Frequency and Electric Field Dependence of the Conductivity of Metallic Polyacetylene

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The temperature (T), frequency (f), and electric field (E) dependent conductivity (σ) of iodine-doped polyacetylene is reported for the concentration regime which encompasses the metal-insulator transition. No f dependence was observed for $f < 500$ MHz. The resistance varied logarithmically with E, while $\sigma \sim \ln T$ and $\sigma \sim \exp[-(T_A/T)^{0.25}]$ were observed. This $\sigma(T, E, f)$ is inconsistent with simple models of metallic regions separated by large barriers and suggests that the known strong disorder plays a dominant role.

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Recent experiments on polyacetylene $(CH)_x$ have shown dramatic increases in the electrical conductivity (σ) upon doping with a variety of strong donors and acceptors.[1,2] These experiments suggest that the material passes from an insulating to a metallic state. However, no sharp metal-insulator transition is observed and in all samples the resistance increases as temperature is decreased in the liquid-helium region and below.[1-5] The usual interpretation of this apparent conflict is that the material consists of metallic regions separated by insulating barriers which dominate the resistance. These barriers are thought to be interfiber contacts or undoped regions, resulting in a picture of small metallic particles in a dielectric medium.[3-5] Both interpretations lead to decreasing σ with decreasing temperature with a nonexponential behavior due to randomness. Such models predict strongly frequency-dependent conductivity[6] and strong nonlinearities in current-voltage characteristics.[4,7]

In this Letter we present measurements of the frequency (f), electric-field (E), and temperature (T) dependent conductivity of $(CH)_x$ doped with iodine in the doping regime which encompasses the "insulator-metal" transition. Our results indicate that the carriers are localized in states between which there is a *fast* transfer rate rather than large barriers. This indicates that disorder plays a fundamental role at low temperatures. Specifically, the observed behaviors resemble recent experiments on the effects of localization in reduced dimensions and suggest that the gradual transition is from a disordered semiconductor (i.e., bandtailing in the gap) to a dirty metal.

Iodine-doped *cis* and mixed *cis-trans* polyacetylene films yielded very similar results. The $\sigma(f)$ was measured from dc through 500 MHz for samples having room-temperature conductivities (iodine concentrations) 0.003 (<0.01), 0.03 (0.01), 0.3 (0.025), 3 (0.12), and 20 (0.20) $(\Omega\ \mathrm{cm})^{-1}$. We measured $R(T)$ down to 10 K in the highly doped $(CH)_x$, down to approximately 150 K in intermediately doped samples, and at room temperature in the lightly doped samples. Within the measuring accuracy (2%), $\sigma(f) = \sigma_{dc}$, in accord with recent microwave σ studies.[8] The small observed differences at 10 GHz at these concentrations may be due to uncertainties in the evaluation of the microwave conductivity. In addition, within our measuring accuracy, we have found no evidence for a capacitive component; i.e., doped $(CH)_x$ can be represented by a frequency-independent resistance with no dispersion up to $f = 500$ MHz. The dependence of σ on E was measured utilizing both two- and four-probe pulsed (~10 μsec) measurement techniques. Frequent checks were made to assure that no heating occurred.

Resistance measurements as a function of E and T are shown in Fig. 1 for a sample of $\sigma(295\ \mathrm{K}) = 3\ (\Omega\ \mathrm{cm})^{-1}$. The resistance of each sample was independent of field for very low electric fields (≤ 10 mV/cm). Upon increasing E, the apparent resistance of the samples decreased slowly, approximately as

$$R = R(E_0, T)[1 - S_v \ln(E/E_0)] \quad (1)$$

with E_0 arbitrary and S_v the logarithmic slope. This effect was quite reproducible and was observed both in two- and four-probe measurements, in samples from different starting materials, in samples of room temperature conductivities of 3 and 20 $(\Omega\ \mathrm{cm})^{-1}$, as well as being measured in-

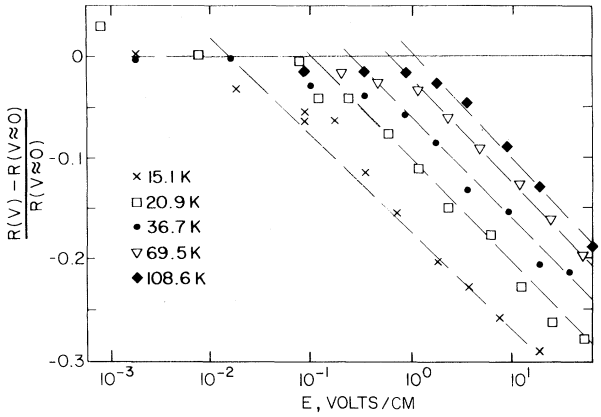

FIG. 1. Deviation from Ohmic (low field) resistance as a function of applied field across a 0.15-cm sample (voltage probe spacing in four-probe measurement). Note $\sigma(300\ \mathrm{K}) = 3\ (\Omega\ \mathrm{cm})^{-1}$. For $\sigma(T)$, see Fig. 3.

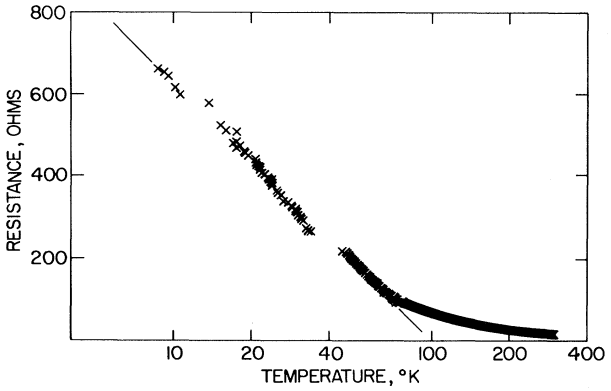

FIG. 2. $R(T)$ (four probe) for a sample of $(CHI_{0.17})_x$ with field behavior similar to Fig. 1. $R(295\ \mathrm{K}) = 15\ \Omega$ and $\sigma(295\ \mathrm{K}) = 5\ (\Omega\ \mathrm{cm})^{-1}$.

dependently in two different laboratories. Samples with resistances of 500 to 500 000 Ω exhibited this behavior. As can be seen in Fig. 1 for a $\sigma(295\ \mathrm{K}) \sim 3\ (\Omega\ \mathrm{cm})^{-1}$ sample the slope, S_v, of the voltage-dependent resistance is nearly temperature independent, whereas the field for its onset increased with increasing temperature.

The (low) electric-field–independent conductivity was measured as a function of temperature for samples of $\sigma(295\ \mathrm{K}) \sim 3\ (\Omega\ \mathrm{cm})^{-1}$ that showed the logarithmic field dependence. Figures 2 and 3 illustrate the two distinct behaviors that were observed (even for samples cut from the same doped film) for the highest doped samples ($y > 0.1$):

$$R = R(T_0, E)[1 - S_T \ln(T/T_0)] \quad (2)$$

and

$$R = R(T_A)\exp[(T_A/T)^{1/4}]. \quad (3)$$

Here T_0, T_A, and S_T are constants. For more lightly doped samples, $R(T)$ follows Eq. (3), with T_A increasing for decreasing y.

Several proposals have been put forth to explain the mechanism of the insulator-metal transition. These include: (a) Mott transition among localized carriers[1]; (b) formation of spinless charged solitons upon light doping; with increased doping these solitons overlap and drive the polymeric bond alternation to zero, rendering $(CH)_x$ a metal[9]; (c) inhomogeneous distribution of the dopant throughout the fiber, forming small metallic particles separated by undoped polymer; that is, with increased doping, the insulator-metal transition occurs at the percolation limit.[3,4] The first two mechanisms predict a sharp insulator-metal transition (as observed by conductivity) and are inconsistent with our results and previous results unless it is assumed that inhomogeneities or barriers between $(CH)_x$ fibrils mask the intrinsic behavior and localize the electrons in metallic regions separated by sizeable barriers. The last mechanism treats the inhomogeneities more directly.

A common feature of composite metal-insulator systems is a decreasing low-field dc conductivity with decreasing temperature[4,7] due to the increased role of the barriers at low temperatures. Various expressions were proposed to account for $\sigma(T)$ and they are all in qualitative agreement with experiments performed in doped $(CH)_x$.[3-5] Another feature is the existence of strongly field[4,7]

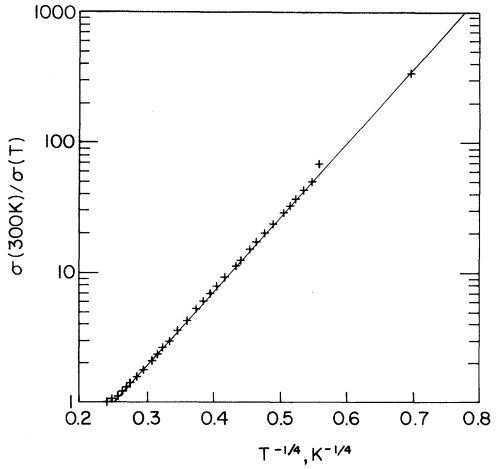

FIG. 3. Ohmic $\sigma(300\ \mathrm{K})/\sigma(T)$ for sample $[(CHI_{0.12})_x]$ whose $\sigma(E)$ is displayed in Fig. 1.

and frequency[6,10] dependent σ.

The field dependence results from the concentration of voltage drop across the highly resistive barriers. It is observed both in metal-dielectric composites[7] and in anisotropic conductors with random bariers.[11] The frequency dependence results from the capacitive coupling between the highly conducting regions and is typically of the form $\sigma \sim \omega^k$ and $\epsilon \sim \omega^{1-\alpha}$. Under the assumption that $\sigma \sim 10^2$ $(\Omega\ \mathrm{cm})^{-1}$ for the conducting and 10^{-3} $(\Omega\ \mathrm{cm})^{-1}$ for the nonconducting regions, with the volume fraction of conducting regions $\frac{1}{3}$ of the volume, the effective medium theory of Springett[6] predicts that the frequency dependence emerges at 10^2 Hz in accordance with experiments on granular metals.[12] The dependence of σ on E should, within these barrier models, follow the fluctuation-induced tunneling theories of Sheng.[4,7] With the assumption of large metal particles, fit[4] of the tunneling theory to $\sigma(T)$ of $(CHI_{0.22})_x$ predicts an exponential behavior of σ on E for fields less than 10^6 V/cm. For small metal particles, the exponential behavior of σ on E^{-1} is predicted.[7] Our experimental results are in marked contrast to such behaviors.

As an alternative explanation of $\sigma(T, E, f)$ we suggest that disorder localization of the wave functions plays a dominant role, especially at low temperatures. Scanning electron microscopic studies[13] demonstrate that both the *cis* and *trans* isomers of $(CH)_x$ are in the form of fibers of ~200 Å diameter, while x-ray studies[14] show the polymer to be only partly crystalline. In addition, microprobe analysis has demonstrated[15] inhomogeneous doping, at least on the scale of 10 μm, increasing the disorder within the $(CH)_x$ fibrils. This disorder should lead to extensive bandtailing and localization of the states at the band edge.

In the light of the intrinsic disorder and of the fibrous structure it is tempting to examine our findings on the highly doped $(CH)_x$ in terms of recent theoretical and experimental work on the question of a maximum metallic resistance.[16-21] [Comparison of the absolute values of the relevant resistance or resistivity with known expressions is not possible for $(CH)_x$ because of its morphology. The measurements are made on a complicated series/parallel fiber network.]

For some time it has been thought that one- and two-dimensional (1D and 2D) disordered systems could be characterized as insulators or metals in terms of the absolute resistance (or resistance per square in 2D) with a crossover of ~8000 Ω (30 000 $\Omega/\square$). More recently both theory and experiment point to the transition being gradual with unusual properties in the "metallic state" at finite temperatures for materials with resistances of order of the crossover values.[16] In particular, for 1D[16] the resistance is expected to increase as T^{-2} and for 2D[17,18] as $\ln T$. Moreover, experiments on the metal films[20,21] have shown an electric-field dependence with resistance decreasing as $\ln E$. This has been interpreted in terms of electron heating which would reflect the temperature dependence of the resistance. The behaviors we have found [expressed in Eqs. (1) and (2)] would indicate a 2D disordered metal. This "dirty metal" interpretation would also explain the lack of a frequency-dependent conductivity up to 10^9 Hz[22] and the gradual transition as a function of doping would be from a dirty semiconductor with bandtailing[23] to a dirty metal with evolving spatially large localized states.

Despite the attractiveness of this interpretation there remain several difficulties. At first glance, doped $(CH)_x$ would appear to be either 3D or 1D depending on the length scale chosen. However, inelastic scattering[24] and magnetic[25] studies suggest that the fibril cores may remain undoped, producing 2D conductivity along an anulus. Considering the present understanding of the mechanism by which the logarithmic field dependence arises, it is disturbing that the $\ln E$ is found for samples which show both logarithmic and exponential temperature dependences. Our results would indicate that the $\ln E$ behavior is more general than is presently thought. The logarithmic and exponential temperature dependencies occur together only in the highest doped samples where $T_A \sim 4 \times 10^4$ K implying marginal applicability of variable range hopping and hence weak localization. The more lightly doped samples fit Eq. (3) with larger T_A (e.g., for $y = 0.01$, $T_A = 3 \times 10^6$ K). Finally, the greatest problem with this interpretation is the applicability of a localized metal model in the temperature range over which our experiments were done. Inelastic scattering delocalizes the electrons and localization effects will only be observed if the inelastic scattering length is larger than the localization length. We have observed logarithmic dependences up to ~100 K where it is unlikely that this condition can be met unless the localization length is extremely small.

It has recently been reported[26] that a more rapid variation of conductivity with applied field is observed for $(CH)_x$ samples doped with AsF_5 in a lower concentration region.

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Electronic Properties of Semiconductors with Negative-U Centers

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The concentration of free charge carriers p as a function of the doping level C [$p(C)$ characteristic] is calculated for a semiconductor containing defects with negative correlation energy U of bound charge carrier pairs. It is shown that in a certain interval $p \sim C^{1/2}$ in contrast to the behavior of defects with positive correlation energy U and of singly charged defects. Therefore, one has a simple criterion to prove experimentally whether a given kind of defect level has the negative-U property or not.

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Chalcogenide glasses show under photoexcitation spin magnetism. On the other hand, without excitation spin magnetism is absent inspite of a large density of localized electrons in these glasses.[1,2] This discrepancy has been successfully explained by a model of defect centers which favor binding of charge carriers by pairs instead of single carriers.[3-5] In order that this electron pairing occur, there is, according to Anderson,[3] a negative correlation energy U between the electrons at one defect site in these materials (negative-U centers). Until now, most publications on negative-U centers have been related to amorphous and glassy semiconductors (for a recent review see Ref. 6). In a recent paper, however, Baraff, Kane, and Schülter[7] showed that centers

