

Solitons in Polyacetylene: Magnetic Susceptibility

S. Ikehata,^{(a),(c)} J. Kaufer,^(a) T. Woerner,^(b) A. Pron,^(b) M. A. Druy,^(b)
A. Sivak,^(b) A. J. Heeger,^(a) and A. G. MacDiarmid^(b)

Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104
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The absolute spin susceptibility of AsF₅-doped *trans*-polyacetylene, [CH(AsF₅)_y]_x, was determined by spin resonance techniques for 0.0004 ≤ y ≤ 0.138. The Curie-law contribution decreases above y = 0.001 to a level less than 1 ppm in the highly conducting regime. The temperature-independent Pauli term is small (≤ 5 × 10⁻⁸ emu/mole) for y < 0.01, remains small up to y = 0.05, and shows an abrupt increase near y = 0.07 to a value of ~ 3 × 10⁻⁶ emu/mole at higher concentrations. The results are consistent with the soliton doping mechanism.

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The possibility of doping through the generation of nonlinear solitons^{1,2} in polyacetylene, (CH)_x, has attracted considerable attention in recent studies. Experimental results from measurements of the magnetic,^{3,4} infrared,^{5,6} optical,⁷ and phototransport⁸ properties of lightly doped samples are in agreement with the soliton mechanism. On the other hand, Tomkiewicz *et al.*⁹ have presented evidence against solitons in (CH)_x. They argue, from measurements of the magnetic susceptibility (χ) at a concentration near y = 0.009, that the properties of doped (CH)_x are determined by an inhomogeneous mixture of metallic islands even at light doping levels, and that the semiconductor-metal (SM) transition is caused by the percolation of such metallic islands. The importance of the magnetic properties has caused us to reexamine the behavior of the susceptibility in a series of samples carefully prepared to achieve maximum uniformity. In this Letter, we present our results from direct measurements of spin susceptibilities of AsF₅-doped *trans*-(CH)_x, i.e., [CH(AsF₅)_y]_x, over the full range from 0.0004 ≤ y ≤ 0.138, well into the high-conductivity regime. Our results are fully consistent with the soliton doping mechanism and indicate that the SM transition is not due to percolation of metallic regions.

(CH)_x films were prepared at -78 °C¹⁰; 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 12 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 12 h the lower cold finger was held at -196 °C for 12 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 12 h, thus repeating the doping process a second time. This entire procedure was repeated a total of 4 times, and after final cryogenic pumping for 12 h, 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 [CH_{1.03}(AsF_{5.98})_{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, this method assures the presence of the AsF₆⁻ species.¹¹

For lightly doped samples (y ≤ 0.0055), the spin susceptibilities were obtained using a standard 10-GHz microwave reflection spectrometer. Absolute susceptibilities were obtained through calibration with a ruby (Cr³⁺ in Al₂O₃) standard. In the higher conductivity regime (y ≥ 0.0055), the technique of Schumacher and Slichter (SS) was used. The ¹H and ¹⁹F NMR and the spin reso-

nance were carried out at 10 MHz using a simple Q -meter continuous-wave spectrometer. The use of the SS technique in the conducting regime was facilitated by the narrow ESR linewidth (~ 0.5 G) and avoided any skin depth problems.

Samples prepared in this manner have a more sharply defined SM transition as a function of y and show higher electrical conductivities in the translational region. For example at $y = 0.002$ we found $\sigma = 0.5 \Omega^{-1}\text{-cm}^{-1}$, and at $y = 0.02$ we found $\sigma = 30 \Omega^{-1}\text{-cm}^{-1}$. These values are much larger than those obtained earlier¹² with use of the more rapid doping (by more than three orders of magnitude for $y = 0.002$ and by more than one order of magnitude for $y = 0.02$). At higher (and lower) concentrations, the conductivities were typical of doped polyacetylene. The thermopower was measured as function of y for the samples prepared for susceptibility measurements as described above. The transition to metallic behavior is more abrupt as a function of y and occurs at a lower concentration than obtained earlier¹² with standard doping procedures. For example, at $y = 0.0004$, $S = 840 \mu\text{V}/^\circ\text{K}$ and at $y = 0.0025$, $S = 20 \mu\text{V}/^\circ\text{K}$ whereas in earlier studies such small values were not achieved until $y > 0.01$. We conclude that for $0.001 < y < 0.02$, the electrical properties are particularly sensitive to the doping process. Inhomogeneous doping can occur resulting in lower-quality electrical properties and a smeared SM transition. The doping technique de-

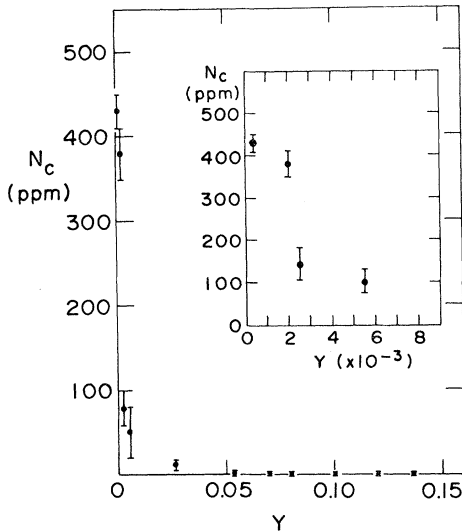


FIG. 1. Concentration (in parts per million, ppm) of Curie-law spins (N_C) as a function of dopant concentration y . The low doping range is shown on an expanded scale in the inset.

scribed above appears to minimize the occurrence of such inhomogeneities.

The measured spin susceptibilities were fitted with

$$\chi(T) = \chi_P + N_C \mu_B^2 / k_B T,$$

where χ_P , N_C , μ_B , and k_B are the Pauli susceptibility, number of unpaired spins, the Bohr magneton, and Boltzmann's constant, respectively. The concentration dependence of N_C is illustrated in Fig. 1; N_C begins to decrease on doping for $y > 0.001$ and falls rapidly with continued doping in agreement with the earlier results of Weinberger *et al.*¹³ In the more heavily doped samples, the spin susceptibility is almost independent of temperature. Typical values for $y = 0.053$ are listed in Table I, implying $N_C < 1$ ppm.

The temperature-independent Pauli susceptibility is shown in Fig. 2 as a function of y ; χ_P is small at all concentrations below $y = 0.053$. At concentrations below $y = 0.005$ the accuracy is limited by the finite Curie-law contribution. However, for each of the low-concentration data points with $y < 0.01$, $\chi_P < 5 \times 10^{-8}$ emu/mole. At higher concentration a finite χ_P emerges; e.g., at $y = 0.053$, $\chi_P = (5 \pm 3) \times 10^{-8}$ emu/mole. The 5.3% sample was cross-checked by comparing the independent results obtained with use of ^1H and ^{19}F as standards; values agreed to within the error. The Pauli term increases rapidly above $y = 0.07$ to a value of about 3×10^{-6} emu/mole at the highest doping levels, in agreement with the results of Weinberger *et al.*¹³ The onset of χ_P is more clearly defined in Fig. 2 and occurs at a somewhat higher value of y (7% here as opposed to $\sim 4\%$ ¹³). This is consistent with the transport data which also yield a smeared transition for rapidly doped samples.¹²

A heavily doped sample (10%) was prepared using *cis*-(CH)_x starting material. The resulting $\chi_P \approx 4.7 \times 10^{-6}$ emu/mole is in agreement with the high-concentration data in Fig. 2 and is consistent with earlier observations^{14,15} of *cis-trans* isomerization during doping.

TABLE I. Susceptibilities for $[\text{CH}(\text{AsF}_6)_{0.053}]_x$ measured at three temperatures.

T (K)	χ_s (10^{-8} emu/mole)
300	6 ± 3
77	5 ± 3
4.2	11 ± 3

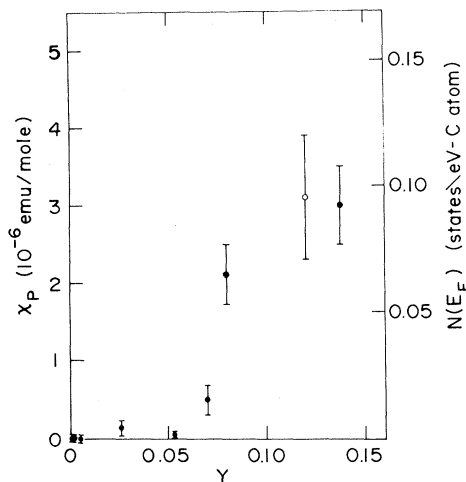


FIG. 2. Pauli susceptibility χ_P vs y . The right-hand scale gives the implied density of states of the Fermi energy. The open-circle datum point is from Ref. 13.

In the transition region χ_P appears to be particularly sensitive to the doping procedure; e.g., $y = 0.026$ gave $\chi_P \approx 10^{-7}$ emu/mole whereas at $y = 0.053$, χ_P was considerably smaller. Given the abrupt increase by two orders of magnitude (Fig. 2), fluctuations in y due to inhomogeneous doping could easily result in an apparent continuous increase. Such fluctuations may well be the source of any residual χ_P for y below ~ 0.05 .

In an attempt to verify that the EPR technique measures all the susceptibility a sample with $y = 0.053$ was placed in an EPR tube and examined with a high sensitivity microwave spectrometer. By turning up the gain and using optimum modulation, a signal-to-noise ratio greater than 10^4 was achieved. No signal other than the narrow $g = 2$ line was observed. In all cases where measurements were carried out at 10 MHz and 10 GHz, the linewidth was the same at both frequencies.

Our results for lightly doped samples are consistent with the soliton doping mechanism²; the Curie-law contribution decreases upon doping, but the Pauli susceptibility is small and apparently zero in the limit of completely homogeneous doping. Thus the localized states generated by dilute doping are nonmagnetic. In view of the dramatic increase in electrical conductivity, we conclude that the charge carriers are spinless. Intuitive arguments would suggest that N_C would begin to decrease when y is approximately equal to the concentration of neutral solitons (~ 400 ppm or $y = 0.0004$). Figure 2 shows the expected decrease, but N_C does not decrease significantly

until $y > 0.001$. The higher experimental value may result from the diffusion kinetics of the dopant molecule into the chain. Even though it would be energetically favorable to ionize a neutral soliton in the center of a fibril, charged solitons may be generated first by charge transfer on the outer portions of the fibril.

χ_P remains small even in the high-conductivity regime as shown for $y = 0.053$ in Table I. The onset of "metallic" behavior is not observed in χ_P until $y > 0.07$, whereas the transport data imply a critical concentration more than an order of magnitude lower. This behavior is inconsistent with the proposal⁹ that the SM transition is due to percolation through metallic islands. In that case, χ_P would turn on smoothly at y well below the percolation threshold indicated by electrical measurements, whereas the data show precisely the opposite behavior.

The small χ_P for $y < 0.05$ is not consistent with the results reported earlier by Tomkiewicz *et al.*⁹ Their higher values apparently result from inhomogeneous doping as suggested in their paper. However, our studies show that these inhomogeneities can be avoided [at least using *trans*-(CH)_x] leading to higher quality electrical properties and a sharp threshold for the onset of χ_P . Thus, our earlier conclusion¹³ that the charge carriers are nonmagnetic at low doping levels is confirmed.

The concentration range $0.005 < y < 0.05$ is of particular interest; χ_P has not turned on, whereas the transport data indicate an excellent conductor. The existence of spinless charge carriers seems to persist well into the highly conducting region where an independent-soliton picture would be inadequate. The increase observed in χ_P near $y = 0.07$ may signify the closing of the energy gap and the onset of single-particle metallic behavior. At higher concentrations, the magnitude of χ_P coincides approximately with that expected from the single-particle band picture.¹⁶

In summary, we have determined the absolute spin susceptibility of $[\text{CH}(\text{AsF}_5)_y]_x$ over the full doping range. For dilute doping, the decrease of the Curie-law contribution with no Pauli susceptibility has been demonstrated: The charge carriers are spinless consistent with the soliton doping mechanism. The Pauli susceptibility remains small well into the highly conducting regime and shows an abrupt increase near $y \approx 0.07$ to values typical of simple metallic behavior. The intermediate range, $0.005 < y < 0.05$, is thus of particular interest, for it can be viewed as a high-conductivity state generated by charged solitons at high

density. The development of a theoretical understanding of the semiconductor-metal transition beginning from the soliton concept remains as a fascinating and important problem.

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^(a)Also at Department of Physics, University of Pennsylvania, Philadelphia, Pa. 19104.

^(b)Also at Department of Chemistry, University of Pennsylvania, Philadelphia, Pa. 19104.

^(c)Permanent address: Department of Physics, University of Tokyo, Tokyo 113, Japan.

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Definite Experimental Evidence against Intrinsic Electron-Hole Superconductivity in Pure CuCl

B. Batlogg and J. P. Remeika

Bell Laboratories, Murray Hill, New Jersey 07974

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Optical absorption measurements on very pure CuCl single crystals, prepared by a novel process, show the exponential drop of the *direct* optical absorption edge to continue below an absorption coefficient $K \sim 10^{-2} \text{ cm}^{-1}$. This rules out unambiguously the existence of an *indirect*-gap absorption below 3 eV, which is not only consistent with band-structure calculations but also excludes pure CuCl from being a suitable candidate for intrinsic high- T_c superconductivity (on the grounds of existing theories).

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Studies of excitons, phonons, piezoelectricity, and ionic conductivity have maintained a steady interest in CuCl for more than two decades. But CuCl suddenly stepped into the limelight when diamagnetic anomalies at as high a temperature as ~ 200 K were reported for a few samples and speculatively assigned to a Meissner-Ochsenfeld effect.¹⁻⁴ So far the theories invoked to explain such an observation of superconductivity in CuCl rely on the existence of a narrow energy gap and the associated excitons.

In a first class of theories (the "extrinsic" way), the electrons in *metallic Cu precipitates* form pairs via exchange of virtual excitons in the adjacent insulating CuCl.⁵⁻⁷ In contrast to this extrinsic mechanism, a second ("intrinsic") possibility for superconductivity in bulk CuCl has also been discussed.⁸⁻¹⁰ If one assumes that the conduction and valence bands cross at different points in reciprocal-lattice space (in CuCl after application of pressure) and the resulting holes are very much heavier than the electrons, then