

## Magnetic susceptibility of doped polyacetylene

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Magnetic susceptibility measurements of  $[\text{CH}(\text{AsF}_5)_y]_x$  over the concentration range  $0 \leq y < 0.13$  and the temperature range 77–295 K are presented. Measurements were performed using both Faraday balance and Schumacher-Slichter magnetic resonance methods. Total susceptibilities were separated into three components: atomic core diamagnetism, local-moment Curie-law paramagnetism, and Pauli paramagnetism. From the onset of the Pauli term as a function of  $(\text{AsF}_5)$  concentration, the critical dopant concentration for the semiconductor-metal transition is determined. The Fermi-surface density of states obtained from the Pauli term is analyzed in terms of various band-structure models. Alternate explanations of anomalously small Curie terms in lightly doped, semiconducting  $(\text{CH})_x$  are discussed, including the possibility of soliton-localized impurity states induced by charge transfer doping.

### I. INTRODUCTION

Polyacetylene,  $(\text{CH})_x$ , has recently been the subject of much experimental study. The undoped polymer is of fundamental importance as it is the simplest linear conjugated polymer. Optical-absorption studies imply that  $(\text{CH})_x$  is a direct-gap semiconductor with a peak absorption coefficient of about  $3 \times 10^5 \text{ cm}^{-1}$  at 1.9 eV.<sup>1</sup> The doped polymer exhibits extraordinary electrical properties; through chemical doping, the room-temperature conductivity of  $(\text{CH})_x$  films can be varied over more than twelve orders of magnitude,  $10^{-9}$ – $10^3 (\Omega\text{-cm})^{-1}$ .<sup>2–6</sup> *N*- and *p*-type doping as well as compensation and junction formation have been demonstrated.<sup>7</sup> Qualitative changes in electrical and optical properties at dopant concentrations above a few atomic percent have been interpreted as arising from a semiconductor-metal (SM) transition.<sup>3,5</sup> Partial orientation of the polymer fibrils has been accomplished by stretch elongation yielding polymer films with anisotropic electrical<sup>4</sup> and optical<sup>2</sup> properties suggestive of a highly anisotropic band structure.

Previous magnetic studies by Shirakawa *et al.*<sup>8</sup> and Goldberg *et al.*<sup>9</sup> utilized magnetic resonance techniques to study the electron-spin resonance of  $(\text{CH})_x$ . Undoped *trans*- $(\text{CH})_x$  was observed to have a narrow spin resonance with *g* value close to the free-electron value and an intensity corresponding to a Curie-law susceptibility from approximately one unpaired spin per 3000 carbon atoms. The tenfold increase in spin density on isomerization<sup>8</sup> from *cis* to *trans*  $(\text{CH})_x$  implies that the observed unpaired spins in pure  $(\text{CH})_x$  arise from defects in the polymer chains. From detailed analysis of the *g* value, Goldberg *et al.*<sup>9</sup> concluded that the resonance arises from a  $\pi$ -electron

defect which they attributed to a  $\pi$ -phase-kink domain wall. Goldberg *et al.*<sup>9</sup> observed that upon exposure of the  $(\text{CH})_x$  to  $\text{AsF}_5$  gas, the line narrowed and increased in intensity, eventually becoming Dysonian in shape in the metallic high-concentration limit.

The magnetic properties of a material can provide important details of its electronic structure. In the heavily doped samples, a temperature-independent paramagnetic contribution to the susceptibility suggests the existence of a degenerate Fermi sea of metallic charge carriers. From the Pauli formula the Fermi-surface density of states  $N(E_F)$  may be obtained;  $\chi_p = \mu_B^2 N(E_F)$ , where  $\mu_B$  is the Bohr magneton and  $N(E_F)$  includes both spin directions. The onset of such a temperature-independent Pauli term in the susceptibility as a function of dopant concentration indicates the transition from the semiconducting to the metallic state.

The susceptibilities of samples with dopant concentrations in the region of the semiconductor-metal transition are of interest in reference to the role of electron-electron correlation effects in the electronic structure of polyacetylene. The question has arisen as to whether the observed optical bandgap of  $\sim 1.5$  eV may be explained solely in terms of single-particle effects<sup>1,10</sup> (bond alternation and a Peierls gap) or requires the introduction of correlations.<sup>11</sup> The existence of strong electron-electron interactions, with accompanying spin-dependent exchange energy, would imply an enhanced Pauli spin susceptibility<sup>12</sup> especially at low carrier densities (i.e., near the SM transition). It has been suggested<sup>13</sup> that the observed temperature and concentration dependences<sup>14</sup> of Si:P spin susceptibilities at dopant levels near the SM

transition may be explained by such correlation effects. Finally, in the lightly doped range, below the SM transition, susceptibility results can suggest the nature of the impurity state. Possible models will be discussed in terms of experimentally determined local magnetic-moment concentrations.

In this paper we present measurements of the static susceptibility of  $\text{AsF}_5$  doped polyacetylene,  $[\text{CH}(\text{AsF}_5)_y]_x$ . Faraday balance measurements were made on samples with dopant concentrations in the range  $0 \leq y < 0.13$ , over the temperature range 77–295 K. These data are supplemented with direct static spin-susceptibility measurements utilizing the Schumacher-Slichter magnetic resonance technique. The experimental details are described in Sec. II, the results are discussed in Sec. III, and the conclusions are summarized in Sec. IV.

## II. EXPERIMENTAL DETAILS

All samples used in this work were unoriented polycrystalline films prepared using techniques similar to those developed by Shirakawa and collaborators.<sup>15</sup> Doping techniques are described elsewhere.<sup>2–6</sup> Dopant concentration levels were determined by measurement of weight uptake. It has been observed that samples with  $\text{AsF}_5$  doping levels approaching saturation ( $y \approx 0.15$ ) lose some  $\text{AsF}_5$  when pumped on, reaching equilibrium concentration after several hours. The  $y = 0.12$  samples used in this work were therefore doped to saturation and pumped on for a minimum of 12 hours prior to weighing.

Static magnetic susceptibilities were measured by two techniques: total susceptibilities using the field gradient Faraday balance method<sup>16</sup> and electron-spin susceptibilities using the resonance technique of Schumacher and Slichter.<sup>17</sup> Samples for use in the Faraday balance were placed inside a gelatin capsule in an argon glovebag. After suspending the sample capsule from the balance, the sample chamber was immediately evacuated to better than  $10^{-3}$  Torr prior to backfilling with  $20 \mu$  He exchange gas. Air exposure time of the samples was limited to less than ten minutes. Sample sizes were in the range  $0.6$ – $2.0 \times 10^{-3}$  moles of  $[\text{CH}(\text{AsF}_5)_y]_x$ . The product  $H(dH/dz)$  was calibrated using a room-temperature aluminum standard, and the deflection of the blank sample holder and capsule was subtracted from each run. Temperatures were monitored with a platinum resistance thermometer.

The Faraday balance measures the total susceptibility of a sample. Consequently, the measured value includes not only the spin susceptibility but other contributions as well, the principal one being the diamagnetism of the atomic core electrons. The Schumacher-Slichter technique, however, isolates one component of the total susceptibility, the component

which gives rise to the observed resonance; the magnetic susceptibility of the electron spins.<sup>17</sup>

A room-temperature spin susceptibility of  $[\text{CH}(\text{AsF}_5)_{0.12}]_x$  was obtained using as calibration the  $\text{F}^{19}$  and  $\text{H}^1$  nuclear magnetic resonances in that sample. The nuclei have a Curie law susceptibility with with absolute magnitude given by

$$\chi_N = NJ(J+1)(\gamma_n \hbar)^2 / 3k_B T,$$

where  $J$  is the nuclear spin ( $J = \frac{1}{2}$  for  $\text{H}^1$  and  $\text{F}^{19}$ ),  $N$  is the number of nuclei per unit volume as determined by the stoichiometry and  $k_B$  is the Boltzmann constant. The experiment was performed at 37 MHz using a simple  $Q$ -meter continuous-wave spectrometer with the electron-spin and reference nuclear resonances observed without changing any rf circuit parameters. Adequate signal-to-noise ratio for the broad (several gauss) nuclear resonances required a large sample of  $\sim 0.5$  g. Typical 37 MHz spin resonance (ESR) and nuclear magnetic resonance (NMR) signals are shown in Fig. 1.

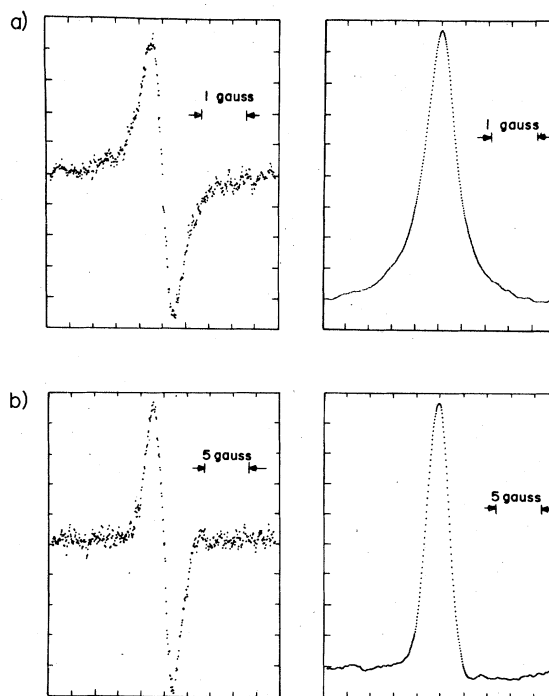


FIG. 1. Typical magnetic resonance data from the 37 MHz Schumacher-Slichter experiment (a) ESR data;  $dX''/dH$  (arb. units) vs  $H$  (gauss) on left, and  $X''$  (arb. units) vs  $H$  (gauss) on right. (b) NMR data;  $dX''/dH$  (arb. units) vs  $H$  (gauss) on left, and  $X''$  (arb. units) vs  $H$  (gauss) on right.

Because of the high conductivity of the metallic heavily doped samples, spin susceptibility measurements must be done at rf frequencies with the NMR reference in order to normalize out any field nonuniformity resulting from the skin effect. For lightly doped samples where skin effect is not a problem, quantitative resonance measurements can be carried out at microwave frequencies using much smaller samples (a few milligrams). Therefore, a  $[\text{CH}(\text{AsF}_5)_{0.006}]_x$  spin susceptibility measurement was performed at 10 GHz in a standard reflection ESR spectrometer. The reference resonance was  $\text{Cr}^{3+}$  ( $\sim 0.5\%$ ) in  $\text{Al}_2\text{O}_3$  (ruby) placed in a  $\text{TE}_{102}$  cavity with  $\sim 1$  mg of the polyacetylene in an equivalent position in the cavity. The ruby susceptibility was independently calibrated with respect to  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  standards. Temperature dependence of the polyacetylene susceptibility was obtained assuming a Curie law for the ruby standard over the range 77–295 K with the temperature being measured by a Ge diode thermometer mounted on top of the cavity. The  $\text{Cr}^{3+}$  resonance in  $\text{Al}_2\text{O}_3$  has an orientation-dependent  $g$  value so that the reference resonance was easily separated from the polyacetylene resonance by proper orientation of the cavity in the static magnetic field. The susceptibility of a  $[\text{CH}(\text{AsF}_5)_{0.006}]_x$  film was measured at several temperatures in this fashion. For comparison we also carried out measurements at 77 and 295 K on undoped *trans*-( $\text{CH}$ ) $_x$  (previously shown to be Curie Law)<sup>8,9</sup> using a piece of the undoped polymer from which the doped sample was made.

In both the rf and the microwave spin-resonance spectrometers field modulation lock-in detection techniques were employed. The lock-ins were interfaced directly to a DEC PDP 11/40 minicomputer which recorded the first derivative absorption curves and performed the numerical integrations. The 37 MHz polyacetylene ESR line occurred at  $H_0 \sim 10\text{G}$  with a width  $\Delta H \sim 0.5\text{G}$ . It had a Lorentzian shape characteristic of solutions to Bloch's equations. The inequality  $\Delta H \ll H_0$  was rigorously satisfied for the 10 GHz ESR lines and the 37 MHz NMR lines as these resonances all occurred at static fields ( $H_0$ ) of several kiloGauss which were large compared to all line widths. Thus, the spin susceptibility could be obtained directly from integration of the resonance curves.<sup>17</sup>

### III. RESULTS

The results of the Faraday balance measurements are listed in Table I and plotted in Fig. 2. Values of the concentrations of ferromagnetic impurities were obtained from a Honda plot analysis.  $N_{\text{Curie}}$ , the concentration of spin- $\frac{1}{2}$  local magnetic moments was obtained by fitting the temperature-dependent susceptibilities to the form  $\chi(T) = \chi_0 + C/T$ .

The measured total susceptibilities for all samples studied were diamagnetic indicating the dominance of atomic core contributions. The diagonal line in Fig. 2 represents an estimate of the diamagnetic core susceptibility of  $[\text{CH}(\text{AsF}_5)_y]_x$  as derived from Pascal's

TABLE I. Static magnetic susceptibility of  $[\text{CH}(\text{AsF}_5)_y]_x$  (Faraday balance).

$y$	$\chi_{\text{meas}}$ (290 K) <sup>a</sup>	$f$ <sup>b</sup>	$N_{\text{Curie}}$ <sup>c</sup>	$\chi_{\text{Pascal}}$ <sup>d</sup>	$\frac{C^e}{T}$ (290 K)	$N^f$ ( $E_F$ )
0	-5.0	5	g	-6.2	g	...
0.005	-6.3	3	360	-6.5	0.47	...
0.011	-6.8	1	g	-7.0	g	...
0.016	-6.7	2	130	-7.3	0.17	0.014
0.04	-5.6	3	<280	-9.2	<0.36	0.11
0.07	-6.8	2	<70	-11.4	<0.09	0.14
0.10	-6.2	15	<140	-13.6	<0.18	0.23
0.13	-9.8	2	g	-15.6	g	0.18

<sup>a,d,e</sup>Units of  $10^{-6}$ (emu/mole-carbon).

<sup>b</sup>Ferromagnetic impurities #Fe / $10^6$  C-atoms.

<sup>c,e</sup>Fitting of  $\chi_{\text{meas}}$  to  $\chi_{\text{meas}}^{(T)} = \chi_0 + C/T$ ,  $N_{\text{Curie}}$  in units of #/ $10^6$  C-atoms.

<sup>d</sup> $\chi_{\text{Pascal}} = -(6.2 + 74.5y) \times 10^{-6}$  emu/mole-carbon; assumes pentavalent As; and a standard correction of  $+2.75 \times 10^{-6}$  emu/mole corresponding to 0.5 double bond/C-atom.

<sup>f</sup>Fermi-surface density of states from  $\chi_{\text{meas}} - \chi_{\text{Pascal}} - C/T = \mu_B^2 N(E_F)$  in units states/eV-carbon atom.

<sup>g</sup>Measurements carried out at room temperature only.

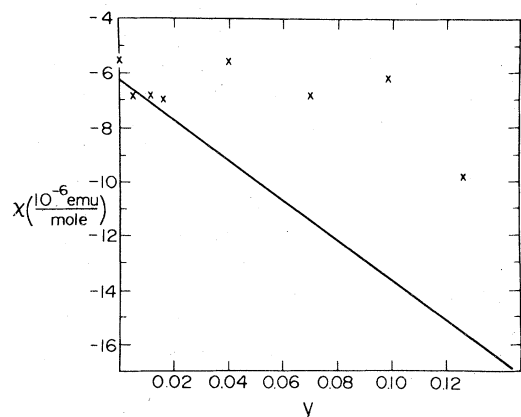


FIG. 2. Static total magnetic susceptibility of  $[\text{CH}(\text{AsF}_5)_y]_x$  (290 K, Faraday balance). The solid line represents the diamagnetic contribution from  $\text{AsF}_5$  as estimated from Pascal's constants (see Ref. 18).

constants.<sup>18</sup> The plotted values for the lightly doped samples ( $y \leq 0.016$ ) have been corrected for the observed paramagnetic Curie term  $C/T$ . The results agree well with the predicted diamagnetic core susceptibilities. For concentrations  $y > 0.02$ , paramagnetic deviations from the diamagnetic background are observed. This may be interpreted as a transition to metallic behavior. This hypothesis is further supported by the temperature independence of this paramagnetic contribution at high doping levels as illustrated in Fig. 3 which compares the temperature dependence of the susceptibility for samples with dopant concentrations above and below the critical concentration ( $y_c$ ) for the SM transition. For  $y < y_c$ , the residual weak Curie law from the defects in the undoped  $(\text{CH})_x$  is evident, decreasing in magnitude as  $y \rightarrow y_c$ .

Treating the paramagnetic deviation from the prediction of Pascal's constants as a Pauli susceptibility, from Eq. (1) the Fermi-surface density of states  $N(E_F)$  is obtained,

$$\chi_{\text{meas}} - \chi_{\text{Pascal}} = \mu_B^2 N(E_F) \quad (1)$$

These results are plotted in Fig. 4. Anisotropies found in the electrical and optical properties of partially oriented films suggest that heavily doped polyacetylene may be described as a quasi-one-dimensional metal. Theoretical one-dimensional band structures predict a divergence in the density of states at the band edge. Plotted in Fig. 4 for comparison is the Fermi-surface density of states for  $[\text{CH}(\text{AsF}_5)_y]_x$  in a one-dimensional rigid-band model assuming  $m^*/m = 1$  and one free hole generated per  $\text{AsF}_5$ . Clearly, the experimental results give no indication of such a one-dimensional band-edge anomaly.

A possible explanation of this result is that above

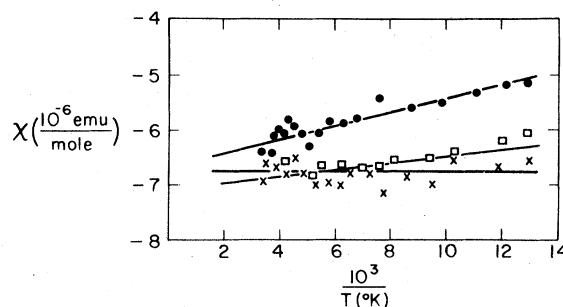


FIG. 3. Representative  $\chi(T)$  for samples above and below the semiconductor-metal transition (Faraday balance).  $\bullet \bullet \bullet$   $[\text{CH}(\text{AsF}_5)_{0.005}]_x$ ,  $\square \square \square$   $[\text{CH}(\text{AsF}_5)_{0.016}]_x$ ,  $\times \times \times$   $[\text{CH}(\text{AsF}_5)_{0.07}]_x$ . Note that for  $[\text{CH}(\text{AsF}_5)_y]_x$  with  $y = 0.04$  and  $0.10$ , the susceptibility is temperature independent as indicated in Table I.

the SM transition bond alternation and the associated energy gap no longer exist. That is, the band structure is that of a one-dimensional metal with a half-filled conduction band. The dashed line in Fig. 4 represents a calculation of  $N(E_F)$  for such a half-filled band in a simple tight-binding model with transfer integral 2.25 eV.<sup>11</sup> Raman spectra of metallic iodine doped  $(\text{CH})_x$ ,<sup>19</sup> however, continue to show the two absorption bands identified with C=C and C-C stretching modes with only minor frequency shifts compared with the pure polymer. Moreover, optical absorption and reflection data imply that the interband transition is present above the SM transition. Thus bond alternation persists into the metallic regime. On the other hand, x-ray photoemission studies<sup>20</sup> indicate nonuniform doping at the highest concentrations. An inhomogeneous metallic state with undistorted metallic domains coexistent with regions of bond-alternated semiconductor is consistent with the data.

Alternatively, the small density of states may result from interchain coupling. From theoretical and spectroscopic studies of short chain polyenes and related ring compounds such as benzene, the  $\pi$ -system transfer integral can be estimated as 2–2.5 eV corresponding to a C-C interchain distance of  $\sim 1.4 \text{ \AA}$ . In contrast, the interchain distance is approximately  $4.4 \text{ \AA}$ ,<sup>21</sup> even greater than the intermolecular distances in molecular crystals such as TTF-TCNQ (tetrathiafulvalenium-tetracyanoquinodimethan), implying a small transverse integral of no more than a few tenths of an eV. It has been suggested,<sup>10</sup> however, that even this small amount of three-dimensional coupling is sufficient to quench the one-dimensional band-edge divergence in the density of states.

Also shown in Fig. 4 are the results of the measurements of the spin susceptibility of a heavily

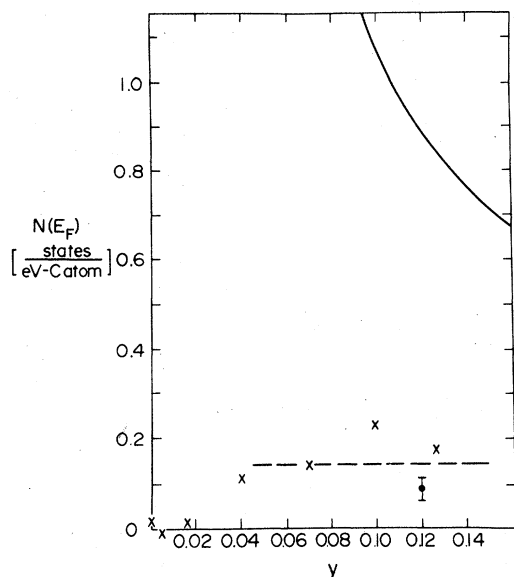


FIG. 4. Fermi-surface density of states vs  $\text{AsF}_5$  concentration. The solid curve represents a rigid band one-dimensional density of state ( $m^*/m=1$ ). The dashed curve would result from a half-filled simple tight-binding band with transfer integral  $t=2.25$  eV (bandwidth of 9 eV).  $\times$  Faraday balance data;  $\bullet$  Schumacher-Slichter.

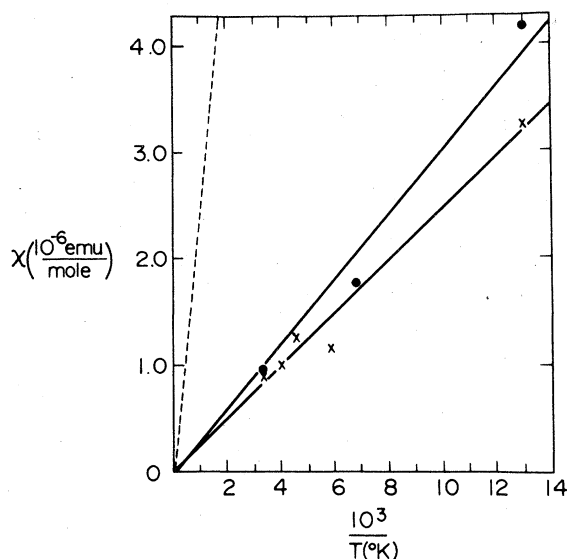


FIG. 5. Spin susceptibility of nonmetallic  $(\text{CH})_x$ :  $\bullet\bullet\bullet$  undoped sample,  $\times\times\times$   $[\text{CH}(\text{AsF}_5)_{0.006}]_x$ . Both samples were from same batch of undoped polymer. The dotted line represents the Curie law expected for  $y=0.006$  assuming  $\text{AsF}_5^-$  with spin  $\frac{1}{2}$ .

doped,  $[\text{CH}(\text{AsF}_5)_{0.12}]_x$ , sample using the Schumacher-Slichter technique. The agreement with the Faraday balance results is satisfactory given the uncertainty in the diamagnetic corrections. At heavy doping levels, core diamagnetism still dominates the total susceptibility so that the value obtained for the Pauli term is very dependent on the accuracy of the core diamagnetism estimate from Pascal's constants. Two different nuclear signals were employed as references:  $\text{F}^{19}$  and  $\text{H}^1$ . Repeated traces were taken on two different samples and spin susceptibility results with  $\text{H}^1$  as the reference were consistently 20–35% lower than those with  $\text{F}^{19}$  as the reference. The proton line is somewhat broader than the fluorine and pulsed NMR measurements yield comparable  $T_1$ 's. However, care in the choice of rf level was taken to avoid saturating either line during the measurement. Small errors in stoichiometry could account for the discrepancy (e.g., due to oxidation or loss of  $\text{AsF}_5$ ). Some loss of  $\text{AsF}_5$  was observed qualitatively over an extended period of about two months as indicated by a slight clouding of the glass sample tube.

The Pauli susceptibility of  $[\text{CH}(\text{AsF}_5)_y]_x$  seems to turn on continuously at  $\text{AsF}_5$  concentrations of a few atomic percent. Within the limits of experimental uncertainty the susceptibility of  $[\text{CH}(\text{AsF}_5)_{0.04}]_x$  is temperature independent (77–295 K). Therefore, the results of this work provide no evidence of strong correlation enhancement of the spin susceptibility near the SM transition.

The 10 GHz resonance measurements on a lightly doped sample ( $y=0.006$ ) and undoped  $\text{trans}-(\text{CH})_x$  are shown in Fig. 5. Both samples exhibited Curie-like susceptibilities between 77 and 295 K. Assuming  $S=\frac{1}{2}$  for the observed spins, the concentrations of unpaired local moments are 850 and 630 per  $10^6$  carbon atoms for  $y=0$  and 0.006, respectively. The local-moment concentration in undoped  $\text{trans}-(\text{CH})_x$  is roughly consistent with previous measurements by Shirakawa<sup>9</sup> and Goldberg<sup>10</sup> of 300/ $10^6$  carbon atoms. Differences are probably due to minor variations in film preparation and isomerization. Significantly, however, the  $\text{trans}-(\text{CH})_x$  showed no enhanced local-moment concentration upon doping. Shown also in Fig. 4 (dashed line) is the Curie-law susceptibility which would correspond to one unpaired spin generated per  $\text{AsF}_5$  for  $y=0.006$ . From these results we conclude that the localized states induced by light doping below the SM transition are nonmagnetic. This result is confirmed by the Faraday balance measurements shown in Fig. 3. The residual weak Curie law from the defects in the undoped  $(\text{CH})_x$  decreases in magnitude as  $y$  increases (below  $y_c$ ) rather than increasing in proportion to the dopant concentration.

The simplest model of the localized donor or acceptor state at light doping ( $y < y_c$ ) follows the traditional semiconductor approach and pictures the elec-

tron or hole, with an effective mass determined by the band structure, loosely bound to the charged center by Coulomb forces in a dielectric medium. In lightly doped  $(\text{CH})_x$ , instead of substitutionally replacing the host as in silicon, the impurity resides very close to the polymer chain, on the surface of the 200 Å fibrils and/or between individual chains. At light doping levels we assume isolated impurities interacting with a single polymer chain. At heavy doping levels impurity interactions will become important, however, well below the SM transition this should not be a problem. The impurity could either donate an electron to, or accept an electron from the chain. In the acceptor case (relevant to  $\text{AsF}_5$  doping), the hole on the chain would be free to delocalize if it were not for the Coulomb binding to the impurity. The resulting localized states are bound states of the hole on the polymer chain in the vicinity of the charged donor or acceptor ion. The binding energies of such quasi-one-dimensional hydrogenic impurity states have been shown<sup>22</sup> to be the same as for donors and acceptors in traditional semiconductors.

In the context of the magnetic studies of this paper, the magnetic properties of such localized bound states are of importance. Because of the spin degeneracy of a single hole (or electron) in a localized state, the magnetic susceptibility would be expected to obey a Curie law. Double occupancy of such weakly bound states in the gap is inhibited by electron-electron Coulomb interactions. However the experimental results (see Figs. 3 and 5) clearly demonstrate that the localized states induced by light doping below the SM transition are nonmagnetic.

Several possible explanations of the absence of magnetic moments for localized hole states in lightly doped  $[\text{CH}(\text{AsF}_5)_y]_x$  can be considered. Double occupancy of such states will lead to spin pairing and corresponding diamagnetism. However, as indicated above electron-electron Coulomb repulsion inhibits double occupancy. Since estimates of the one-electron binding energy<sup>22</sup> yield  $E_B \approx 0.1$  eV, the doubly occupied configuration would surely be ionized at room temperature.

Nonmagnetic doubly occupied states can also occur by means of a continuum of states in the gap, resulting from disorder. Such effects must certainly be considered in the present case, since the  $(\text{CH})_x$  films are only partially crystalline<sup>8,15,21</sup> (~80%) before doping. In such a case, the Fermi level may be determined by the disorder induced states in the gap rather than the impurity induced states. As a result, the impurity states would not be occupied and thus would be nonmagnetic. However the observation of doping phenomena at very dilute levels<sup>2-6</sup> argues against such an explanation. For example, dramatic increases in electrical conductivity are observed at dopant levels well below 0.1%. Moreover, well-defined infrared absorption modes are observed upon

doping at impurity concentrations in the range  $0.01\% < y < 0.1\%$ .<sup>22</sup> Thus, the gap is evidently relatively free of disorder induced states. Moreover, *p-n* junction<sup>7</sup> and Schottky barrier formation<sup>23</sup> have been observed implying that doping can be used to set the Fermi level. These results imply that the Fermi level is determined by the localized states induced by doping at least in the range of 0.1% or greater so that such states should be occupied and therefore magnetic.

The situation is somewhat complicated by uncertainties in our knowledge of the  $\text{AsF}_5$  dopant species. Since  $\text{AsF}_5$  has an even number of electrons,  $\text{AsF}_5^-$  would have an unpaired spin with a Curie-law susceptibility. However the absence of a Curie law at all doping levels is inconsistent with the formation of  $\text{AsF}_5^-$ . Measurements of the static magnetic susceptibility of the metallic  $\text{AsF}_5$ -intercalated graphite compound<sup>24</sup>  $\text{C}_8\text{AsF}_5$  similarly show no trace of paramagnetic  $\text{AsF}_5^-$ . Anderson model<sup>25</sup> formation of a virtual nonmagnetic bound state due to mixing of the localized level with conduction states was suggested.<sup>23</sup> Such a model could explain the lack of Curie-law paramagnetism in heavily doped  $(\text{CH})_x$  but fails for lightly doped nonmetallic samples for which no unoccupied band states exist at the Fermi level. Interpretation of valence electron photoemission and chemical shift data<sup>20</sup> leads to the conclusion that the chemisorbed species are not simple molecular entities like  $\text{AsF}_5^-$  but may be  $\text{AsF}_6^-$  or more complex species, e.g.,  $(\text{As}_2\text{F}_{10})^{2-}$ , which exhibit a net As:F ratio near 1:5. It is conceivable that the spin on the chain and that on the impurity couple antiferromagnetically quenching any magnetism. This idea, however, seems improbable as the complete absence of any enhanced magnetism as high as 295 K would imply an exchange interaction and corresponding transfer integral (between the chain and the dopant ion) inconsistently large compared with the small measured binding energy of the impurity state.<sup>22</sup>

The bond-alternation energy gap in polyacetylene may be viewed as due to the  $2k_F$  instability in a quasi-one-dimensional metal.<sup>22</sup> The effect of charge transfer doping, then would be to change  $2k_F$  to preserve the energy gap at the Fermi level. However, since  $(\text{CH})_x$  corresponds to the half-filled band case (one  $\pi$  electron per carbon atom), doping would pull the resultant charge-density wave (CDW) condensate out of commensurability with the lattice with an accompanying loss of commensurability energy. To avoid this loss of energy, the CDW could remain commensurate with the lattice except in localized domain-wall regions. The result would be a soliton-like kink in the bond-alternated structure. Although similar to the phase-kink excitations of the CDW studied earlier,<sup>26-31</sup> the domain wall would in general involve both amplitude and phase distortions and would be present in the ground state of the system.

Soliton kinks of  $\pi$  and  $2\pi$  are conceivable as illustrated in Figs. 6(a) and 6(b). The former represents the removal of one  $\pi$  electron, the latter two  $\pi$  electrons (an entire  $\pi$  bond). Significantly, both structures have *no* unpaired spins so that this doping model would predict no enhanced local-moment concentration due to doping. Fig. 6(c) shows a  $\pi$  kink in *undoped trans*-(CH)<sub>x</sub>. Note that such a structure has an uncharged magnetic defect which could be the source of the observed spin resonance in undoped *trans*-(CH)<sub>x</sub>.<sup>9</sup>

#### IV. CONCLUSIONS

To summarize, the magnetic susceptibility of heavily doped [CH(AsF<sub>5</sub>)<sub>y</sub>]<sub>x</sub> contains a temperature-independent paramagnetic contribution, suggestive of Pauli conduction-electron paramagnetism. The onset of this term indicates a transition from the semiconducting to the metallic state at a dopant level of ~2 at. %. The metallic polymer films have small Fermi-surface densities of states [ $N(E_F) \approx 0.1$  state/eV/C atom] consistent with either the model of a broad band quasi-one-dimensional metal in which the band-edge divergence in the density of states has been quenched by a small amount of transverse coupling or that of a nondistorted uniform bond length metal. The smooth turn on and temperature independence of the small Pauli susceptibility provides no indication of the effects of electron-electron correlations.

The lightly doped semiconducting polymers have anomalously small Curie-law susceptibility components indicating that the localized states induced by doping below the semiconductor-metal transition are nonmagnetic. Several possible explanations are discussed. Of particular interest is the possibility of soliton doping; viewing (CH)<sub>x</sub> as a quasi-one-dimensional metal driven semiconducting by the

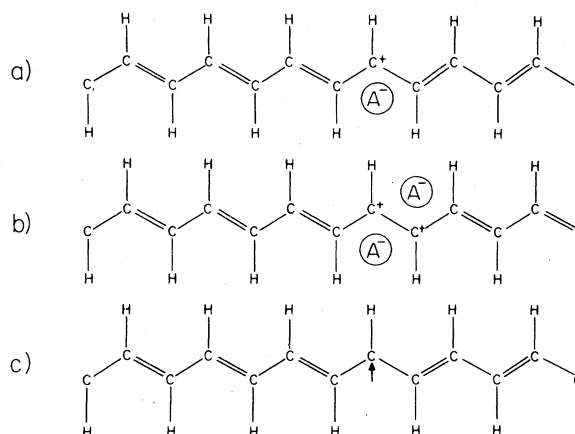


FIG. 6. Kink defects in *trans*-(CH)<sub>x</sub>. (a)  $\pi$  kink with charge transfer. (b)  $2\pi$  kink. (c)  $\pi$  kink neutral defect in *undoped trans*-(CH)<sub>x</sub> showing unpaired spin;  $A^-$  represents charged acceptor molecules. For simplicity, the phase kinks are shown localized to one lattice site. In general, such kinks will be spread over several lattice sites similar to domain walls.

Peierls instability leads to localized domain-wall-like charged donor-acceptor states induced through charge transfer doping.

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