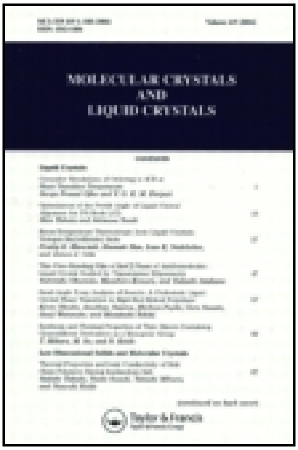

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Far-Infrared absorption in polyacetylene below the nonmetal-metal transition

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FAR-INFRARED ABSORPTION IN POLYACETYLENE BELOW THE NONMETAL-METAL TRANSITION

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Far infrared (20-700 cm^{-1}) transmission measurements have been made on in situ iodine-doped polyacetylene $(CH[I_3]_y)_x$ at doping levels from zero to the metallic state, $0<y<0.02$. A broadband absorption, too weak to be the pinning mode of a soliton, was observed; it increased with doping level. The data yield estimates for the ac conductivity and the dielectric constant of the material. At low doping levels the ac conductivity far exceeds the dc conductivity, while at higher levels the two conductivities are the same. The dielectric constant diverges as the nonmetal-metal transition ($y_c \approx 0.0215$) approaches.

INTRODUCTION

Although trans-polyacetylene[1] resembles in many ways a simple semiconductor (in that it has a modest bandgap, exhibits photoconductivity, and may be doped with acceptors or donors for control of electrical properties[2]), anomalies in the infrared spectrum and in the magnetic susceptibility indicate that a semiconductor model is not correct. When trans-polyacetylene is lightly doped, the number of unpaired (Curie) spins decreases[3,4], rather than increasing as would happen in a simple semiconductor, and infrared absorption at half the bandgap is observed.[5] The magnetic susceptibility appears to remain small when the doping level is large enough to give a relatively high conductivity.[3,4] This result is also contrary to the picture of a simple semiconductor, which predicts an appearance of a temperature independent (Pauli) susceptibility above the semiconductor to metal transition. The soliton mechanism[6,7] for doping has been proposed to explain this behavior. Alternatively, on the basis of ESR studies of magnetic susceptibility[8] and electric field dependent conductivity[9] of AsF_5 doped samples, it has been proposed[8] that the properties of doped $(CH)_x$ are dominated by the formation of metallic islands separated by undoped polymer. The non-metal to metal transition is then viewed as a percolation transition of such metallic islands[8]. However other studies of magnetic susceptibility[4] and frequency dependent conductivity[10] of iodine doped polyacetylene and magnetic[3] and optical[5] studies of AsF_5 doped $(CH)_x$ indicate that although the dopant distribution may be nonuniform, it is not segregated into metallic islands. The predictions of these two models for the far infrared properties differ substantially. We have made infrared transmission measurements on iodine doped trans-polyacetylene, $(CH[I_3]_y)_x$, in an attempt to explore this controversy.

EXPERIMENT

Trans-polyacetylene films were prepared at the Xerox Webster Research Center using standard techniques.[11] In situ doping was done at Ohio State by admitting small amounts of vapor from iodine crystals maintained at 23°C to the sample chamber. The sample resistance was monitored during the doping process and this resistance was used to estimate the iodine concentration.[12] By repetition of this procedure, the same polyacetylene film could be doped to progressively increasing iodine concentration without making any other changes in it. Iodine concentrations in $(CH[I_3]_y)_x$ from $y=0$ to $y=0.02$ were obtained. The doping technique was slow; it took ∿24 hours to reach the maximum concentration. The samples were compensated with ammonia in a similar manner.

Far infrared transmission measurements were made in the frequency range 20-700 cm^{-1} (2.5-85 meV) using a Michelson interferometer.[13] Measurements were made at sample temperatures of 77K and 300K.

RESULTS

The absorption coefficient, α, for a series of iodine doped samples is shown in Figure 1. This quantity is given by

$$\alpha(\omega) = -(1/d)\ln T(\omega) + (2/d)\ln(1 - R) \qquad (1)$$

where d is the thickness, T the transmittance and R the reflectance of the film. A broadband increase in the frequency dependent absorption coefficient with increasing iodine concentration was observed. There was no sharp structure in the absorption coefficient; instead, the absorption coefficient increased almost linearly with frequency. The broadband absorption decreased upon compensating an iodine doped sample with ammonia as shown in figure 2.

The oscillations in the absorption coefficient at low frequencies are caused by the interference of the light multiply reflected between the front and back surfaces of the film. The period of these oscillations is related to

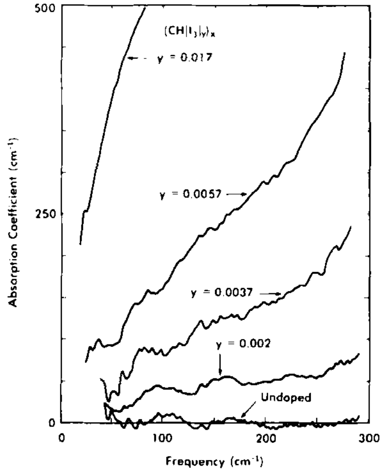

Figure 1 Far infrared absorption coefficient for lightly iodine doped <u>trans</u>-polyacetylene.

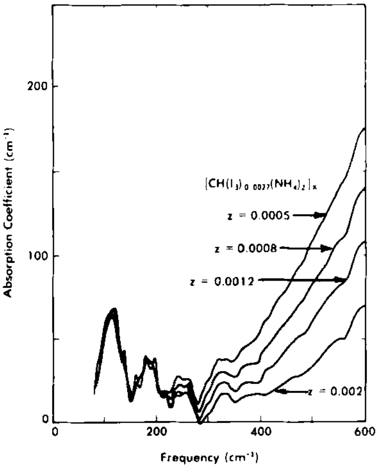

Figure 2 Far infrared absorption in a lightly iodine doped sample compensated with ammonia.

the refractive index of the sample by

$$n = 1/(2d\Delta\omega) \tag{2}$$

where $\Delta\omega$ is the frequency spacing (in cm^{-1}) of the maxima or minima of the oscillations. The absorption coefficient is linear in frequency implying that the extinction coefficient,

$$\kappa = \alpha/2\omega, \tag{3}$$

has little frequency dependence. The dielectric constant ε is related to the refractive index and the extinction coefficient by

$$\varepsilon = n^2 - \kappa^2. \tag{4}$$

Figure 3 shows the dielectric constant as a function of iodine concentration for $(CH[I_3]_y)_x$. Because n and κ have little frequency dependence in the far infrared, the data should be close to the static dielectric constant of the polyacetylene film. The dielectric constant is observed to diverge at ~2% $[I_3]^-$ as would be expected for the nonmetal-metal transition[2] at this doping level.

The ac conductivity was determined by extrapolating the absorption coefficient to zero frequency and calculated from

$$\sigma(\omega) = n\,\alpha(\omega)/(120\pi). \tag{5}$$

The concentration dependencies of the ac and dc conductivities are shown in Figure 4. At low iodine concentrations the ac conductivity is much larger than the dc conductivity while at higher concentrations the two conductivities are almost the same. This result is in agreement with measurements of the frequency dependence of the conductivity at low doping levels[14,15].

DISCUSSION

Our far infrared absorption coefficient data differ in detail from the predictions of both the soliton model and the small metallic particle picture. The soliton model[16] predicts a strong far infrared absorption by the pinned charged soliton at 300 cm^{-1}. The absorption should have an electronic oscillator strength because the soliton has an effective

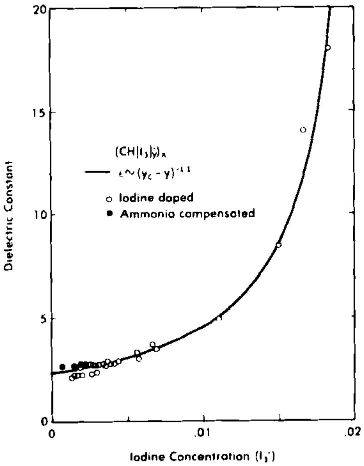

Figure 3 Dopant concentration dependence of the dielectric constant for iodine doped and ammonia compensated trans-polyacetylene.

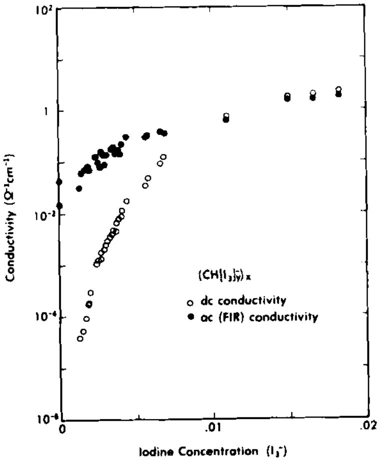

Figure 4 Dc and far infrared conductivities as a function of dopand concentration for lightly doped trans-polyacetylene. Dc conductivity from ref. 12.

mass $m^* \sim 7 m_e$. The increasing broadband absorption observed in our data could result from a spread in pinning energies of the soliton due to impurities or nonuniform doping. (Variations in the distance between the dopant molecule and the charged pinned soliton could cause the frequency of the absorption to vary.) However, the small oscillator strength of our far infrared absorption leads to a large effective mass, $m^* \sim 500\ m_e$. It has been suggested that interactions between the pinned soliton and acoustic phonons might cause a reduction in the oscillator strength.[17]

The far infrared absorption by small metal particle composites is known to be quadratic in frequency as observed, for example, in Pd/KCl and Ag/KCl composite systems.[18,19] In polyacetylene the absorption coefficient is nearly linear in frequency. Our absorption coefficient data are thus inconsistent in detail with both the soliton and the small particle pictures of lightly doped polyacetylene.

In many materials the insulator-metal transition is heralded by an increase in the dielectric constant. At the transition, the dielectric constant diverges[20,21] as

$$\varepsilon \sim |y_c - y|^{-s} \tag{6}$$

where y_c is the critical value of the parameter y for the transition. (Here, y is the iodine concentration.) For a percolation transition in three-dimensions, such as occurs in random small particle systems[22] or random resistor networks[23], $s \approx 0.7$. In contrast, the dielectric constant for phosphorous doped silicon diverges with $s=1.1$ at the Anderson nonmetal-metal transition.[24] A least squares fit of our dielectric constant data to equation 6 gave $s=1.1$ and a critical concentration $y_c = 0.0215$ $[I_3]^-$. Hence, the critical exponent is in agreement with that found for doped silicon and differs markedly with that found in composite systems.

The far infrared conductivity observed for our lightly doped samples is much greater than the dc conductivity. The two are almost equal at higher iodine concentrations. The only temperature dependence observed was a slight increase at low temperatures, suggestive of metallic behavior. The frequency dependence of the infrared conductivity would be linear because the absorption coefficient measured was linear in frequency (equation 5). Composite systems have an ac conductivity much larger than the dc conductivity for low concentrations of metallic constituent and the two become approximately equal at the critical concentration. For low metal concentrations, the temperature dependence of the conductivity is governed by the semiconducting host and should decrease rapidly with decreasing temperature, while the frequency dependence of the ac conductivity would be quadratic. Thus, while the concentration dependence of our far infrared conductivity is in qualitative agreement with that for the composite system, the temperature and frequency dependences are not.

Soliton systems might well have an ac conductivity much greater than the dc conductivity if the restoring force for the pinned soliton is weak or, alternatively, if hopping dominates the conduction properties. Recently a model has been proposed for charge transport via intersoliton electron hopping[25] which gives a very good account of the frequency (dc to 10^6 hz) and temperature dependence of the conductivity of trans-$(CH)_x$[14] and lightly doped trans-$(CH)_x$.[26] Extension of this model to higher frequencies is necessary for comparison with the experiments described here.

In summary, we have observed systematic changes in the far infrared absorption in polyacetylene as a result of doping with iodine and of compensation with ammonia. Our results differ considerably from those usually found for a material which undergoes percolative nonmetal-metal transition. In addition, we have failed to detect the predicted soliton pinning mode. The concentration dependence of the dielectric constant suggests the possibility of an Anderson-type transition in $(CH)_x$.

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