Role of Solitons in Nearly Metallic Polyacetylene

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A correlated study of the structural, optical, magnetic, and transport properties of polyacetylene, doped with iodine to nearly the metallic doping levels, shows that essentially all charges go into solitonlike states. The measurements are in quantitative agreement with charge transport via variable-range hopping among solitonlike levels.

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Polyacetylene, (CH)$_x$, is a semiconducting polymer whose electrical conductivity ($\sigma$) may be increased to metallic levels by doping the cis or trans isomer with acceptor or donor ions. Early conductivity studies$^{1,2}$ suggested that disorder-induced localized states play an important role in the transport properties of (CH)$_x$. Many subsequent experiments$^{3-8}$ on undoped and on lightly doped trans-(CH)$_x$ demonstrated that solitons$^9$ play an important role at low doping levels. trans-(CH)$_x$ samples doped to concentrations of 0.01 to 0.05 (I$_y$)$^+$ or (AsF$_5$)$^-$ per carbon have been shown to have simultaneously magnetic susceptibility ($\chi$) much lower than that of the metallic state and high conductivity ($\sigma$)$^{2,4,5,8}$ This anomalous low-$\chi$, high-$\sigma$ behavior led to a suggestion$^{10}$ that the conduction in this regime is by unpinned charged solitons. In contrast, in a detailed model of a disordered Peierls insulator, in which the soliton centers are pinned, electronic transport was suggested to arise from a finite Fermi-level density of localized one-electron states.$^{11}$

In this Letter we report the results of structural,$^{12}$ optical, magnetic, dc conductivity, and thermopower ($S$) measurements of [CH(I$_y$)$_x$, with $0.01 < y < 0.05$. Our measurements show that essentially all excess charge on the polymer chain goes into solitonlike states, even at the highest dopant concentrations studied, [CH-(I$_y$)$_{0.05}$)$_x$. Further, at these doping levels, doped cis-(CH)$_x$ and doped trans-(CH)$_x$ have similar properties.$^{12,13}$ Our data for nearly metallic (CH)$_x$ are in quantitative agreement with a model that charge transport is via variable-range hopping among solitonlike levels in the vicinity of the Fermi level.

Our freestanding (CH)$_x$ films$^{14}$ are ~90% crystalline$^{15}$ and are composed of ~500-Å diam fibrils. The samples were doped with iodine by the "slow-doping" technique.$^4$ After doping, all measurements were performed on sections of the same film. X-ray diffraction measurements$^{12}$ of doped cis-(CH)$_x$ show the same pattern as doped trans-(CH)$_x$, with about one-third of the fibril volume$^{15}$ undoped. The x-ray reflections are in agreement with intercalation$^{16}$ of iodine between (CH)$_x$ planes. Room-temperature reflectance measurements were made between 20 and 20 000 cm$^{-1}$; Kramers-Kronig analysis gave the frequency- ($\omega$-) dependent conductivity $\sigma(\omega)$. The temperature- ($T$-) dependent $\chi$ was measured from 4 to 320 K with a calibrated$^4$ Faraday technique. $S(T)$ 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.

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 ~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 dc 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.$^5$ 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, $\gamma < 0.01$. The strength per dopant molecule is unchanged up to $\gamma = 0.048$, showing that doping proceeds through the formation of solitonlike states. If we assume that the oscillator strength per dopant molecule for transitions from the valence band to the mid-gap soliton states is also unchanged, the total oscillator strength from excitation to the soliton states is exhausted by $\sim 3000$ cm$^{-1}$; thus the 3000-
cm$^{-1}$ peak must result from both transitions to the soliton levels and across a partially closed band gap.

The $\chi(T)$ is a sum of $\chi^{\text{Curie}}$ and $\chi^{\text{Pauli}} = 2\mu_B^2 N(E_F)$, where $\mu_B$ is the Bohr magneton and $N(E_F)$ is the density of states at the Fermi level. The density of Curie spins decreased dramatically upon doping, in agreement with the soliton mechanism, for (CH)$_n$ with zero band gap is expected to be $\sim 0.16-0.20$ states/eV C atom. Table I shows that $N(E_F)$ for the two initially trans doped samples is nearly as low as that reported earlier for low-susceptibility, slow-doped samples. The initially cis-(CH)$_n$ samples exhibit a larger $N(E_F)$ than trans-(CH)$_n$ samples doped to the same level. Though $N(E_F)$ for the highly conducting doped trans sample is an order of magnitude lower than the expected metallic level, it is much larger than that of an uncompensated amorphous semiconductor such as amorphous Si where $N(E_F) \sim 10^{19}$ to $10^{20}$ states/eV cm$^{-2}$.

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

$$\sigma(T) = \left[0.39\left(N(E_F)/\alpha \kappa B T\right)^{1/2} \nu_0 \nu^2\right] \times \exp\left[-\left(T_0/T\right)^{1/4}\right],$$

(1)

where $T_0 = 16\alpha^3/k_B N(E_F)$, $\alpha^{-1}$ is the decay length of a localized state, and $\nu_0$ is a hopping attempt frequency. The fit of $\sigma(T)$ by the functional form $T^{-1/2} \exp\left[-(T_0/T)^{1/4}\right]$ is shown as a solid line for each sample in Fig. 2, with the one adjustable parameter, $T_0$, given in Table I. Fits with other behaviors, e.g., $\exp\left[-(T_0/T)^m\right]$ with $m$ other than $1/4$, were not as good. Using $N(E_F)$ and $T_0$ we find $\alpha^{-1} = 5$ Å, varying slightly from sample to sample (see Table I).

With $N(E_F)$ and $\alpha^{-1}$ taken from Table I, plus the usual assumption that $\nu_0$ is an optical phonon frequency ($\nu_0 = \nu_{370} = 3.6 \times 10^{13}$ sec$^{-1}$), Eq. (1) is evaluated at 295 K and given in Table I as $\sigma_M$.

<table>
<thead>
<tr>
<th>Starting (CH)$_n$</th>
<th>$N(\epsilon_F)$ (st/eV C)</th>
<th>$N(\epsilon_F)$ (10$^{20}$ st/eV cm$^3$)</th>
<th>$\sigma(295 \text{ K})$ (Ω$^{-1}$ cm$^{-1}$)</th>
<th>$T_0$ (10$^3$ K)</th>
<th>$\alpha^{-1}$ (Å)</th>
<th>$\sigma_M$ (Ω$^{-1}$ cm$^{-1}$)</th>
<th>$\sigma_{CN}$ (Ω$^{-1}$ cm$^{-1}$)</th>
<th>$R$ (Å)</th>
<th>$N^{-1}dN/d\epsilon$ (eV$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans</td>
<td>0.017</td>
<td>0.014</td>
<td>7.0</td>
<td>2.5</td>
<td>19</td>
<td>5.2</td>
<td>0.0027</td>
<td>1.9</td>
<td>0.046</td>
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<tr>
<td>cis</td>
<td>0.033</td>
<td>0.045</td>
<td>23</td>
<td>8</td>
<td>29</td>
<td>3.1</td>
<td>0.0014</td>
<td>9.1</td>
<td>0.42</td>
</tr>
<tr>
<td>trans</td>
<td>0.042</td>
<td>0.027</td>
<td>14</td>
<td>20</td>
<td>3.8</td>
<td>7.1</td>
<td>0.088</td>
<td>3.1</td>
<td>0.60</td>
</tr>
<tr>
<td>cis</td>
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<td>0.069</td>
<td>35</td>
<td>50</td>
<td>4.6</td>
<td>4.9</td>
<td>0.088</td>
<td>12</td>
<td>1.9</td>
</tr>
</tbody>
</table>

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FIG. 2. $T^{1/3} \sigma(T)/\sigma(295 \text{ K})$ vs $T^{-1/4}$ for slow-doped \([\text{CH}_2\text{I}_9]_x\). The solid lines are from theoretical fits described in the text.

As usually occurs, the calculated $\sigma$ is a factor of $10^2$ to $10^3$ low. Colson and Nagel have suggested\(^{15}\) that $\nu_0 = \nu_0' \exp(2\alpha R)$, where $R$ is the separation between hopping sites. The modified $\sigma(295$ K) calculated with use of Eq. (1) with this $\nu_0$, $\sigma_{\text{CN}}$, is in Table I. These values are in good agreement with experiment.

$S(T)$ measured during the $\sigma(T)$ study is shown in Fig. 3. For VRH,\(^{18}\)

$$S_{\text{VRH}}^{k}(T) = \frac{1}{2}(k_{B}/e)\xi(T)^{1/2}(N^{-1}dN/d\epsilon)$$

(2)

while for a metal,\(^{18}\)

$$S^{*}(T) = (2\pi^2/3)(k_{B}/e)\xi(T)(N^{-1}dN/d\epsilon).$$

(3)

The best fit by these expressions (for the one adjustable parameter $N^{-1}dN/d\epsilon$) is shown in Fig. 3 by solid lines. Equation (2) gives a good fit for $y = 0.017$ and $0.033$ with $N^{-1}dN/d\epsilon = 0.4 \text{ eV}^{-1}$, that is, $N(\epsilon)$ is slowly varying. For $y = 0.048$, $S(T)$ is intermediate between VRH and delocalized (metallic) behavior. From Eq. (2), $N^{-1}dN/d\epsilon = 0.6 \text{ eV}^{-1}$. For $y = 0.042$, $S(T) \propto T$ reflecting nearly delocalized behavior, consistent with the large $\alpha^{-1}$. With Eq. (3), $N^{-1}dN/d\epsilon = 1.9 \text{ eV}^{-1}$.

From the optical data presented above, it is 

suggested that the high density of states in the reduced valence-to-conduction band gap may be associated directly with an empty condensate band which persists\(^{11}\) at these high dopant concentrations. $E_F$ then lies in the gap between the valence band and the condensate band. 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. These states should retain a large solitonlike character. In fact, the effective dimensionally averaged decay length of a noninteraction soliton, $\xi = (\xi_x^2 \xi_z^2)^{1/2}$, $3.6 \text{ Å}^{14,20}$ is in very good agreement with the $\alpha^{-1}$ values in Table I. The larger $\alpha^{-1}$ of $7.1 \text{ Å}$ found for the $y = 0.042$ sample reflects the lower $T_0$ and is indicative of the near overlap of the solitonlike states at this high density. In this sample VRH must be applied with care, as the concentration may approach the transition\(^{11,15,21}\) to delocalization and formation of a metallic state. It is important to consider the applicability of alternative models for nearly metallic \([\text{CH}_2\text{I}_9]_x\). However, detailed predictions of $\sigma(T)$, $S(T)$, etc., are currently unavailable for concepts such as the depinning of the charged solitons to form a soliton liquid.\(^{10}\)

In summary, analysis of $\sigma(\omega)$, $\sigma(T)$, and $\chi(T)$ is in agreement with VRH among solitonlike sites for the regime studied. Hence, \textit{trans-}\([\text{CH}_2\text{I}_9]_x\) has three distinct regions for charge transport: (a) $\gamma < 0.001$ is well fitted by interisoliton electron hopping\(^{4,20}\); (b) $0.01 < \gamma < 0.05$, VRH\(^{14,2,11,18}\); (c) $\gamma > 0.05$, disordered metallic behavior.\(^{11}\)

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