands are no longer sharp [40], the states in the band edges and band tails will be localized and the location of the mobility edge will depend on the individual dopant configuration [41]. Because the samples with small $N(E_F)$ are usually doped in a particularly gentle manner (*e.g.*, slow intercalation in *trans*-($\text{CH})_x$ and use of very thin 50 Å fibrils), it is plausible that the resulting doped polymer is much less disordered. The corresponding electronic structure is schematically as shown in Fig. 2(b), with the states at the band edges being more 'extended' than those in Fig. 2(a).

For acceptor (donor) doping, thermodynamic equilibrium requires excitation of a finite number of electrons from the occupied valence (soliton) band to the unoccupied soliton (conduction) band, which is located at an energy 2δ higher. An estimate of the number of charge carriers available at room temperature can be made using reasonable parameters for $N(E)$ and 2δ . For simplicity, we assume here that the density of states for the valence, soliton (or condensate) and conduction bands is independent of E and has the same value in each band. More detailed assumptions for $N(E)$ do not substantially change our results. Assuming [8] the density of states at the band edge is $\sim 0.2 \text{ state/eV C}$ (probably an underestimate because of the one-dimensional band structure) and, from the infrared data (*e.g.*, Fig. 1)

and magnetic data [8], that $2\delta = 0.3$ eV, the number of holes (electrons) excited at room temperature is given by

$$n(T) \approx N(E)k_B T \exp(-\delta/k_B T) \quad (4)$$

or $n(300\text{K}) = 3 \times 10^{17} \text{ cm}^{-3}$. An equal number of electrons (holes) are excited into the soliton band. A more detailed treatment of carrier excitation in thermal equilibrium is given by Conwell [42]. At this concentration of electrons or holes, the magnetic susceptibility would be below that reported [14] for small $N(E_F)$ samples. For an electrical conductivity [14] of $1 \text{ ohm}^{-1} \text{ cm}^{-1}$, and assuming that the holes (electrons) in the valence (conduction) band and the electrons (holes) in the soliton band are equally mobile, $\sigma = ne\mu$ requires a mobility of $11 \text{ cm}^2/\text{V s}$ for the excited charge carriers. This number is quite reasonable; it is even smaller than what is expected for polyacetylene. For comparison, the segregated stack charge transfer salt (tetrathiafulvalenium)-(tetracyanoquinodimethanide) [(TTF)(TCNQ)] has a mobility at 300 K of $4 \text{ cm}^2/\text{V s}$ [43], while the 300 K mobility for electrons at the bottom of the conduction band of polyparaphenylene has been calculated [44] to be $\sim 600 \text{ cm}^2/\text{V s}$. The mobility for ordered polyacetylene was expected [44] to be similar to that calculated for polyparaphenylene.

The total measured conductivity of a particular $(\text{CH})_x$ sample is then a sum of contributions from hopping at the Fermi level, σ_H , and activation of carriers to the band edges, σ_A :

$$\sigma = \sigma_A + \sigma_H \quad (5)$$

With increasing disorder, σ_H is expected to increase (through increased $N(E_F)$) while σ_A decreases (through decreasing μ). As a result the conductivity of samples doped under a variety of conditions can remain in the range 10^{-1} to $10^{+2} \text{ ohm}^{-1} \text{ cm}^{-1}$ for $0.01 \leq y \leq 0.05$ despite a widely varying $N(E_F)$.

8. Summary

In summary, the charges in nearly metallic polyacetylene are accommodated in soliton-like states. The detailed coordinated measurements of the structural, optical, magnetic and transport properties of polyacetylene doped with I_3 to $0.01 \leq y \leq 0.05$ are in quantitative agreement with charge transport via variable range hopping among soliton-like levels. It is shown how the conductivity of samples of much lower susceptibility may be accounted for by the thermal activation of carriers to extended states.

Acknowledgements

This work is funded in part by National Science Foundation Solid State Chemistry Grant No. DMR-8218021. We acknowledge useful discussions with E. M. Conwell, P. Robin, J. P. Pouget and R. Comes.

References

- 1 C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau and A. G. MacDiarmid, *Phys. Rev. Lett.*, **39** (1977) 1098.
- 2 A. J. Epstein and E. M. Conwell (eds.), *Proc. Int. Conf. on Low-Dimensional Conductors, Boulder, CO, Aug. 9 - 14, 1981*, (*Mol. Cryst. Liq. Cryst.*, **77** (1981) and **83** (1982)); see also these Proceedings.
- 3 M. J. Rice, *Phys. Lett.*, **71A** (1979) 152.
- 4 W. P. Su, J. R. Schrieffer and A. J. Heeger, *Phys. Rev. Lett.*, **42** (1979) 1698 and *Phys. Rev. B*, **22** (1980) 2099.
- 5 C. R. Fincher, Jr., M. Ozaki, A. J. Heeger and A. G. MacDiarmid, *Phys. Rev. B*, **19** (1979) 4140; E. J. Mele and M. J. Rice, *Phys. Rev. Lett.*, **45** (1980) 926.
- 6 B. Horovitz, *Solid State Commun.*, **41** (1983) 593, 729.
- 7 A. Feldblum, A. J. Heeger, T. C. Chung and A. G. MacDiarmid, *J. Chem. Phys.*, **77** (1982) 5114.
- 8 A. J. Epstein, H. Rommelmann, M. A. Druy, A. J. Heeger and A. G. MacDiarmid, *Solid State Commun.*, **38** (1981) 683.
- 9 S. Ikehata, J. Kaufer, T. Woerner, A. Pron, M. A. Druy, A. Sivak, A. J. Heeger and A. G. MacDiarmid, *Phys. Rev. Lett.*, **45** (1980) 423.
- 10 A. J. Epstein, H. Rommelmann, M. Abkowitz and H. W. Gibson, *Phys. Rev. Lett.*, **47** (1981) 1549, and *Mol. Cryst. Liq. Cryst.*, **77** (1981) 81.
- 11 N. Suzuki, M. Ozaki, S. Etemad, A. J. Heeger and A. G. MacDiarmid, *Phys. Rev. Lett.*, **45** (1980) 1209.
- 12 D. Moses, A. Denenstien, J. Chen, A. J. Heeger, P. McAndrew, T. Woerner, A. G. MacDiarmid and Y. W. Park, *Phys. Rev. B*, **25** (1982) 7652.
- 13 A. Feldblum, J. W. Kaufer, H. W. Gibson and A. J. Epstein, to be published.
- 14 T. C. Chung, F. Moraes, J. D. Flood and A. J. Heeger, to be published.
- 15 A. J. Epstein, H. W. Gibson, P. M. Chaikin, W. G. Clark and G. Gruner, *Phys. Rev. Lett.*, **45** (1980) 1730, and *Chem. Scr.*, **17** (1981) 135.
- 16 A. J. Epstein, H. Rommelmann, R. Bigelow, H. W. Gibson, D. M. Hoffman and D. B. Tanner, *Phys. Rev. Lett.*, **50** (1983) 1866.
- 17 R. R. Chance, J. L. Brédas and R. Silbey, to be published.
- 18 T. Ito, H. Shirakawa and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **12** (1974) 11; **13** (1975) 1942.
- 19 P. Robin, J. P. Pouget, R. Comes, H. W. Gibson and A. J. Epstein, *Phys. Rev. B*, **27** (1983) 3938.
- 20 A. J. Epstein, H. Rommelmann, R. Fernquist, H. W. Gibson, M. A. Druy and T. Woerner, *Polymer*, **23** (1982) 1211.
- 21 K. D. Cummings, D. B. Tanner and J. S. Miller, *Phys. Rev. B*, **24** (1981) 4142.
- 22 D. M. Hoffman, H. W. Gibson, A. J. Epstein and D. B. Tanner, *Phys. Rev. B*, **27** (1983) 1454.
- 23 D. M. Hoffman, D. B. Tanner, A. J. Epstein and H. W. Gibson, *Mol. Cryst. Liq. Cryst.*, **83** (1982) 1175.
- 24 M. Nakahara and K. Maki, *Phys. Rev. B*, **24** (1981) 1045.
- 25 S. Kivelson, unpublished results.
- 26 G. B. Blanchet, C. R. Fincher, T. C. Chung and A. J. Heeger, *Phys. Rev. Lett.*, **50** (1983) 1938.
- 27 S. Kivelson and A. J. Epstein, *Phys. Rev. B*, in press.
- 28 E. J. Mele and M. J. Rice, *Phys. Rev. B*, **23** (1981) 5397; M. J. Rice and E. J. Mele, *Chem. Scr.*, **17** (1981) 121.
- 29 N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, Clarendon Press, Oxford, 1979.
- 30 P. Robin, J. P. Pouget, R. Comes, H. W. Gibson and A. J. Epstein, *Polymer*, **24** (1983) 1558; *J. Phys. (Paris) Colloq.*, **44** (1983) C3-87.
- 31 A. J. Epstein, H. Rommelmann and H. W. Gibson, to be published.

- 32 S. L. Hsu, A. J. Signorello, G. P. Pez and R. H. Baughman, *J. Chem. Phys.*, **69** (1978) 106.
- 33 Y. Tomkiewicz, T. D. Schultz, H. B. Brom, A. R. Taranko, T. C. Clarke and G. B. Street, *Phys. Rev. B*, **24** (1981) 4348.
- 34 A. J. Epstein, H. Rommelmann, R. W. Bigelow, H. W. Gibson, D. M. Hoffman and D. B. Tanner, *Phys. Rev. Lett.*, **51** (1983) 2020.
- 35 R. Colson and P. Nagel, *J. Non-Cryst. Solids*, **35** (1980) 129.
- 36 S. Kivelson, *Phys. Rev. B*, **25** (1982) 3798.
- 37 A. J. Epstein, H. Rommelmann, R. Bigelow, H. W. Gibson, D. M. Hoffman and D. B. Tanner, *J. Phys. (Paris) Colloq.*, **44** (1983) C3-61.
- 38 A. Feldblum, R. Bigelow, H. W. Gibson, A. J. Epstein and D. B. Tanner, *Mol. Cryst. Liq. Cryst.*, in press.
- 39 A. J. Epstein, A. Feldblum, R. W. Bigelow and H. W. Gibson, to be published.
- 40 D. Vanderbilt and E. J. Mele, *Phys. Rev. B*, **22** (1980) 3939.
- 41 W. P. Su, to be published.
- 42 E. M. Conwell, to be published.
- 43 A. J. Epstein, E. M. Conwell and J. S. Miller, *Annal. N.Y. Acad. Sci.*, **313** (1978) 183.
- 44 C. Menendez and F. Guinea, *Phys. Rev. B*, **28** (1983) 2183.