

Effect of nonuniform doping on electrical transport in *trans*-(CH)_x: Studies of the semiconductor-metal transition

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Owing to the strong dependence of the resistivity on the dopant concentration, nonuniformity across the thickness of a sample leads to an apparent anisotropy in the resistivity (measured parallel to and perpendicular to the plane of the film). Thus the magnitude of the *apparent* anisotropy (for nonoriented samples) offers a convenient means for quantifying the degree of dopant nonuniformity in *trans*-(CH)_x. This technique is used to evaluate the uniformity achieved in [CH(AsF₅)_y]_x by conventional vapor-phase doping as compared with the slow-doping technique developed earlier for susceptibility studies. Using samples which have been demonstrated in this manner to be uniform, we reexamine the semiconductor-metal transition. From the transport data, we find that the better the uniformity in the distribution of dopant, the more abrupt is the transition at $y_c \approx 0.002$. A generalized soliton picture, involving delocalized carriers, appears to be implied by the combination of optical, magnetic, and transport data.

I. INTRODUCTION

There is extensive current interest in the prototype conducting conjugated organic polymer polyacetylene, (CH)_x. Doping this semiconductor with donors or acceptors results in more than 12 orders of magnitude increase in the conductivity σ and the formation of a metallic state.¹ The mechanisms of doping and transport in conducting polymers are of fundamental importance, since they appear to differ markedly from those in ordinary semiconductors. In particular, theoretical analysis shows that neglecting electron-electron interactions, single-particle excitations are always unstable to the formation of soliton pairs; discommensurations which reverse the magnitude of the bond alternation.²⁻⁶ Each of these defects produces a midgap level which is half-filled (spin $\frac{1}{2}$) when neutral, but which can accommodate an excess carrier in a charged, spin-zero state. Addition of carriers, therefore, leaves the doped (CH)_x chains diamagnetic; the added carriers are self-trapped in the localized states associated with the formation of amplitude solitons.

Experimental results of magnetic,⁷ infrared,⁸⁻¹⁰ optical,¹¹ and transport^{12,13} measurements on

doped (CH)_x support the soliton mechanism for doping. Moreover, photoconductivity¹⁴ and light scattering¹⁵ experiments are consistent with calculations which show that photo-injected electron-hole pairs in *trans*-(CH)_x rapidly interact with the bond alternated chain structure and form soliton-antisoliton pairs in a time of the order of 10^{-13} sec.¹⁶

Alternatively, Tomkiewicz *et al.*¹⁷ argued against soliton formation in polyacetylene on the basis of magnetic susceptibility (χ) measurements carried out primarily on *cis*-(CH)_x samples lightly doped with AsF₅. They observed a Pauli susceptibility which increased linearly with dopant concentration and therefore proposed that the properties of doped (CH)_x are dominated by the formation of metallic islands separated by undoped polymer. The semiconductor-metal (SM) transition in their view would be a percolation transition; the effect of changing the concentration would be to increase the number and size of the metallic islands until the percolation threshold is achieved.

Subsequent studies⁷ of the magnetic properties of *trans*-(CH)_x carefully doped using a technique designed to achieve optimum uniformity, demonstrated the nonmagnetic character of the doped polymer [CH(AsF₅)_y]_x for concentrations below

about $y = 0.07$. In contrast to the predictions of the percolation model, the susceptibility was found to increase abruptly to values characteristic of the Pauli spin susceptibility of a broad band metal, $\chi_p \approx 3 \times 10^{-6}$ emu/mol.

In situ optical studies during electrochemical doping have recently shown¹⁸ that doping *cis*-polyacetylene to a fixed dilute concentration induces partial *cis-trans* isomerization. "Undoping" back to neutral $(\text{CH})_x$ converts that portion of the sample which was doped back into undoped *trans*- $(\text{CH})_x$. Subsequent doping to the same level (or to lower levels) redopes only that portion which is already *trans*. Although doping to a higher level induces additional isomerization, complete isomerization is not achieved until dopant levels reach those characteristic of the metallic state. The optical absorption results obtained during electrochemical isomerization are consistent with ¹³C NMR data¹⁹ which show major inhomogeneity for *cis*- $(\text{CH})_x$ samples doped to intermediate levels, but more nearly uniform doping in *trans*- $(\text{CH})_x$. Thus, because of the doping-induced isomerization, the results indicate that doping of *cis*- $(\text{CH})_x$ may be necessarily inhomogeneous and limited to regions of doped *trans*- $(\text{CH})_x$ within the primarily *cis* polymer. However, this conclusion is not in any way in contradiction with the predictions associated with soliton doping. In fact, the demonstration that in partially isomerized films, the *trans* regions dope first (and only afterwards is there additional isomerization) provides confirming evidence of the validity of the soliton doping mechanism. Only in *trans*- $(\text{CH})_x$, where the ground state is truly degenerate, is it possible for the doping to proceed through the formation of low-energy solitons via the zero-energy midgap state. Doping of *cis*- $(\text{CH})_x$ would require generation of higher energy polarons.^{20,21} Evidently, in the event of charge transfer, it is energetically favorable for *cis*- $(\text{CH})_x$ to locally convert to *trans*- $(\text{CH})_x$ with the charge accommodated in soliton midgap states. Therefore, since the dopant uniformity in *cis*-rich samples is determined by the history of partial isomerization and by the simultaneous isomerization induced during doping, the present study is restricted to doped *trans*- $(\text{CH})_x$.

Previous studies of dopant uniformity in doped $(\text{CH})_x$ were reported by Janossy *et al.*²² and by Rolland *et al.*²³ who employed an energy dispersive x-ray analysis microprobe. Janossy *et al.*²² pointed out two scales for which nonuniformity is to be considered; from the exterior of the film toward

the interior, and radially within an individual $(\text{CH})_x$ fibril. They concluded that polyacetylene doped in the usual way, typical of most of the work in the field, is nonuniform on both these scales. They furthermore inferred a typical gradient through the film thickness with a characteristic length of $\sim 50 \mu\text{m}$, so that with care and the use of relatively thin films, this macroscopic nonuniformity can be avoided. Concentration gradients within the $(\text{CH})_x$ fibrils result from the relatively slow solid-state diffusion of the dopant ions; such intrafibril gradients were proposed by Epstein *et al.*²⁴ for iodine doped *trans*- $(\text{CH})_x$. However, Epstein *et al.*²⁴ demonstrated that this effect could be minimized (even for the relatively massive iodine molecule) by application of the slow-doping procedure.

In this paper we focus on the nature of the SM transition in doped *trans*- $(\text{CH})_x$ with emphasis on the relation between dopant uniformity and the intrinsic features of the SM transition. An experimental technique for monitoring the degree of uniformity of the doped sample is described. We have found that the anisotropy $\rho_{\perp}/\rho_{\parallel}$ in the resistivity, measured parallel to (ρ_{\parallel}) and perpendicular to (ρ_{\perp}) the plane of the film (for nonoriented samples), is directly correlated with the degree of uniformity of doping. Owing to the strong dependence of the resistivity on the dopant concentration, nonuniformity across the thickness of the sample leads to an apparent anisotropy. On the other hand, for uniform doping the anisotropy remains near unity at all levels of doping. Thus the magnitude of the *apparent* anisotropy offers a convenient means for quantifying the degree of dopant nonuniformity in *trans*- $(\text{CH})_x$. We use this technique to evaluate the uniformity achieved in $[\text{CH}(\text{AsF}_5)_y]_x$ by conventional vapor-phase doping as compared with the slow-doping technique developed for the susceptibility studies. We then present transport data, electrical conductivity and thermopower versus concentration, on a series of samples demonstrated to be uniformly doped. The results indicate that the nature of SM transition in doped *trans*- $(\text{CH})_x$ differs qualitatively from an impurity band insulator-metal transition in a conventional semiconductor. Moreover, the data for *trans*- $(\text{CH})_x$ are not consistent with the metallic "islands" model. From the transport data, we find that the better the uniformity in the distribution of dopant, the more abrupt is the SM transition at $y_c \approx 0.002$. On the other hand, magnetic studies⁷ of identical samples $[\text{CH}(\text{AsF}_5)_y]_x$ show the onset of Pauli spin

susceptibility only for $y > 0.07$.

In Sec. II, we give the experimental details of the doping procedure used to optimize uniformity. We also describe the Montgomery-configuration sample holder used for the determination of $\rho_{\perp}/\rho_{\parallel}$. Section III contains a description of the experimental results, which are discussed in more detail in Sec. IV. A summary and conclusion are given in Sec. V.

II. EXPERIMENTAL TECHNIQUES

(CH)_x films were prepared at -78°C (Ref. 25); the doping utilized a technique developed to achieve a homogeneous distribution of dopant ions. A large flat *trans*-(CH)_x film (~ 130 mg after doping) was placed in the center of a 500-ml bulb to which two cold fingers were attached, one entering at the top, the other at the bottom. The film rested on small glass supports, thus permitting both sides of the film to be exposed evenly to the AsF₅ vapor. A fixed amount of purified AsF₅, ~ 10 – 20% in excess of that required for a given doping level, was transferred to the upper cold finger and the apparatus was evacuated and sealed. Doping was carried out by first holding the upper cold finger at -131°C for 6 h. Independent mass spectroscopic studies showed that the vapor of AsF₅ (vapor pressure < 0.1 Torr) over the AsF₅ contained no HF or AsF₃. After 6 h the lower cold finger was held at -196°C for 6 h during which time the upper cold finger was gradually permitted to warm to approximately room temperature. After this time all the AsF₅ had been cryopumped into the lower cold finger. The lower cold finger was then held at -131°C and the upper cold finger at room temperature for 6 h, thus repeating the doping process a second time. This entire procedure was repeated a total of 4 times. After cryopumping for 12 h, the films were separated into samples for magnetic resonance and for transport measurements. For transport studies, samples were cut into convenient dimensions; for resonance, the films were weighed and loaded into either an NMR tube (~ 100 mg of sample) or an EPR tube (~ 2 mg of sample). The use of large samples of film permitted an accurate determination of sample composition. The large volume of the reaction bulb and the small vapor pressure of AsF₅ (which would decrease still further during the reaction) leads to very slow doping. For the film having a 7% nominal AsF₅ content, an elemental analysis gave the composition $[(\text{CH})_{1.03}(\text{AsF}_{5.96})_{0.067}]_x$. The sum of the analytical

percentages of the constituent elements was 99.13%. It is therefore assumed that all films contained the AsF₆ species. Although different anions can be generated by AsF₅ doping,^{26,27} this method assures the presence of the AsF₆⁻ species.

For comparison, additional samples were doped using the conventional technique of exposing the (CH)_x film to the vapor pressure of AsF₅. The AsF₅ was initially precooled to 77 K, and the stopcock was subsequently opened to the doping vessel. The temperature of the AsF₅ reservoir was then slowly raised while monitoring the resistivity of a test sample; the doping was allowed to proceed until the desired resistivity was achieved.

The resistivity components along and perpendicular to the film surface were measured by the Montgomery method.²⁸ In this method a sample is cut in the form of a rectangular prism, the faces of which edges along the directions of the two resistivity components to be measured. Small electrodes are attached at the four corners of this face. The ratio of voltages between two adjacent electrodes to the current between the other two electrodes is measured; then a similar measurement is made with all connections rotated by 90° . From these measurements and the dimensions of the sample, two components of the resistivity tensor can be calculated. In the unstretched films that we have studied only two components of ρ are to be determined (ρ_{\parallel} and ρ_{\perp}) since there is in-plane isotropy. The (CH)_x films used had a typical thickness of about 80 to 100 μm . In such thin samples, successful application of Montgomery's method requires that the distance between the attached electrodes be comparable to the sample thickness. Furthermore, since the relations between the voltages and currents in the sample are extremely sensitive to the positions of the contacts, the locations of the electrodes must be precisely determined.

In order to meet the stringent conditions (needed in particular for the more highly conducting samples) a specially designed sample holder was constructed for carrying out the anisotropy measurements. The (CH)_x film is clamped between two polished epoxy surfaces. The electrodes are gold wires imbedded in the bulk of the epoxy in a direction perpendicular to the polished surfaces. There are eight contacts (gold wires with diameter 0.0075 cm separated by 0.02 cm), four on each side of the (CH)_x film (see Fig. 1). The device is constructed in such a way that the upper contacts are located exactly on top of the lower ones which are on the opposite side of the sample. The precise alignment

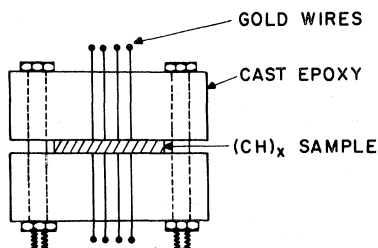


FIG. 1. Schematic diagram of sample holder for Montgomery measurements on thin films of $trans$ -(CH)_x.

was accomplished by building the sample holder as follows: Two pieces of hard epoxy were polished and one was subsequently grooved along the polished face. Four gold wires were then placed in the four grooves, after which the second polished part was glued on to the first one. After drying, the composite piece was cut in a direction perpendicular to the wires. Before the final cutting, holes for clamping screws were drilled. Finally, the newly cut surfaces were polished and the exact locations of the contact wires were measured with a microscope.

The values of $\rho_{||}$, ρ_{\perp} and the ratio $\rho_{||}/\rho_{\perp}$ were determined by using a selected set of four-point contacts located close to each other (two on the top surface of the (CH)_x film and two on the bottom surface). The values of the resistivity components were self-consistently checked by using a second set of four contacts (next-nearest neighbor). The results were found to be in excellent agreement.

Techniques for the resistivity (ρ) and thermopower (S) measurements as a function of temperature were standard, and were described in detail in an earlier publication.¹³

III. EXPERIMENTAL RESULTS

A. Anisotropy as an indicator of dopant uniformity

The anisotropy of the electrical resistivity was measured for pure $trans$ -(CH)_x and for $trans$ -(CH)_x doped with AsF₅. Two types of doped material were investigated: samples prepared with the slow-doping technique, and samples doped in the more conventional manner, both described in Sec. II. The resulting anisotropy data $\rho_{\perp}/\rho_{||}$ measured for various dopant concentration, are summarized in Table I. For pure nonstretched $trans$ -(CH)_x, we find $\rho_{\perp}/\rho_{||} \approx 2$. The implied modest orientation of the (CH)_x fibrils (for nonstretched films) apparently results from interaction with the glass surface on which the films were grown. The observation of some anisotropy in as-grown film suggests that with proper substrate preparation, it may be possible to achieve truly oriented films.

Doped samples, prepared with the slow-doping technique described in Sec. II, yielded $\rho_{\perp}/\rho_{||} \approx 2$ at all doping levels (Table I). Thus, although the absolute resistivity increased by many orders of magnitude on doping, the anisotropy remained essentially constant. The constant anisotropy implies *uniform doping throughout* the film thickness. If the center were undoped (or if there were a significant gradient), the resistivity of the center portion would be high while that of the outer surfaces could be low. Since $\rho(y)$ is a strong function, such a dopant nonuniformity would lead to a large apparent anisotropy. Such an anisotropy is indeed obtained on samples doped in the more conventional manner (see Table I). For such samples we typically find $\rho_{\perp}/\rho_{||} \sim 25-35$.

TABLE I. Apparent resistivity ($\rho_{\perp}/\rho_{||}$) and $\rho_{||}$ obtained from Montgomery measurements on nonstretched films of $trans$ -(CH)_x.

	Sample	$\rho_{\perp}/\rho_{ }$	$\rho_{ }$ (Ω cm)	$\rho_{ }$ (4-probe)
undoped	$trans$ -(CH) _x	2.0	6.7×10^5	7.1×10^5
rapidly doped (see Sec. II)	$trans$ -[CH(AsF ₅) _{0.10}] _x	23	9.0×10^{-2}	
	$trans$ -[CH(AsF ₅) _{0.12}] _x	33	2.9×10^{-3}	2.5×10^{-3}
slowly doped (see Sec. II)	$trans$ -[Ch(AsF ₅) _{0.036}] _x	2.0	7.1×10^{-3}	9.1×10^{-3}
	$trans$ -[Ch(AsF ₅) _{0.12}] _x	2.2	4.0×10^{-3}	4.6×10^{-3}

B. Semiconductor-metal transition in uniformly doped *trans*-(CH)_x

The concentration dependence of the conductivity $\sigma(y)$ for uniformly doped $[\text{CH}(\text{AsF}_5)_y]_x$ is presented in Fig. 2. Compared with earlier data,¹³ the results indicate a somewhat more sharply defined SM transition as a function of y and show higher electrical conductivities in the transitional region. For example, at $y = 0.002$, $\sigma = 0.5 \Omega^{-1} \text{cm}^{-1}$, more than 3 orders of magnitude larger than obtained earlier using more rapid doping. Similarly, at $y = 0.02$, $\sigma = 30 \Omega^{-1} \text{cm}^{-1}$, again more than an order of magnitude greater than samples prepared with known nonuniformity (i.e., apparent anisotropy of ~ 25). At higher (and lower) concentration, the conductivities were typical of doped polyacetylene.

The concentration dependence of the thermopower $S(y)$ for uniformly doped $[\text{CH}(\text{AsF}_5)_y]_x$ is shown in Fig. 3. Again, the transition to "metallic" behavior is more abrupt as a function of y and occurs at a lower concentration than reported earlier for samples prepared with standard doping procedures. For example, at $y = 0.0004$, $S = 840 \mu\text{V}/\text{K}$, and at $y = 0.002$, $S = 20 \mu\text{V}/\text{K}$, whereas in earlier studies such small values were not achieved until $y > 0.01$. The temperature dependence of the thermopower $S(T)$ is shown in Fig. 4 for the $y = 0.0025$ sample (i.e., just above transition shown in Fig. 3); $S(T)$ is small and quasi-linear, consistent with the sharp transition. This

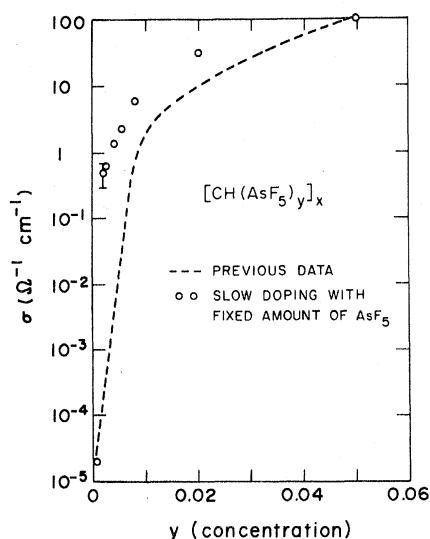


FIG. 2. Conductivity vs dopant concentration (y) for $[\text{CH}(\text{AsF}_5)_y]_x$. — — —, previous data (Ref. 13); $\circ\circ\circ$, slow-doping technique (see text).

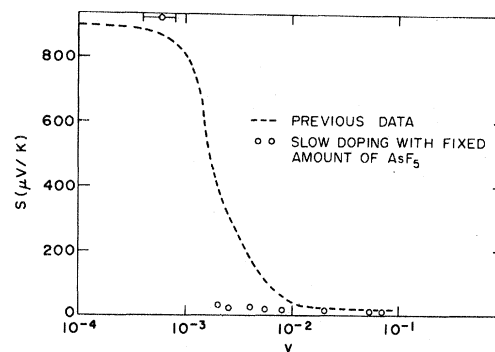


FIG. 3. Thermopower (s) vs dopant concentration (y) for $[\text{CH}(\text{AsF}_5)_y]_x$. — — —, previous data (Ref. 13); $\circ\circ\circ$, slow-doping technique (see text).

transition is also observed in the temperature dependence of the conductivity. In the dilute regime, $\sigma(T) \sim T^n$ with $n \simeq 13$. This strong dependence persists until $y \simeq 0.001$. At higher concentrations the dependence of σ upon T becomes extremely weak. For example, if one evaluates the slope $d(\ln\sigma)/d(T^{-1})$ at room temperature, the value drops from 0.31 eV below $y = 0.001$ to ~ 0.02 eV at $y \simeq 0.002$. Thus, major changes in the magnitude and temperature dependence of both the thermopower and conductivity occur at $y \simeq 0.001$.

IV. DISCUSSION

A. Nonuniform doping in *trans*-(CH)_x; Origin and effect on transport and magnetic data

The anisotropy measurements lead to the conclusion that the slow-doping procedure (Sec. II)

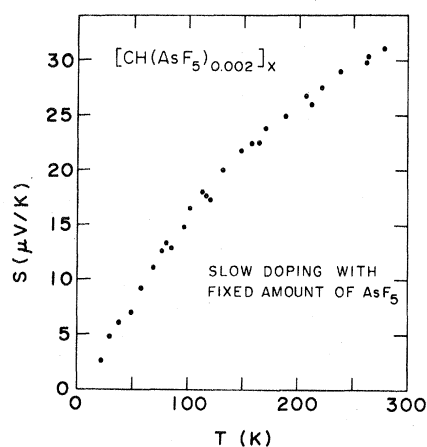


FIG. 4. Thermopower (s) vs temperature (T) for $[\text{CH}(\text{AsF}_5)_{0.002}]_x$ prepared using the slow-doping technique (see text).

does, in fact, result in uniform doping across the thickness of the $trans\text{-}(\text{CH})_x$ film. Such measurements are relatively insensitive to intrafibril concentration gradients. However, the slow-doping procedure with cyclic cryopumping allows considerable time for the establishment of a uniform equilibrium concentration throughout the $\sim 200\text{-}\text{\AA}$ diameter fibrils. The higher degree of intrafibril dopant uniformity is confirmed by the essentially complete disappearance of the (neutral soliton) Curie-law susceptibility in such samples at intermediate doping levels. We point out here that by uniform doping, we mean that the density averaged over any small macroscopic volume does not depend on the region of the sample over which the average is taken. Thus, even for uniform doping, statistical fluctuations will always give rise to local variations on a small enough scale.

The observation that the SM transition is much sharper in samples which are macroscopically uniform ($\rho_{\perp}/\rho_{\parallel} \approx 2$) as compared with samples with known nonuniformity (as evidenced by an apparent anisotropy, $\rho_{\perp}/\rho_{\parallel} \sim 25$) is particularly important. Smearing of the transition by concentration gradients is to be expected if the behavior (for example S vs y , or χ vs y , etc.) is abrupt. This was demonstrated explicitly for the Pauli susceptibility by Epstein *et al.*²⁴

Concentration gradients across the sample thickness lead directly to an understanding of the apparent anisotropy

$$\rho_{\perp} = t^{-1} \int_0^t \rho[y(x)] dx, \\ \rho_{\parallel} = \left[t^{-1} \int_0^t \sigma[y(x)] dx \right]^{-1},$$

so that the apparent anisotropy would be given by

$$\frac{\rho_{\perp}}{\rho_{\parallel}} = t^{-2} \left[\left[\int_0^t \rho(y) dx \right] \left[\int_0^t \sigma(y) dx \right] \right],$$

where $\rho(y) \equiv 1/\sigma(y)$ is the resistivity (versus y) for nonoriented $trans\text{-}(\text{CH})_x$ and t is the film thickness. The resulting values depend on the detailed form of the concentration profile $y(x)$. However, the general features are certainly consistent with the data.

The origin of the concentration gradients obtained using conventional doping procedures is of interest. Janossy *et al.*¹² suggested that concentration gradient across the film thickness results from a decrease in the dopant vapor pressure from the surface to the interior as the reaction takes place. Alternatively, we note that electron microscopy studies²⁹ have revealed significant swelling of the

$(\text{CH})_x$ fibril after doping with AsF_5 . As a result, the interfibril spaces close up during doping. Since this would occur initially on the outer surface of the $(\text{CH})_x$ film, subsequent diffusion toward the center may be somewhat inhibited. More work is clearly needed in order to determine the dynamic evolution of the dopant concentration profile under different doping conditions.

B. The semiconductor-metal transition in $trans\text{-}(\text{CH})_x$

The transport data obtained from uniformly doped samples (Figs. 2–4) together with the magnetic susceptibility results presented earlier, define the SM transition. For $y < 0.002$, the thermopower and conductivity data (versus temperature and pressure) indicate hopping transport. Using the soliton theory as a basis, a quantitative understanding of the hopping transport in $trans\text{-}(\text{CH})_x$ at dilute doping levels has been demonstrated.^{30–32} Kivelson's theory of transport by intersoliton hopping³⁰ accounts for the magnitude, temperature dependence,³¹ pressure dependence,³¹ and frequency dependence³² of the electrical conductivity, and for the magnitude and sign of the temperature-independent thermopower.³¹ Alternatively, attempts to explain the results in terms of variable range hopping³³ predicted conductivity values off by 15 orders of magnitude and predicted pressure and frequency dependences which are not consistent with the experimental results.³¹ Thus, using the soliton theory as a basis, a quantitative understanding of electrical transport in lightly doped $trans\text{-}(\text{CH})_x$ has been demonstrated.

In the heavily doped regime, $y > 0.07$, doped polyacetylene is truly metallic. The Pauli susceptibility,⁷ linear term in the heat capacity,³⁴ linear temperature dependence of the thermopower,¹³ and infrared-absorption data,³⁵ which are observed in the high concentration regime, all imply metallic behavior with a density of states at the Fermi energy, $N(E_F) \approx 0.1$ states/eV C atom, consistent with a broad energy band. Optical absorption³⁶ and electrical energy loss³⁷ experiments suggest that the energy gap of pure $(\text{CH})_x$ has closed (or at least reduced to a value less than a few tenths of an eV). Thus in the high-concentration limit relatively simple and traditional metallic behavior is observed. The question of whether the bond alternation goes to zero in this regime or whether the reduced gap is filled in by a combination of disor-

der and interchain coupling remains to be settled.⁶

The results of Figs. 2–4 are inconsistent with the percolation model proposed by Tomkiewicz *et al.*¹⁷ The essential feature of such a percolation transition would be the presence of disconnected metallic regions at concentrations well below the critical value (y_c). One would therefore expect χ_p to increase linearly at concentrations well below y_c at which point the regions would connect leading to metal-like transport. The observation of a semiconductor-metal transition from transport data at $y \simeq 0.002$ with the onset of χ_p only at much higher concentrations, therefore, rules out the percolation model for *trans*-(CH)_x.

Frequency-dependent conductivity studies have been useful for checking the “metallic islands.” Grant and Krounbi³⁸ found the room-temperature conductivity to be frequency independent (10 Hz to 10 MHz) for all levels of doping with AsF₅. Similarly Epstein *et al.*³⁹ investigated the frequency dependence of σ from dc through 500 MHz at intermediate doping levels. In all cases, they found that for doped (CH)_x the conductivity was frequency independent up to their maximum frequency. On the other hand, any model of serial segregation into metallic and insulating regions would predict an increasing conductivity at higher frequencies. A frequency dependence has been observed³² for undoped *trans*-(CH)_x with magnitude and function dependence in agreement with Kivelson’s³⁰ theory of intersoliton hopping. Mihaly *et al.*⁴⁰ extended the data through microwave measurements (9 GHz) and obtained the ratio σ_{ac}/σ_{dc} as a function of iodine concentration. In contrast to the behavior expected for metallic islands, Mihaly *et al.*⁴⁰ found σ_{ac}/σ_{dc} to decrease from about 10^3 at $y = 0$ to around unity at $y = 0.03$. These results rule out the possibility of nonuniformity in the shape of metallic islands. Moreover, these studies were carried out on samples prepared with conventional doping techniques where dopant nonuniformity is known to exist. We conclude that the proposed metallic islands do not exist in *trans*-(CH)_x; whatever nonuniformity is present in either macroscopic across the film thickness, or radially through the cross section of the fibrils.

The intermediate regime $0.002 < y < 0.07$ is particularly interesting. The thermopower and spin susceptibility results are compared directly in this regime in Fig. 5. We emphasize that identical uniformly doped samples were used for both the transport and magnetic measurements (Sec. II), so that direct comparison is justified. The thermo-

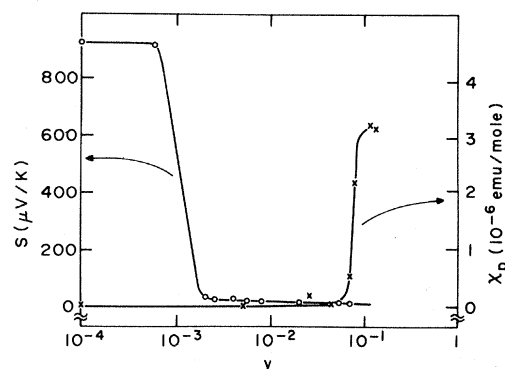


FIG. 5. Comparison of the thermopower data and Pauli susceptibility (Ref. 7) for $[\text{CH}(\text{AsF}_5)_y]_x$. Identical doped samples were used in the transport and magnetic measurements (see Sec. II).

power data imply a transition at a concentration of about $y \simeq 0.001$. The transition in the transport mechanism at $y \simeq 0.001$ is also seen in the dramatic change in the temperature dependence of the conductivity as described above. However, the Pauli susceptibility (and hence the density of states) remains small until concentrations in excess of $y \simeq 0.07$. In this regime it has been demonstrated⁷ that it is possible to prepare highly conducting samples ($\sigma \sim 100 \Omega^{-1} \text{cm}^{-1}$) with fewer than 1 ppm Curie spin (compared with 300 ppm before doping) and with $\chi_p \leq 1 \times 10^{-7}$ emu/mol. Moreover, for concentrations less than $y \simeq 0.07$, any small residual temperature-independent susceptibility appears to be the result of residual nonuniformity in doping. The magnetic susceptibility results for AsF₅-doped *trans*-(CH)_x are therefore fully consistent with the soliton-doping mechanism.

The results appear to imply the existence of two transitions. Indeed, optical studies on samples chemically doped¹¹ with AsF₅ and optical studies carried out *in situ* during electrochemical doping⁴¹ show that at these concentrations, both the midgap transition and the interband transition are experimentally well defined, characteristic of the formation of midgap states due to soliton generation. These distinct features persist until concentrations of about $y \simeq 0.05$; only in the most heavily doped regime does the absorption become like that due to free carriers. Thus, the transition at $y \simeq 0.001$ does not signify the onset of metallic behavior in the traditional sense.

V. CONCLUSION

In conclusion, we have developed a technique for using the apparent anisotropy in nonoriented *trans*-(CH)_x films as a means of investigating the nonuniformity in dopant profile generated by different doping techniques. We find that the slow-doping procedure developed for the magnetic susceptibility studies on [CH(AsF₅)_y]_x leads to more uniform doping as indicated by a measured anisotropy which remains near unity at all concentrations. On the contrary, conventional vapor-phase doping results in an apparent anisotropy, $\rho/\rho_{||} \sim 25-35$, indicative of a dopant profile with a concentration gradient across the thickness of the film (the center being more dilute than the outside).

Using samples which have been demonstrated to be uniform in the above manner, we have reinvestigated the semiconductor-metal transition. We find a more sharply defined transition as a function of *y* and higher electrical conductivities in the transitional region. The combination of transport and magnetic data from uniformly doped *trans*-(CH)_x are not consistent with a percolation transition of metallic islands.

The transition from the dilute regime, characterized by Kivelson's intersoliton hopping, to the non-

magnetic intermediate regime is most clearly demonstrated in the thermopower data. The small values and quasilinear (with temperature) behavior are suggested of delocalized carrier transport. However, these carriers cannot arise from simple band states. In this concentration range, there is no evidence of a finite density of states at the Fermi energy. Moreover, optical studies show the simultaneous existence of the midgap transition (originating from the soliton-bound state) and the interband transition. Thus a generalized soliton picture, involving delocalized carriers, appears to be implied by the combination of optical, magnetic, and transport data.

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¹For references, see the following review paper: A. J. Heeger and A. C. MacDiarmid, in *The Physics and Chemistry of Low Dimensional Solids*, edited by Luis Alcacer (Reidel, Dordrecht, 1980), p. 353. The following paper in this volume (p. 393) focuses on the chemical aspects.

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