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COORDINATED STUDY OF NEARLY METALLIC POLYACETYLENE : ROLE OF SOLITONS

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Résumé - Nous présentons ici les résultats d'une étude des propriétés structurales, optiques, magnétiques et de transport de films de cis et trans $(CH)_x$ dopés lentement avec l'iode jusqu'à l'état métallique, c'est-à-dire $[CH(I_3)_y]_x$, $1,0 < y < 5,0$. Les systèmes cis et trans une fois dopés ont des structures similaires, avec essentiellement des états de solitons chargés. Les résultats sont en accord avec un nouveau mécanisme de transport dans le $(CH)_x$, par saut d'amplitude variable parmi des états de type soliton.

Abstract - We report here the results of a coordinated study of the structural, optical, magnetic and transport properties of cis and trans polyacetylene slow doped with iodine to nearly metallic levels, i.e., $[CH(I_3)_y]_x$, $1.0 < y < 5.0$. Cis and trans doped material have similar structure, with essentially all charges going into soliton states. The data are shown to be in agreement with a new mechanism of charge transport in polyacetylene, variable range hopping among soliton-like levels.

Considerable experimental and theoretical interest has focused upon the conducting polymer, polyacetylene, $(CH)_x$, and its two isomeric forms cis and trans /1,2/. According to the soliton model /3,4/, undoped $(CH)_x$ is a semiconductor due to a commensurate Peierls distortion. For the trans isomer the two phases of dimerization are degenerate in energy, hence the formation of solitons is favored in this system. These solitons are either neutral with a spin or charged with no spin. For cis- $(CH)_x$ (cis-transoid) a change in phase of dimerization results in the trans-cisoid structure which is not degenerate in energy. Hence other excitations such as bipolarons are favored in this system /5,6/. The conductivity, σ , at room temperature of both isomers increases from nonmetallic levels (10^{-9} (ohm cm) $^{-1}$ for cis and 10^{-5} ohm $^{-1}$ cm $^{-1}$ for trans) to metallic levels (10^{+2} - 10^{+3} ohm $^{-1}$ cm $^{-1}$) upon doping with acceptors such as I_3 , AsF_5 or ClO_4 or donors such as Li /7/ to levels of ~ 0.06 per polyacetylene carbon atom. Optical /8,9/ and structural /10/ studies have demonstrated that upon doping the cis isomer evolves to the doped trans isomer configuration. Magnetic susceptibility (χ) /11,12/, dc and ac transport /13,14,15/, and optical /16/ and infrared /9/ absorption studies of undoped or lightly doped trans- $(CH)_x$ support the soliton picture /3,4/.

Samples slowly doped to concentration of 0.01 to 0.05 I_3^- per carbon of trans- $(CH)_x$ have been shown /11/ to have magnetic susceptibility much

lower than that of the metallic state, χ^{Pauli} , yet have high conductivity. Similar results were reported for AsF_6 slowly doped trans samples /12,14/. This led to the suggestion /17/ that unpinned charged solitons determine the transport in the low χ^{Pauli} regime. Larger χ^{Pauli} were reported for cis-(CH)_x doped with AsF_5 to near one percent concentration /18/. On the basis of this and temperature dependent transport data, a model of formation of metallic islands separated by undoped polymer was proposed /18/. However, magnetic /11,12/, optical /16/ and transport /14,15,19/ studies of doped (CH)_x have shown that though the dopant distribution may be nonuniform, it is not segregated into metallic islands.

Here we report the results of an extensive series of coordinated measurements of $[\text{CH}(\text{I}_3)_y]_x$ with $0.01 < y < 0.05$, in the range where the doped polymer has been reported to have high conductivity with low susceptibility ($\chi^{\text{SPIN}} \ll \chi^{\text{Pauli}}$). Structural, optical, magnetic and conductivity and thermopower (S) studies were performed on sections of the same films. The results are inconsistent with clusters of small metal particles. The data show that both cis and trans doped material are very similar with similar structure and all charges, up to the highest levels studied here, $(\text{CH}(\text{I}_3)_{0.048})_x$ going into solitonlike states. On the basis of the data presented here, a different mechanism of charge transport is proposed, variable range hopping among soliton levels. The data are shown to be in quantitative agreement with this picture.

Polyacetylene was prepared by the Shirakawa technique /20/. The films are 90% crystalline /10/ and are composed of 500 Å diameter fibrils /21/. The "slow doping" technique /11/ was used to prepare samples. Between experiments, samples were stored in sealed evacuated vessels at 193K. Pieces of the same films were used for all experiments reported here. The temperature (T) dependent χ was measured using a very sensitive Faraday technique from 4K to 320K /11/. The calibration of the apparatus was verified by measurement of an aluminum standard provided by the National Bureau of Standards. Room temperature reflectance measurements /22/ were made between 20 and 700 cm^{-1} (0.002-0.09 eV) using a Michaelson interferometer. A grating monochromator was used for reflectance measurements between 700 and 7000 cm^{-1} (0.09-0.9 eV). A Kramers-Kronig analysis of the reflectance was performed in order to calculate the frequency dependent conductivity and dielectric function. S(T) and the four-probe $\sigma(T)$ and its electric field (E) dependence were measured during the same run.

The X-ray diffraction study /10/ of cis-(CH)_x slow doped to $(\text{CH}(\text{I}_3)_y)_x$ with $y = 0.033$ and $y = 0.048$ yields nearly the identical results as those for trans-(CH)_x slow doped to $y = 0.017$ and $y = 0.042$, in agreement with the earlier optical /9/ and transport studies of light doping ($y < 0.01$) of the cis isomer resulting in doped trans. For all iodine doping levels studied, about one-third of the sample volume remains undoped. As a uniform iodine distribution is observed in energy dispersive X-ray analysis /21/, these undoped regions are in the centers of the 500 Å diameter fibrils. Three broad X-ray reflections are found for $[\text{CH}(\text{I}_3)_y]_x$ corresponding to interplanar spacings of 7.9 Å, 4.1 Å and 2.9 Å, in agreement with a model /23/ of intercalation between polyacetylene planes. The transverse coherence length for the doped (CH)_x is 20 ± 5 Å.

The frequency dependent conductivity obtained by Kramers-Kronig analysis of the reflectance data samples of $y = 0.033$, 0.042 and 0.048 is shown in Figure 1 for frequencies up to 7000 cm^{-1} . These doped samples each have a strong absorption centered at 2800-3800 cm^{-1} , with the tail of this absorption extending to zero frequency. The zero frequency conductivity

FIGURE 1

Frequency dependent conductivity of slow doped $[\text{CH}(\text{I}_3)_y]_x$.

FIGURE 3

$T^{1/2} \sigma(T)/\sigma(295\text{K})$ versus $T^{-1/4}$ for slow doped $[\text{CH}(\text{I}_3)_y]_x$.

FIGURE 2a

FIGURE 2b

FIGURE 2

Spin susceptibility versus temperature for (a) $\text{cis}-(\text{CH})_x$ and iodine doped $\text{cis}-(\text{CH})_x$, and (b) $\text{trans}-(\text{CH})_x$ and iodine doped $\text{trans}-(\text{CH})_x$.

FIGURE 4

Thermopower versus T for $[\text{CH}(\text{I}_3)_y]_x$. The solid lines are fits to Eqs. 2 and 3, see text.

obtained is approximately 1.0 to 2.0 times the measured room temperature dc conductivity. Extension of $\sigma(\bar{r})$ to 20,000 cm^{-1} for $y = 0.042$ shows that the original interband transition of trans-(CH)_x /1,11/ is no longer observed.

Two strong maxima are observed, a narrow one at 1370 cm^{-1} and a broader one centered at 900 cm^{-1} . These features are associated with the formation of charged solitons created by chemical doping /24/. The oscillator strength for each mode was calculated after subtracting off the low energy tail of the main absorption at 3000 cm^{-1} . The results are shown in the insert in Figure 1. The data for these nearly metallic samples show the same oscillator strength per I_3^- as reported /9,24/ for lower doping concentrations. Hence doping with iodine to concentrations of I_3^- as high as 0.048 results in approximately as many charged solitons even at these high concentrations. This is just below the concentration of 0.07 where 15 carbon unit long solitons will overlap /3,4/.

Assuming excitation from the valence band to soliton levels is the origin of a large part of the strong absorption centered at 3000 cm^{-1} , one can utilize the oscillator strength per soliton and the known doping concentration to determine at what frequency soliton contributions to this strong absorption are exhausted. For each of the three curves shown in Fig. 1, the oscillator strength for soliton contributions is exhausted before the peak in the absorption. Hence this peak includes contributions of excitations from valence band to soliton levels and valence band to conduction band across a reduced bandgap /11,25/. These results are inconsistent with the expectations of the model /18/ of doping into isolated metallic regions.

The temperature dependent spin susceptibilities (χ^{SPIN}) for the starting cis-(CH)_x and cis-(CH)_x doped to 0.033 (I_3^-) and 0.048 (I_3^-) are shown in Figure 2a, while the results for trans-(CH)_x and the trans-(CH)_x doped to 0.017 (I_3^-) and 0.042 (I_3^-) are shown in Figure 2b. The core diamagnetism was experimentally established /11/ for (CH)_x and iodine and subtracted from all data. The remaining χ^{SPIN} is well represented as a sum of $\chi^{\text{CURIE}} = N^{\text{C}} g^2 \mu_B^2 / 3k_B T$ and $\chi^{\text{PAULI}} = 2\mu_B^2 N(E_F)$. Here μ_B is the Bohr magneton, k_B the Boltzmann constant, N^{C} the density of Curie spins and $N(E_F)$ the density of states at the fermi level for both directions of spin, assuming no Coulomb enhancement of χ^{PAULI} .

The starting cis material had $N^{\text{C}} = 188$ ppm probably as a result of the presence of 10-15 percent trans in it. The trans sample which was obtained by isomerization in vacuo at 207°C for 98 minutes, had $N^{\text{C}} = 583$ ppm. As was reported /11,12/ earlier, N^{C} decreases dramatically with doping, in agreement with the soliton mechanism of doping. For the trans starting material, approximately one-third to one-fifth of the Curie spins remain even after doping to 12.5 percent iodine ($y = 0.042$). This is consistent with the X-ray diffraction results /10/ which show about one-third of the trans-(CH)_x remaining undoped. The highly doped cis-(CH)_x sample ($y = 0.048$) has no localized Curie spins, though the X-ray diffraction studies /10/ also showed that the undoped regions of the initially cis film have isomerized to the trans structure. Isomerization at room temperatures (the temperature during doping) probably produces few crosslinks. Hence mobile solitons in the undoped trans regions of the initially cis film would be able to migrate to regions where there are dopants present and be oxidized to spinless charged solitons. The results of the magnetic studies are summarized in Table I.

TABLE I
SUMMARY OF RESULTS FOR $[\text{CH}(\text{I}_3)_y]_x$

Starting $(\text{CH})_x$	<u>trans</u>	<u>cis</u>	<u>trans</u>	<u>cis</u>
y	0.017	0.033	0.042	0.048
N^c , ppmC	186	193	110	0
$N(E_F)$, states/eV-C	0.014	0.045	0.027	0.069
$N(E_F)$, states/eV-cm ³	7.0×10^{20}	2.3×10^{21}	1.4×10^{21}	3.5×10^{21}
σ_{exp} , ohm ⁻¹ cm ⁻¹	2.5	8	20	50
T_0 , K	1.9×10^6	2.9×10^6	3.8×10^5	4.6×10^5
α^{-1} , Å	5.2	3.1	7.1	4.9
σ_M , ohm ⁻¹ cm ⁻¹	2.7×10^{-3}	1.4×10^{-3}	8.8×10^{-2}	8.8×10^{-2}
σ_{CN} , ohm ⁻¹ cm ⁻¹	1.9	9.1	3.1	12
R, Å	17	14	13	12
$N^{-1} dN/dE$, eV ⁻¹	0.46	0.42	0.60	1.9

The results for the two initially trans doped samples show an $N(E_F)$ nearly as low as that reported earlier /11,12/ for low susceptibility slow doped samples. The initially cis-(CH)_x samples exhibit a larger $N(E_F)$ than trans-(CH)_x samples doped to the same level. Though $N(E_F)$ for the highly conducting trans doped samples is an order of magnitude down from the expected metallic level (0.16-0.20 states/eV-C atoms), it is much larger than that of an uncompensated amorphous semiconductor such as amorphous Si where $N(E_F) \sim 10^{19} - 10^{20}$ state/eV-cm³/26/.

The $\sigma(295\text{K})$ of these samples is reported on Table I. The conductivity decreases slowly with decreasing T. For each of the nearly metallic samples studied $\sigma(T)$ is best fit by $\sigma(T) = AT^{-1/2} \exp[-(T_0/T)^{1/4}]$, as seen in Fig. 3. As $N(E_F)$ is below the metallic value yet very high for a semiconductor, it is tempting to analyze the data in terms of the Mott variable range hopping (vrh) model /26/, where $T_0 = 16\alpha^3 / (k_B N(E_F))$ and

$$\sigma(T) = 0.39 (N(E_F) / \alpha k_B T)^{1/2} v_0 e^2 \exp[-(T_0/T)^{1/4}] \quad (1)$$

Here α^{-1} is the decay length of a localized state, v_0 is a hopping attempt frequency, and e is the charge per electron. Using $N(E_F)$ and T_0 for each sample in Table I, α^{-1} is evaluated ~ 5 Å, varying slightly from sample to sample.

Utilizing $N(E_F)$ and α^{-1} from Table I and assuming, as is usually done /26/, that v_0 is an optical phonon frequency /24/ ($v_0 = v_{\text{ph}} \sim 3.6 \times 10^{13} \text{ sec}^{-1}$), the prefactor in Eq. 1 may be evaluated. The results, evaluated at 295K are given in Table I as σ_M . The absolute value of σ calculated from Eq. 1 is two to three orders of magnitude too low. This shortcoming of the absolute value of $\sigma(T)$ as calculated in vrh is common, occurring also for amorphous tetrahedral semiconductors such as amorphous Si/26/. Colson and Nagels have suggested/27/ that $v_0 = v_{\text{ph}} e^{2\alpha R}$, where R is the separation between hopping sites. Using R and α^{-1} from Table I for each y, a corrected σ_{CN} is evaluated. The results for y = 0.017 and 0.033 are in very good agreement with experiment. The results for y = 0.048 and 0.042 are off by factors of

4 and 6 respectively, in agreement with their small αR product implying the impending delocalization. Ohmic behavior for electric fields up to 5×10^4 volts/cm at temperatures as low as 8K for $y = 0.042$ and 0.048 are in agreement with the expectations of variable range hopping /26/.

$S(T)$ may now be examined in the context of these concepts. For vrh /26/,

$$S^{\text{vrh}}(T) = 1/2(k_B/e)k_B(T_0 T)^{1/2} N^{-1} dN/dE \quad (2)$$

while for a metal /26/,

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

where N is the energy dependent density of states. The best fit of these expressions to the experimental $S(T)$ is shown in Fig. 4 by the solid lines. Eq. 2 gives a good fit for $y = 0.017$ and 0.033 with $N^{-1} dN/dE \sim 0.4 \text{ eV}^{-1}$. That is, $N(E)$ is slowly varying. For $y = 0.048$, $S(T)$ is intermediate between vrh and delocalized (metallic) in behavior. Using Eq. 2, $N^{-1} dN/dE = 0.6 \text{ eV}^{-1}$. For $y = 0.042$, $S(T) \propto T$ reflecting a nearly delocalized behavior, consistent with the large α^{-1} . Using Eq. 3, $N^{-1} dN/dE$ is evaluated as 1.9 eV^{-1} . These results are given in Table I.

From the optical data presented above, it is suggested that the high density of states in the reduced valence to conduction bandgap may be associated directly with an empty condensate band which persists /25/ at these high doping concentrations. The small values of $N^{-1}(dN/dE)$ obtained from vrh analysis of $S(T)$ imply that E_F is near the minimum in $N(E)$ between the valence band and condensate band as shown schematically in Fig. 5. $N(E_F)$ is nonzero due to states being pulled out of the valence and condensate bands by the I_3 disorder /25/. These states should retain a large soliton-like character /25/. In fact, the effective dimensionally averaged decay length $\langle \xi \rangle$ of a non interacting soliton, $\xi = (\xi_{\perp}^2 \xi_{\parallel})^{1/3}$, is $3.6 \text{ \AA}$ /13,15,28/ is in good agreement with the α^{-1} values of Table I. The larger α^{-1} of $7.1 \text{ \AA}$ found for the $y = 0.042$ sample reflects the lower T_0 and is indicative of the near overlap of the solitons at this high density. In this sample vrh must be applied with care as it may be near the transition /25,29/ for delocalization and formation of the metallic state.

FIGURE 5

Schematic diagram of the electronic structure of nearly metallic polyacetylene

In sum, we have carried out an extensive series of coordinated experiments on cis and trans $(\text{CH})_x$ doped to the nearly metallic regime. Results show that the system is composed of a dense array of solitons in the solid. Quantitative analysis of $\sigma(T, E)$, $S(T)$, $\chi(T)$, optical reflectivity and X-ray structure is in agreement with a new model of variable range hopping among a dense array of soliton-like states. Trans-($\text{CH}(\text{I}_3)_y$) $_x$ has three distinct regimes for charge transport: (a) $y < 0.01$, well fit by intersoliton electron hopping /13,14,15,28/, (b) $0.01 < y < 0.05$, vrh among soliton-like sites, and (c) $y > 0.05$, disordered metallic behavior /19/.

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