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Nearly Metallic $[CH(1_3)_y]_x$ - Importance of Solitons, Crystal Order, Hopping and Band Conduction

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ABSTRACT

Polyacetylene doped in the range of one to five percent has been shown to have low Pauli susceptibility yet high electrical conductivity. Earlier studies of polyacetylene doped with iodine to these nearly metallic levels show that essentially all charges go into soliton-like states. The conductivity (σ) and thermopower (S) of many samples are in quantitative agreement with charge transport via variable range hopping among soliton-like levels. Other doped samples have a lower density of states at the Fermi level with differing $\sigma(T)$ and $S(T)$. The strong sensitivity of the density of states to disorder leads to the proposal of a parallel conduction mechanism of thermal activation of charge carriers to "high mobility" extended band states. This mechanism may dominate in less disordered samples.

I. INTRODUCTION

Polyacetylene, the simplest of the long chain polyenes, has attracted considerable experimental and theoretical interest in the last several years [1]. Experimental interest was sparked by the discovery [2] that the conductivity of polyacetylene could be increased by over eight orders of magnitude through exposure to the vapours of acceptor or donor chemical species. In its pristine state, polyacetylene is a semiconductor due to a commensurate Peierls distortion leading to alternation in bond lengths. *Trans*-$(CH)_x$ has one of two degenerate ground states depending on the phase of the bond alternation. In contrast, for the *cis*-$(CH)_x$, reversal of phase of the bond alternation (order parameter) leads to the nondegenerate *trans-cisoid* structure. The soliton model [3,4] has been successful in accounting for the transport, spectroscopic and magnetic properties [5-15] of undoped and doped polyacetylene. At high doping levels, above approximately six percent, the soliton picture breaks down and, experimentally, bandgap closure is reported along with a sizeable density of states at the Fermi level ($N(E_F)$) and high conductivities. The highly doped $(CH)_x$ system can then be viewed as a disordered quasimetallic system [5,16].

There remains a transitional regime with dopant concentration per carbon of between one and five percent ($0.01 < y < 0.05$), that needs to be understood. In this region, the magnetic susceptibility yields a density of states at the Fermi energy $N(E_F)$, substantially lower than that of metallic $(CH)_x$ ($y \sim 0.05$), yet the conductivity σ is "nearly metallic" ($10^2 \gtrsim \sigma \gtrsim 10^{-1}$ ohm^{-1} - cm^{-1}) [11,12,14,17,18]. Several different proposals have been put forward to explain the behavior in this regime, including: variable range hopping [5,16] among pinned soliton-like centers [19], collective transport by mobile spinless charged solitons [17], interchain hopping of bipolarons [20], and thermal activation of charge carriers to "high mobility" extended states [21].

In this paper we demonstrate how under some conditions, variable range hopping is the dominant transport mechanism. We then show that under slightly different conditions, other mechanisms play dominant roles. It is proposed [21] that this sensitivity of the transport mechanism to the exact details of the doping and/or isomerizing conditions reflects the central role of crystalline order in nearly metallic $(CH)_x$. Variations in the degree of disorder due to changes in doping conditions, dopants, etc., can explain the broad differences seen in the experimental data. In particular, for situations when the disorder is minimal, thermal activation of charge carriers to extended states may dominate the observed conductivity.

II. SAMPLE PREPARATION

Free standing polyacetylene films were prepared by the Shirakawa technique [22]. The films are ~90% crystalline [23] and are composed of ~500 Å diameter fibrils [24]. The samples were doped with iodine to obtain $(CH(I_3)_y)_x$ using the 'slow-doping' technique [12]. After doping, all measurements were performed on sections of the same film.

For this first part of the study, two *cis*-$(CH)_x$ films were doped to y=0.033 and y=0.048 and two *trans*-$(CH)_x$ films, isomerized at 207°C for 98 minutes, were doped to y=0.017 and y=0.042. X-ray diffraction measurements [25] of the doped *cis*-$(CH)_x$ shows the same pattern as the doped *trans*-$(CH)_x$, in agreement with earlier optical [6,10] and transport [26] studies indicating that the doping into *cis*-$(CH)_x$ results in a doping induced isomerization to doped *trans*-$(CH)_x$. For all the films studied (those of Fig. 1, see below), the x-ray measurements indicated that about one-third of the sample volume remains undoped, probably in the centers of the fibrils. Three new broad x-ray reflections are found in agreement with a model of intercalation between polyacetylene planes [27], though the coherence length perpendicular to the chain was reduced from 100 Å to only 20±5 Å [24]. Sample properties are summarized in Table I.

III. EXPERIMENTAL RESULTS

The temperature dependent conductivity of a series of iodine doped samples is shown in Fig. 1 with corresponding thermopower data given in Fig. 2. Figure 3 shows the $\sigma(T)$ for another sample of *cis*-$(CH)_x$ doped to y=0.024 with I_3^-. It is plotted both versus $T^{-1/4}$ and versus T^{-1}. The temperature dependent thermoelectric power for this sample is shown in Fig. 4.

The density of states at the Fermi level, Table I, is obtained from the susceptibility. It is substantially smaller than the metallic value for all five samples, with the initially *cis*-$(CH)_x$ samples having a higher $N(E_F)$ than the initially *trans*-$(CH)_x$ samples doped to nearly the same level. At the same time, although $N(E_F)$ for these highly conducting doped *trans*-$(CH)_x$ samples are an order of magnitude lower than the expected metallic level, they are much larger than that of an uncompensated amorphous semiconductor such as amorphous Si where $N(E_F)$ is $\sim 10^{19}$ to 10^{20} states/eV-cm^3.

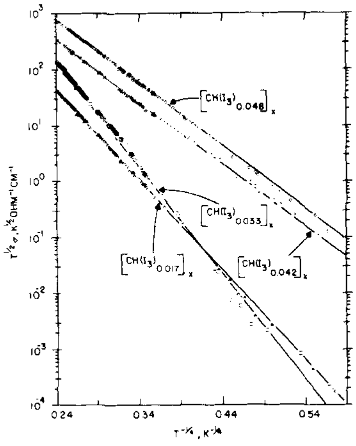

FIGURE 1. $T^{1/2}\ \sigma(T)$ vs. $T^{-1/4}$ slow-doped $[CH(I_3)_y]_x$. The solid lines are from theoretical fits described in the text (Eq. 1).

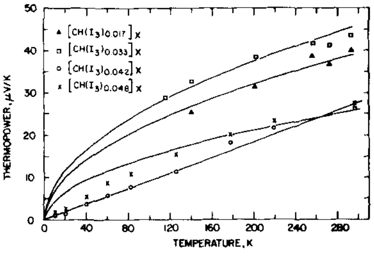

FIGURE 2. S vs. T for $[CH(I_3)_y]_x$ samples of Fig. 1. The solid lines are for theoretical fits described in the text.

TABLE 1. Summary of results for $[CH(I_3)_y]_x$

Starting $(CH)_x$	y	T_0 10^5K	$N(E_F)$ st/eVC	α^{-1} Å
trans	0.017	19	0.014	5.2
cis	0.033	29	0.045	3.1
trans	0.042	3.8	0.027	7.1
cis	0.048	4.6	0.069	4.9
cis	0.024	3.50	0.013	2.0
–	>0.05	~0.3	–	–

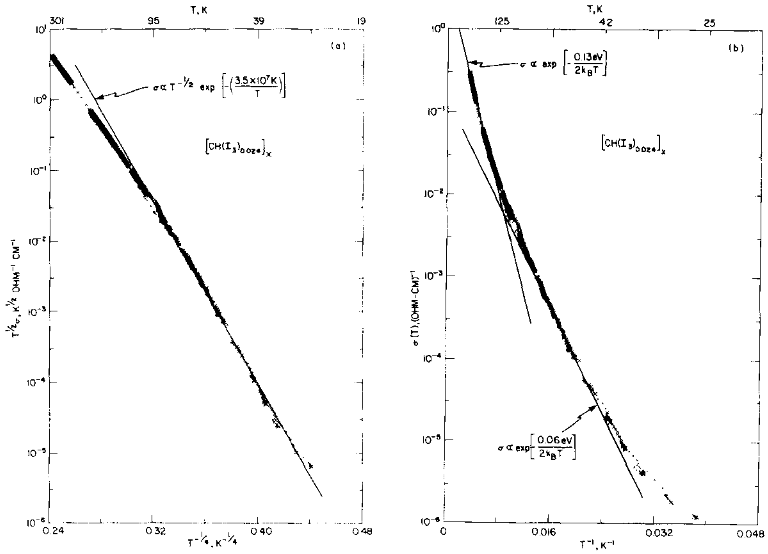

FIGURE 3. Temperature dependent conductivity of slow doped $[CH(I_3)0.024]x$. (a) $T^{1/2}\sigma(T)$ vs. $T^{-1/4}$; (b) $\sigma(T)$ vs. T^{-1}.

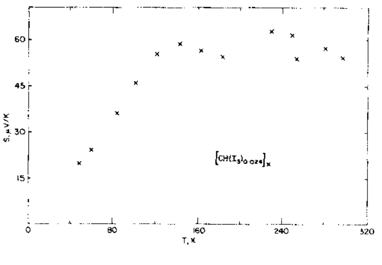

FIGURE 4. S vs. T for $[CH(I_3)_{0.024}]_x$ sample of Fig. 3.

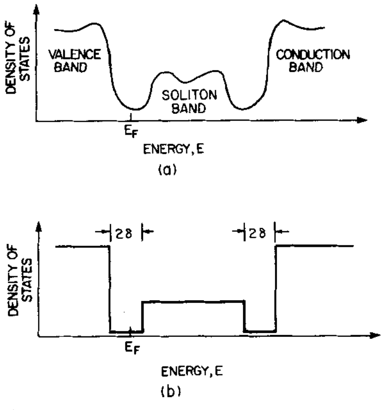

FIGURE 5. Schematic electronic structure for doped polyacetylene. The Fermi energy is shown for acceptor doping (a) Disorder strong. (b) Disorder weak. 2δ is the energy gap between the valence (conduction) band and the soliton band.

The infrared reflectance studies [19] for the samples in Figure 1 show a narrow peak in $\sigma(\omega)$ at 1370 cm^{-1} and a broad maximum at 700-900 cm^{-1}. These modes had earlier been established [7-9] as an internal mode and the pinned mode of a soliton respectively. The oscillator strength of these modes quantitatively establishes that essentially all charges introduced by the doping process go into soliton states. The optical and structural data suggest that the $N(E_F)$ is nonzero as a result of states being pulled out of the valence and soliton bands by the I_3 disorder [5], as illustrated schematically in Figure 5a.

IV. ANALYSIS

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 [28]. In this model, the conductivity can be written as:

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

where

$$T_0 = 16\alpha^3/k_B N(E_F) \qquad (2)$$

α^{-1} is the decay length of a localized state and ν_0 is a hopping attempt frequency. In Fig. 1, $\log(T^{1/2}\sigma(T))$ is plotted vs $T^{-1/4}$, with the solid line for each sample the fit to Eq. 1, with the one adjustable parameter, T_0, given in Table I. The absolute value of the conductivity as well as the functional form can be compared with the VRH formalism. Using the suggestion of Colson and Nagel [29] that ν_0 be given by $\nu_{ph}\exp(2\alpha R)$, where R is the separation between hopping sites and ν_{ph} is an optical phonon frequency ($\sim 3.6 \times 10^{13}$ sec^{-1}), there are no more adjustable parameters. The VRH conductivities can then be evaluated and are in good agreement with the experimental values [19].

The temperature dependent thermopower is an independent probe of the transport mechanism. The VRH thermopower is given by [28]

$$S^{VRH}(T) = \tfrac{1}{2}(k_B/e)k_B(T_0T)^{1/2}(N^{-1}dN/dE)$$

while for a metal [28]

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

The S(T) measurements were made on the same samples during the $\sigma(T)$ measurements. The experimental results along with fits to S^{VRH} and S^m are given in Fig. 2. Clearly for $y = 0.017$ and $y = 0.033$, the data, are fit well by the S^{VRH} with the one adjustable parameter $N^{-1}dN/dE$ indicating that N(E) is only slowly varying, consistent with the assumption of the VRH model. The *cis* doped to $y = 0.048$ shows a behavior which at low temperatures appears like $S^m(T)$ but then bends over at high temperature to be closer to $S^{VRH}(T)$. The calculated $N^{-1}dN/dE$ shows a more strongly varying N(E). For the *trans*-$(CH)_x$ doped to 0.042, the thermopower is linear with T indicating an $S^m(T)$ behavior. The conductivity data on the other hand, is of VRH form, although α^{-1} is much larger (~ 7 Å).

The optical data and magnetic data support that E_F lies in the gap between the valence and soliton bands (Fig. 5a). Here, $N(E_F)$ is nonzero as a result of states being pulled out of the valence and condensate bands by the I_3 disorder [30]. These states should retain a large soliton like character. In fact, the effective dimensionally averaged decay length of a noninteracting soliton [31], $\xi=(\xi_\perp^2\xi_\parallel)^{1/3} \approx 4$ Å is in very good agreement with the α^{-1} values of the samples of Figure 2, Table I. The larger α^{-1} of the $y = 0.042$ sample reflects the lower T_0 and is indicative of the near overlap of the soliton states at this density.

Analysis of the data for *cis*-$(CH)_x$ doped to $y=0.024$, Figs 3a and 4, provides a marked contrast. Though the sample qualitatively has a similar $\sigma(T)$ to those in Fig. 2, the T_0 obtained in fitting the data to Eq. 1 is 3.5×10^7K, much larger than T_0 for the other samples. Using the measured $N(E_F)=6.5 \times 10^{20}$ state/eV-cm^3 in Eq. 2, we obtain $\alpha^{-1} = {\sim}2$ Å. This localization length is much smaller than the three dimensionally averaged soliton length. It suggests that the charges are localized in single bonds or perhaps that the original VRH model [19] is not appropriate for this sample. Using the known parameters in Eq. 1 demonstrates that the calculated σ(300K) is several orders of magnitude smaller than the measured σ(300K). The $\sigma(T)$ for the $y = 0.024$ sample is replotted in Fig. 3b versus T^{-1}. The results show two regions, one with activation energy δ ~0.065 eV ($\sigma \propto \exp(-\delta/k_BT)$ for $T > 125$K, and the second with δ ~0.031 eV for $T < 125$K. The thermopower results in Fig. 4 are qualitatively different from those samples in Fig. 2 that are well fit by VRH. Indeed, S(T) shows a break in behavior at 125K in agreement with the activated conductivity analysis.

Samples doped more heavily [16] typically have a $\sigma(T)$ that agrees with Eq. 1 but $T_0 \sim 10^5$K. Analysis of T_0 in terms of Eq. 2 suggests that α^{-1} now is so large, that the original soliton picture [19] is no longer appropriate, in agreement with the high density of state [12] for these samples.

V. DISCUSSION

It is clear that a variety of behaviors are observed as a function of initial condition (*e.g.*, *cis* or *trans*-$(CH)_x$), doping concentration, and doping procedure. It was shown earlier [19,32,33] that variable range hopping among pinned soliton-like levels is in quantitative agreement with the structural, optical, magnetic and transport properties of many iodine doped samples. These localized states were associated with the phase disordering of the Peierls insulator due to the presence of the I_3^- dopants. Figure 5a schematically illustrates the electronic structure. However, data such as that shown in Fig. 3 as well as some ClO_4^- doped $(CH)_x$ [18] and Na^+ doped $(CH)_x$ [17] samples in the same concentration range have Pauli susceptibilities ($N(E_F)$) too small for the use of Eq. 1. This has lead to the suggestion of the importance of collective transport by mobile spinless charged solitons [17], and interchain hopping of bipolarons [20].

We note that the detailed N(E) for energies in the neighborhood of E_F will be extremely sensitive to initial doping conditions, dopant concentration and doping procedure. The measured conductivity is then better represented by

$$\sigma(T) = \int f(E,T)\,\sigma(E,T)\,dE \qquad (3)$$

where f(E,T) is the Fermi function and $\sigma(E,T)$, the conductivity per carrier of energy E, depends on both N(E) and a mobility $\mu(E,T)$.

The details of N(E) and $\mu(E,T)$ will be very sensitive to the local order in the system. For example, samples that are less disordered may be better represented by the schematic electronic structure of Fig. 5b. The phase disordering will be less pronounced, producing a lower density of states in the gaps and a higher mobility for the states at the band edges. Thermal activation of charge carriers to higher mobility "extended" states may then be expected to dominate the conductivity.

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 first that the density of states at the band edge is ~0.2 state/eV-C (probably an underestimate because of the one-dimensional band structure) and second that $2\delta \approx 0.3$ eV (consistent with the infrared and magnetic data [12,19]), then the number of holes (electrons) excited at room temperature is given by

$$n(T) \approx N(E)k_BT \exp(-\delta/k_BT) \qquad (4)$$

or $n(300K) = 3x10^{17}$ 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 [34]. At this concentration of electrons or holes, the magnetic susceptibility would be below that reported [17,18] for small $N(E_F)$ samples. For an electrical conductivity [17] of 1 $ohm^{-1}cm^{-1}$, and an assumed equal mobility for holes (electrons) in the valence (conduction) band and the electrons (holes) in the soliton band, then $\mu = \sigma/ne = 11$ cm^2/volt-sec. 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 300K of 4 cm^2/volt-sec [35], while the 300K mobility for electrons at the bottom of the conduction band of polyparaphenylene has been calculated [36] to be ~600 cm^2/volt-sec. The mobility for ordered polyacetylene was expected [36] to be similar to that calculated for polyparaphenylene.

The data of Figs 3b and 4 may be reexamined in light of Eqs 3 and 4. The experimental activation energy, δ~0.065 eV is consistent with the measured susceptibility and the schematic diagram shown in Fig. 5b. Using Eq. 4, we find $\mu(300K) \approx 0.3$ cm^2/volt-sec. This small μ suggests that conduction in this sample may be better described as thermal activation of carriers to the tails of the valence and soliton bands, and subsequent hopping of these carriers among the localized states of these band tails. The nearly flat S(T) for $T > 125K$, Fig. 4, is in contrast with the VRH behavior of the other I_3 doped samples presented here. Below 125K both the effective δ and S(T) change. Referring to Eq. 3, this may reflect the change in relative contribution of various energy states to the total conductivity as the temperature is reduced.

VI. SUMMARY

An extensive series of experiments have been carried out for samples of $(CH)_x$ doped to the range of one to five percent. It was demonstrated that variable range hopping among soliton-like sites is often the predominant transport mechanism for this regime. A generalized approach based upon the sensitivity of N(E) and $\sigma(E)$ to crystalline order was proposed and shown to be consistent with this data.

The total measured conductivity of a particular $(CH)_x$ sample is then a sum of contributions from hopping at the Fermi level, σ_H, and activation of carriers to the band edges and band tails, σ_A, Eq. 3. 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 of 10^{-1} to 10^{+2} $ohm^{-1}cm^{-1}$ for $0.01 \lesssim y \lesssim 0.5$ despite a widely varying $N(E_F)$.

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