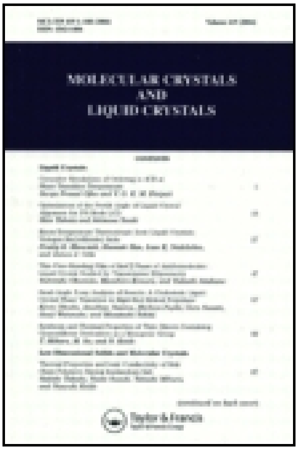

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Density of States and Hopping Conductivity in Nearly Metallic Polyacetylene

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DENSITY OF STATES AND HOPPING CONDUCTIVITY IN NEARLY METALLIC POLYACETYLENE

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ABSTRACT Nearly metallic polyacetylene doped to the level, y, of ~0.01 to 0.05 acceptors or donors per carbon has a high, "nearly metallic" conductivity yet susceptibility very much less than the metallic value. We present here the results of an extensive study of the transport properties of this regime coordinated with magnetic, optical and structural experiments, using ClO_4^- and I_3^- doped $(CH)_x$. We conclude that for all samples studied, the charge conduction is via three dimensional variable range hopping among states near the Fermi level, ϵ_F. The variation of the density of states, $N(\epsilon)$, near ϵ_F, is measured using susceptibility, and shown to determine the detailed transport behavior. Our results are in agreement with the transition to an incommensurate Peierls semiconductor for higher doping levels, with disorder leading to a gapless condition.

I. INTRODUCTION

The report that the electrical conductivity (σ) of the semiconducting polymer polyacetylene, $(CH)_x$, may be increased to nearly metallic levels by doping the *cis* or *trans* isomer with acceptor or donor ions led to intense study of this system[1]. In many experiments[1] on undoped and lightly doped *trans*-$(CH)_x$, it was demonstrated that solitons[2,3] play an important role. Their continued presence has been verified to concentrations of $y \approx 0.05$.[4] Despite the similarity in $\sigma(y)$ for each dopant, the variation of susceptibility (χ) with y changes significantly with dopant and doping condition[4,5,6], Fig. 1.

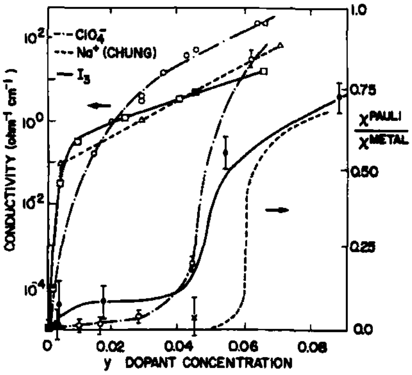

FIGURE 1. σ_{DC} (300K) vs. y (left hand scale) and χ^P vs. y (right hand scale). Data for $(I_3)^-$, ClO_4^- and Na^+ are from Refs. 4, 5, and 6 respectively.

It was early on suggested[7] that in a detailed model of a disordered Peierls insulator, in which soliton centers were pinned, electronic transport arose from the finite Fermi level density of localized one-electron states. A later correlated experimental study[4] of the structural[8], optical, magnetic, and transport properties of I_3^- doped $(CH)_x$ in the range of $0.01 < y < 0.05$ was in quantitative agreement with charge transport via three-dimensional variable hopping (VRH) among pinned soliton-like levels. However, study of Na doped $(CH)_x$[6] showed that the density of states (derived from susceptibility) in this material was too small for VRH[2,9] to account for the magnitude and temperature dependence of $\sigma(T)$ of these samples. It was proposed that the charge conduction in this nearly metallic regime was by charged soliton diffusion[6], melting of the soliton glass to form a soliton liquid[10], interchain hopping of charged soliton pairs (bipolarons)[11] and/or activation of charged carriers to high mobility conduction (or valence) band edge states[12,13].

We have carried out an extensive study of the transport properties of polyacetylene doped with ClO_4^- and I_3^- correlated with the magnetic, structural[14] and optical[15] properties of the same samples. Through ClO_4^- electrochemical doping of 200 Å fiber diameter films prepared by the Shirakawa technique several sets of "standard" samples were prepared. Pieces of the same film were used for transport, magnetic, structural and optical studies. The density of states at the Fermi energy ($N(\epsilon_F)$) was found to vary both in value and curvature. Several samples were prepared with susceptibility so low (less than 0.008 χ^{Metal}) that the earlier[4] VRH formalism could not be successfully applied, in accord with results for Na^+ doped[6] $(CH)_x$. We show here that when the probable curvature in $N(\epsilon)$ near E_F is taken into account, a modified VRH in the presence of an energy dependent $N(\epsilon)$ can readily account for the experimental results.

II. EXPERIMENTAL APPROACH

Polyacetylene films were synthesized using the Shirakawa catalyst[16] by techniques detailed elsewhere[17]. Electrochemical doping was carried out using $LiClO_4$ electrolyte in acetonitrile[5]. The samples were annealed at room temperature in argon (< 0.8 ppm O_2) or in vacuo for several weeks before beginning experimental studies. The samples were then stored at ~200 K between experiments in order to prevent redistribution of dopants or degradation.

The density of states was measured using the temperature dependent $\chi(T)$ obtained with a sensitive Faraday balance [4]. The Pauli susceptibility for $N(\epsilon) = \rho_0 + \frac{1}{2}\rho_2 (E-\epsilon_F)^2 + \ldots$ is

$$\chi^P = 2\mu_B^2 [\rho_0 + \frac{\pi^2}{6} (K_BT)^2 \rho_2 + \ldots] \qquad (1)$$

where μ_B is the Bohr magneton, and ρ_0 and ρ_2 are constants. χ^P may be evaluated in convenient limits. For a 10 eV wide half filled one-dimensional tight binding band (with no Coulomb interaction), i.e., metallic polyacetylene, $\rho_0 = 0.13$ st/eV-C atom and $\chi^P = 3.9\times10^{-6}$ emu/mole. We define this value of χ^P as χ^{Metal} and normalize all subsequent results to it. In contrast, if there is a small gap of 0.2 eV at ϵ_F with $N(\epsilon)$ varying as $\frac{1}{2}\rho_2 (\epsilon - \epsilon_F)^2$ from a value of zero at ϵ_F to a value of 0.13 st/eV-c atom at $|\epsilon - \epsilon_F| = 0.1$ eV, then $\rho_2 = 25$ st/(eV)^3-C atom. Using Eq. 1, this N(E) leads to a T-dependent χ^P with χ^P (300K) = 0.2 χ^{Metal} The four-probe $\sigma(T)$ and thermopower (S(T)) were obtained during the same experiment.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows some typical experimental results for $\chi(T)$ of ClO_4 electrochemically doped samples. A Curie-like ($\chi \propto T^{-1}$) contribution to χ equivalent to ~150 ppm carbon spins was observed for all samples and subtracted from the data. These numbers of spins may be intrinsic due to the presence of an effective Hubbard U (Coulomb repulsion) of ~50-100K. This reduced U is consistent with the measured delocalization lengths at ϵ_F (see below). For y = 0.015, χ^P < 0.008 χ^{Metal}, while for y = 0.030, $\chi^P \approx 0.05$ χ^{Metal} for T < 200K, increasing with T at higher temperatures. More highly doped samples showed larger and more temperature dependent χ^P until the y > 0.06, when χ became large (~0.8 χ^{Metal}) but nearly T-independent. Figure 3 shows the schematic densities of states corresponding to these samples derived from this experimental $\chi^P(T)$. The results are in agreement with the optical studies[15] and the increasing disorder with doping[14]. The y = 0.061 sample corresponds to a sample beyond the commensurate to incommensurate transition[15].

In light of experimental $N(\epsilon)$, we compare the predictions of the various conduction models with the transport results for the individual samples. Table I summarizes the predictions assuming the density of states schematically shown in Fig. 3. The full gap (valence to conduction band) is 2Δ, the gap between the valence (or conduction) band and soliton band is 2δ. The Fermi energy for acceptors (donors) lies between the valence (conduction) and soliton bands. Disorder[4,8,14] leads to a finite density of localized states in the gaps 2δ. The

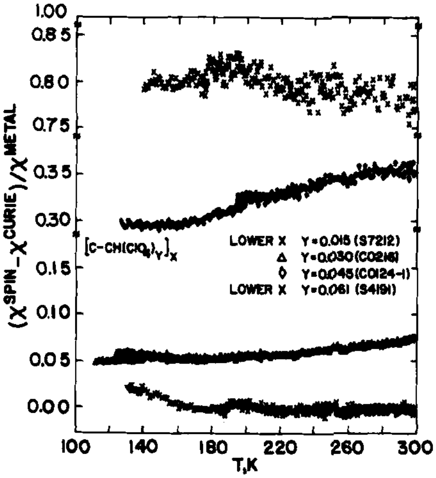

FIGURE 2. χ^P vs. T for $[CH(ClO_4)_y]_x$. See text.

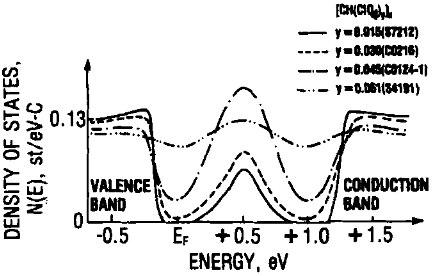

FIGURE 3. Schematic diagram of electronic structure of $[CH(ClO_4)_y]_x$ derived from χ^P (T), Fig. 2.

density of states in the vicinity of ε_F can then be expanded in powers of ε (defining $\varepsilon_F = 0$) as $N(\varepsilon) = \rho_0 + \rho_1\varepsilon + \frac{1}{2}\rho_2\varepsilon^2 + \ldots$ The results for VRH for nearly constant $N(\varepsilon)$ ($\rho_1 \approx \rho_2 \approx 0$) are well known[9], Table I. Kivelson has recently extended[18] this model to include the more general $N(\varepsilon)$ The results for $\rho_0 = \rho_1 = 0$ are included in Table I. Also shown are simple predictions for a semiconductor model[12,13]. Here ξ is the (three-dimensionally averaged) localization length, k_B is Boltzmann's constant, ν_0 is an attempt frequency which we take as ~$3\text{x}10^{13}\text{sec}^{-1}$[4], e the electron charge, S the thermoelectric power, μ the mobility of band edge states, P_0 ~ 16[8], P_2 ~ 18[16], and T_0, C_0 and C_2 are constants.

The correlated transport results for more than a dozen samples were obtained for 0.01 < y < 0.05. In general, all of the samples were self consistently analyzed in terms of VRH and the measured N(E). Though high mobility band edge states are predicted[19] to be present, in none of the samples studied was a significant Hall voltage (to 8.5 tesla) (which would signify dominance of charge conduction via activation of carriers to these band edge states) observed. As the mobility in these states is sensitive to disorder, such a mechanism may apply to more ordered specimens, e.g., Na doped material[20].

Three representative examples are discussed here: $(CH)_x$ doped with ClO_4^- to $y=0.015$, with I_3^- to $y=0.017$[4], and with ClO_4^- to $y=0.045$. We conclude that VRH dominates in all three cases with $N(\epsilon) \propto \frac{1}{2}\rho_2\epsilon^2$, ρ_0, and $\rho_0 + \frac{1}{2}\rho_2\epsilon^2$ respectively. The starting material, dopant and doping procedure influence the final $N(\epsilon)$ for each sample, and hence the detailed transport behavior.

The $\chi^P(T)$ of $[CH(ClO_4)_{0.015}]_x$ is shown in Fig. 2. $\chi^P(300K) < 0.008\ \chi^M$, with $\sigma(300K) = 0.04\ (ohm.cm)^{-1}$. If a constant $N(\epsilon)$ is assumed, then $\rho_0 < 0.001$ st/eV-C. The $\sigma(T)$ may be fit to $\sigma_0 \exp(-(T_0/T)^{1/4})$ for VRH with $T_0 = 1.4 \times 10^8$K. However, using ρ_0 and T_0, the calculated value of σ_0 is five orders of magnitude too small to fit the experimental σ. In addition, S(T) is ~ constant at 90 μV/K for T > 150K, in contradiction to the predicted[9] $T^{1/2}$ behavior. If alternatively we assume a contribution to $N(\epsilon)$ proportional to ϵ^2, then Eq. 1 gives $\rho_2 < 3\ st/(eV)^3$ C. This value implies a smooth increase from $N(\epsilon) = 0$ at ϵ_F to $N(\epsilon) = N^{Metal}$ at 0.3 eV below ϵ_F (see Fig. 2) in agreement with optical absorption measurements on lightly doped material[4,15]. The fit of $\sigma(T)$ to $\exp(-(T_0/T)^{1/2}]$ is shown in Fig. 4, with $T_0 = 2.8 \times 10^4$K. Utilizing the ρ_2 noted above, we obtain $\xi \sim 14$ Å, suggesting that the average localized states participating in the three dimensional hopping process are several times the size of a soliton. This is in agreement with the structural studies of these ClO_4 doped samples which show clusters of ~four ClO_4 units between layers of polyacetylene chains[14]. Using these values in the prefactor, σ_0, $\sigma_{calc} \approx \sigma_{exp}$. In addition, the measured S(T) is in agreement with expectations of this model, as are the small $\sigma(E)$ and $\sigma(H)$ [5]. A similar analysis may apply to Na^+ doped $(CH)_x$[6] where $\chi^P < 0.01\ \chi^{Metal}$.

Comparison to the proposed models of charged soliton conduction[6,10,11] is difficult in the absence of detailed predictions. The lack of shift of the pinning frequency (900 cm^{-1}) at these doping levels as compared with very lightly doped $(CH)_x$ [4,15] supports the conclusion that few, if any, of the charged solitons are mobile even at room temperature. (The agreement of the infrared conductivity with the dc σ at room temperature is in accord with predictions of VRH [21].) Even if it is assumed that all of the charged solitons are diffusing, the Einstein relation yields a diffusion coefficient for charged solitons at 300K, $D_{||}^+$ (300K), of $\sim 10^{-4}$ cm^2/sec, nearly the same as that for neutral solitons ($D_{||}^0$) in the absence of Coulomb interaction and disorder [1]. Further, $D_{||}^0$ for the neutral solitons in undoped *trans*-$(CH)_x$ is ~constant from 200K to 300K[1], while $D_{||}^+$ continues to increase above $D_{||}^0$ at higher temperatures.

The $(CH)_x$ doped to $y=0.017$ I_3^-, though nearly identical in y, has significantly different behavior[4]. The $\chi^P \approx 0.11\ \chi^{Metal}$ and is weakly T-

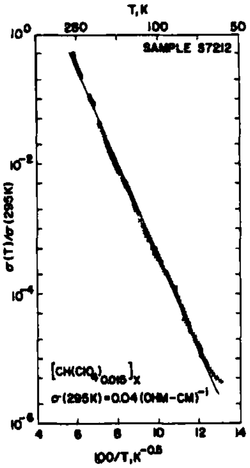

FIGURE 4. $\sigma(T)/\sigma(295K)$ vs. $T^{-1/2}$ for $[CH(ClO_4)_{0.015}]_x$

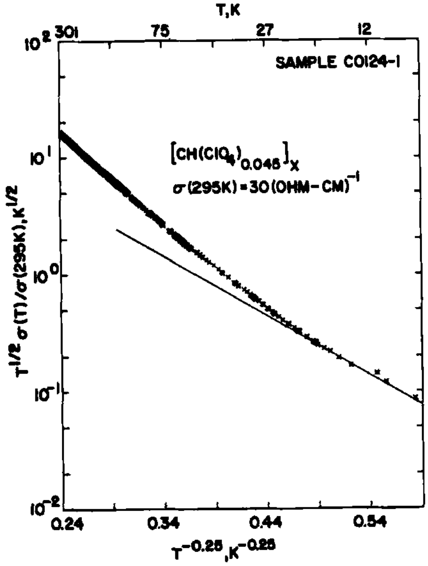

FIGURE 5. $T^{1/2}$ $\sigma(T)/\sigma(295K)$ vs. $T^{-1/4}$ for $[CH(ClO_4)_{0.045}]_x$.

dependent [4,22], implying $N(\varepsilon)=\rho_0=0.014$ st/eV-C. The $\sigma(T,\omega)$ and S(T) data quantitatively fit three-dimensional VRH with a nearly constant N(E). Analysis of the S(T) [4,22] yields $dN(\varepsilon)/d\varepsilon=0.5N(\varepsilon)/eV$, i.e., self consistently slowly varying $N(\varepsilon)$.

A final example is given by a sample of $[CH(ClO_4)_{0.045}]_x$. As seen in Fig. 2, χ^P is both sizable at low temperatures and strongly T dependent, with $\chi^P(T < 30K) \approx 0.25\ \chi^{Metal}$ and $\chi^P\ (300K) \approx 0.44\ \chi^{Metal}$, leading to estimate of $\rho_0=0.032$ st/eV-C and $\rho_2 \approx 8.2$ st/(eV)^3 C, as suggested schematically in Figure 3. This sample is thus near the commensurate to incommensurate transition (at ~0.05) and has significant number of states pulled into the gap by disorder. Figure 5 displays the $T^{1/2}$ σ vs. $T^{-0.25}$ for this sample. A fit at low temperatures gives $T_0=2.3\times10^4$ K. Using Table I, this leads to $\xi=19$ Å and quantitative agreement with the magnitude of σ. Above 50K, $\sigma(T)$ deviates from the simple $T^{0.25}$ law as expected [18] for this small T_0 and energy dependent $N(\varepsilon)$. The S(T), σ(E) and σ(H) are in agreement with VRH [5].

IV. SUMMARY

In sum, we have investigated the nearly metallic regime of $(CH)_x$ doped with acceptors. The detailed $N(\varepsilon)$ was found to vary in absolute value and energy dependence with dopant, doping conditions and concentration. Together with structural studies, this supports that the detailed $N(\varepsilon)$ is determined by the disordering of the Peierls semiconductor. We have measured the transport parameters $[\sigma(T,H,E,\omega)]$ of these samples and shown that they can be self consistently understood in terms of three dimensional variable range hopping among the independently determined density of (localized) states near the Fermi energy. The inclusion of the structure of N(E) into the VRH formalism leads to qualitative changes in the predicted charge transport parameters, and quantitative agreement with experiment.

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TABLE I. Transport Properties for VRH for Constant and Quadratic N(E), and Activation to "High Mobility" Extended States (ES)

	VRH $N(E) = \rho_o$	VRH $N(E) = \frac{1}{2}\rho_2\varepsilon^2$	ES $E_g = 2\delta$
σ_{DC}	$\sigma_o \exp\left[-\left(\frac{T_o}{T}\right)^{1/4}\right]$	$\sigma_o \exp\left[-\left(\frac{T_o}{T}\right)^{1/2}\right]$	$\sigma_o \exp\left[-\left(\frac{T_o}{T}\right)\right]$
T_o	$\sim \frac{P_o}{k_B\rho_o\xi^3}$	$\sim \left[\frac{360\ P_2}{k_B{}^3\rho_2\xi^3\pi}\right]^{1/3}$	δ
σ_o	$0.4\left[\frac{\rho_o\xi}{k_BT}\right]^{1/2} \nu_o e^2$	$40\frac{T_o}{\xi}\ \nu_o\ e^2$	$e\mu$
S	$\frac{1}{2}\frac{k_B{}^2}{e}(T_oT)^{1/2}\frac{d\ln N(\varepsilon)}{d\varepsilon}$	$\sim \frac{k_B{}^2}{e}\frac{d\ln N(\varepsilon)}{d\varepsilon}$	$\propto T^{-1}$
$\sigma(E)$	$\propto (1 + C_oE^2)$	$\propto (1 + C_2E^2)$	—
$\sigma(H)$	SMALL	SMALL	$\propto \mu H^2$
Hall Voltage	SMALL	SMALL	$\propto H$

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