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# Solitons at high density in *trans*-$(CH)_x$: Collective transport by mobile, spinless charged solitons

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Coordinated measurements of the magnetic susceptibility, optical absorption, and dc conductivity on the same samples of $[(Na^+)_y(CH)^{y-}]_x$ in a sealed apparatus demonstrate that the Pauli susceptibility remains small ($<10^{-8}$ emu/mole) for $y<0.05$. These data imply that the excess charge is stored in spinless soliton states and that the electrical conductivity arises directly from transport of charged solitons.

The possibility that solitonlike excitations of the coupled electron-lattice system may play an important role in the physics of *trans*-$(CH)_x$ has recently stimulated considerable research activity.[1] Photogeneration studies demonstrated that the charged photoexcitations have all the spectroscopic signatures[2–6] predicted for solitons[7–10] and that these excitations obey the reversed spin-charge relation[7] *unique* to charged solitons.[11] The one-to-one correspondence between the photoinduced features[5] and those induced by doping[12,13] indicate that charge-transfer doping also takes place through the formation of charged soliton pairs.

Because of the complications which arise from the possibility of nonuniform doping, and from uncertainty in the precise nature of the dopant species (e.g., $AsF_4^-$ and/or $AsF_6^-$), the mechanism of the semiconductor-metal transition and the nature of the transitional regime have been controversial. Ikehata *et al.*[14] were the first to present data indicating that the magnetic susceptibility ($\chi$) was insensitive to dopant concentration and remained much smaller than that of the metallic state throughout the translational regime ($\sim 1$ to 5 mole%). The simultaneous existence of high electrical conductivity ($\sigma$) in this regime led to the suggestion[15] that the conduction is due to unpinned charged solitons and that the final transition to truly metallic behavior occurred abruptly at dopant levels above 5 mole%. The persistance of the midgap transition and the soliton-induced infrared modes throughout this regime[16] provide support of this interpretation. On the other hand, Tomkiewicz *et al.*[17] presented data which showed a continuous increase in the Pauli susceptibility ($\chi_p$) and argued that this resulted from the continuous formation of metallic islands with the final transition to the metallic state being coincident with the percolation threshold.

*Through coordinated measurements of the magnetic susceptibility, optical properties, and dc conductivity on the same samples of* $[(Na^+)_y(CH)^{y-}]_x$ *in a sealed apparatus,* we demonstrate in this paper that $\chi_p$ remains small ($<10^{-8}$ emu/mole) for $y<0.05$. At $0.05<y<0.06$, we find an increase by more than two orders of magnitude to $\chi_p \simeq 2\times10^{-6}$ emu/mole, typical of the metallic state. The measured dc conductivity in the transitional regime is in the range 1 to 10 $\Omega^{-1}cm^{-1}$. These observations, together with the corresponding optical transmission data, lead us to conclude that (1) the excess charge is stored in soliton states, and (2) the conductivity arises directly from the transport of these charged solitons. Previous experimental difficulties have been avoided by using thin films of *trans*-$(CH)_x$ ($\sim 0.2$ $\mu$m) to optimize dopant uniformity. Uniform doping is assured both by the thin films and by the fact that the fibril diameters in such thin films are $\sim 50$ Å [compared with $>200$ Å for free standing $(CH)_x$ films].[18] Moreover, these thin films completely avoid the microwave skin depth problems which have complicated the analysis of earlier magnetic resonance data.[19]

Semitransparent *trans*-$(CH)_x$ films (thickness 0.1–0.3 $\mu$m) were synthesized on glass or quartz substrates. The chemical Na doping of *trans*-$(CH)_x$ was carried out by exposing to a solution of sodium benzophenone in tetrahydrofuron, $Na^+B^{\dot{-}}$ (THF),

$$(CH)_x + xyNa^+B^{\dot{-}} \rightarrow [(Na^+)_y(CH)^{y-}]_x + xyB \ .$$

Contrary to the complexities involved with $AsF_5$ or $I_2$ doping, the $Na^+$ species is a simple, closed-shell, nonreactive ion.

An apparatus was designed for *in situ* doping and measurement of ESR and optical spectra on the same sample in a completely sealed system. It was constructed with three "arms:" a quartz EPR tube containing the $(CH)_x$ film on substrate, a reservoir (10 cm long by 1 cm diameter), and a storage container (25 cm$^3$) for $Na^+B^{\dot{-}}$ solution. All three arms were sealed to a common connecting glass tube. With this, a technique was developed to carry out the doping, washing, and measurements entirely within the sealed system, avoiding any exposure to air. The apparatus used for the *in situ* combined measurements of $\sigma$ and optical transmission was similar except that the EPR tube was replaced by a rectangular tube containing the semitransparent $(CH)_x$ on a glass substrate onto which four gold contacts were evaporated prior to polymerization. Contacts to the gold electrodes were made with Pt wires which were brought out through a glass-metal seal. Again, this allowed doping, washing, and measurement entirely within the sealed system.

The visible–near-ir absorption measurements utilized a computer controlled McPherson EU700 spectrophotometer. The spin resonance measurements were made with an IBM Instruments E-200D ESR spectrometer, with sensitivity enhanced through a Nicolet 1270 signal averager. A National Bureau of Standards (NBS) ruby standard was attached to the EPR tube (near the sample) for calibration of absolute magnetic susceptibilities. Symmetric ESR lines and accurate $\chi$ values were obtained, since the sample thickness ($\simeq 2000$ Å) was much less than the microwave skin depth, even at the highest concentrations.

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Our methodology was to first obtain a visible-ir spectrum at each doping level to assure dopant uniformity and to determine the dopant concentration, using the previously published optical data obtained as a function of dopant concentration.[13] The apparatus was then immediately moved to carry out the ESR or $\sigma$ measurements. The sealed apparatus design resulted in excellent sample stability. Magnetic resonance data were monitored over several days and found to be fully reproducible. After the conductivity measurements, $\sigma$ was monitored over a period of several weeks with no significant change in value.

The room-temperature magnetic-susceptibility data are shown as a function of dopant concentration in Fig. 1. Each data point was obtained by direct comparison with the ruby standard. The $(CH)_x$ film area was directly measured, and the thickness was obtained from the magnitude of the optical density[12] prior to doping. The absolute susceptibilities obtained in this way were in excellent agreement with previously published values for both the undoped and fully metallic limits.[14,20,21] Moreover, the qualitative features of Fig. 1 are consistent with the results of Francois *et al.*[22] The corresponding ESR linewidth is shown versus $y$ in the inset to Fig. 1. In all cases, the ESR spectrum consisted of a single, symmetric line even through the linewidths in the transitional regime and the metallic regime differed by a factor of 20, *a result which demonstrates uniform doping.* The data in Fig. 1 were obtained from six completely independent experiments starting with the construction of a new sealed apparatus and a freshly prepared $(CH)_x$ film. The reproducibility is excellent.

The $y$ values $(Na^+)$ were obtained from the series of spectra shown in Fig. 2. Again, we found excellent stability; the spectra were reproducible over many days. Note that the midgap transition remains evident even at concentrations as high as 4.5%, implying the presence of solitons at high density.

As described earlier,[14,20,21] the initial susceptibility due to neutral solitons decreased with doping to a value averaging about $8\times10^{-8}$ emu/mole in the region for $0.005<y<0.04$. In this intermediate regime the linewidth (peak to peak) reduced to $\simeq 0.5$ G and then increased dramatically to $\simeq 9.5$ G in the metallic state. The broad line in the metallic state[23] for heavily doped $[(Na^+)_y(CH)^{y-}]_x$ arises from spin-flip scattering due to the relatively large spin-orbit coupling to the $Na^+$ ions. The narrow line $0.005<y<0.05$ therefore does not arise from metallic islands with locally high dopant concentrations. More importantly, temperature-dependence measurements of the narrow line show a Curie law with an upper limit for any $T$-independent $\chi_p < 10^{-8}$ emu/mole. As the linewidth and $\chi$ begin to increase, $\chi$ becomes $T$ independent; e.g., at 5.7%, $\chi_p = 3.5\times10^{-7}$ emu/mole. The narrow line with Curie-law susceptibility at $y<0.05$ implies a mobile neutral species (if it were charged, Coulomb binding to the $Na^+$ would yield a broad line comparable with that of the metallic state). The precise origin of this residual small Curie-law susceptibility is currently under investigation.

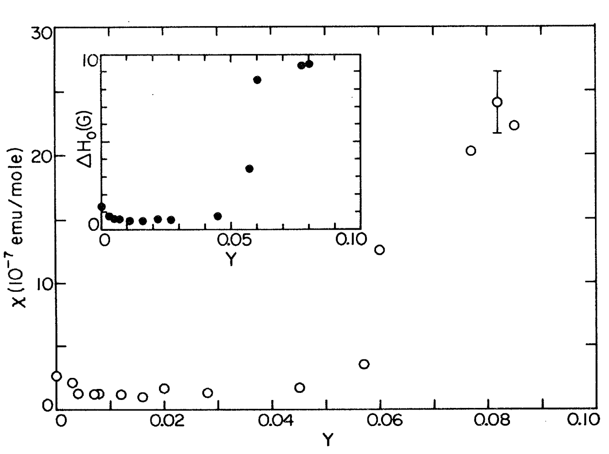

FIG. 1. Magnetic susceptibility (room temperature) for $[(Na^+)_y(CH)^{y-}]_x$ vs $y$. The inset shows the concentration dependence of the ESR linewidth.

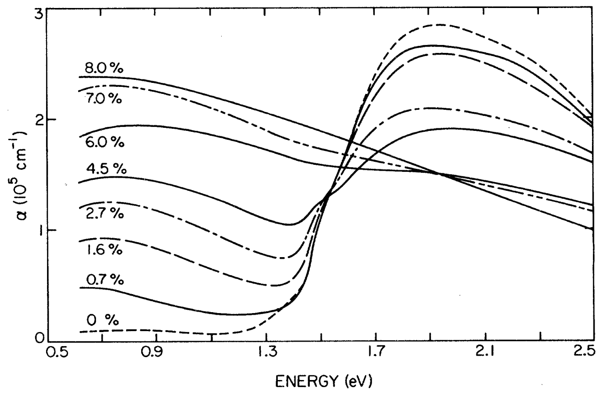

FIG. 2. Optical absorption coefficient ($\alpha$) vs photon energy for $[(Na^+)_y(CH)^{y-}]_x$. The data were obtained from the identical samples used in Fig. 1 (see text).

The results are summarized in Fig. 3, where we plot $\chi_p$

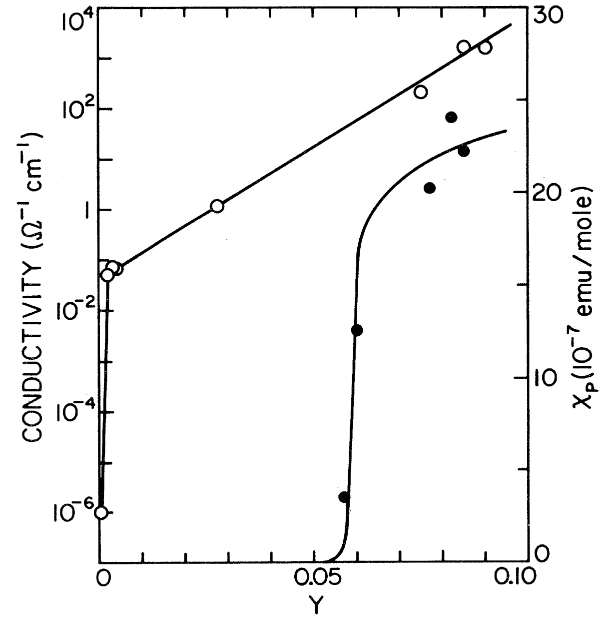

FIG. 3. $\chi_p$ vs $y$ (right-hand scale) and $\sigma_{dc}$ (300 K) vs $y$ (left-hand logarithmic scale). For $y<0.05$, $\chi_p<10^{-8}$ emu/mole.

(right-hand scale) and $\sigma$ (300 K) (left-hand logarithmic scale) for direct comparison. We conclude that $\chi_p < 10^{-8}$ emu/mole for $y < 0.05$, whereas $\sigma$ is quite high, e.g., $1-10\ \Omega^{-1}\mathrm{cm}^{-1}$ in the dopant range from 2–4 mole%. The quality of the sample and procedures can be further evaluated by noting that in the heavily doped metallic regime, $\sigma$ is in excess of $10^3\ \Omega^{-1}\mathrm{cm}^{-1}$, more than an order of magnitude greater than previously reported.[24]

Flood and Heeger[11] demonstrated that the charged species generated by photoexcitation are nonmagnetic. The extensive infrared studies[5,6] have demonstrated unambiguously that the same charged state is induced by doping and by photoexcitation. The results presented in Fig. 3 close the loop; they demonstrate that below about 5% the charged species generated by doping are also nonmagnetic. Thus we conclude that the dominant charge excitations in *trans*-$(CH)_x$ are solitons and that these solitons are stable and dominate the physical properties at concentrations up to about 5%.

The data of Fig. 3 indicate a density of states (both signs of spin), $\eta_0 < 3\times10^{-4}$ states/eV C-atom. Such a small value rules out hopping models for the transport in this high-density soliton regime. Epstein *et al.*[25] have attempted to explain the conductivity in terms of the variable range hopping (VRH) model,[26] in which the conductivity is quite sensitive to the density of states, $\sigma = A\eta_0^{1/2}\times\exp(-\Gamma\eta_0^{1/4})$; $A$ and $\Gamma$ are defined in Ref. 25. Using $\eta_0 = 2.7\times10^{-2}$ states/eV C-atom, Epstein *et al.*[25] estimate $\sigma$ (300 K) $\simeq 0.1\ \Omega^{-1}\mathrm{cm}^{-1}$. Our results indicate, however, an upper limit for the density of states which is two orders of magnitude smaller, leading to an estimate for $\sigma_{\mathrm{VRH}} < 2\times10^{-7}\ \Omega^{-1}\mathrm{cm}^{-1}$; i.e., *more than seven orders of magnitude too small.*

The fact that all the excess charge is stored in the soliton states, the observation of an abrupt onset of $\chi_p$ (increasing by more than two orders of magnitude at $0.05 < y < 0.06$), and the demonstration that the magnitude of the dc conductivity is incompatible with variable range hopping through the small density of states implied by $\chi_p$ lead us to conclude that in the transitional regime, the electrical conductivity arises directly from the transport of charged solitons. Thus the transitional regime consists of mobile, spinless, charged solitons at high density, a state not previously observed. The demonstration of charged spinless solitons in *trans*-$(CH)_x$ is the first direct experimental manifestation of fermion charge fractionalization through soliton formation (charge $\frac{1}{2}$ for each sign of spin), a phenomenon first predicted in the mathematical physics of field theory.[27,28]

*Note added in proof.* Kivelson (private communication) has pointed out that conductivity ($\sigma$) via variable range hopping involves states well away from the Fermi energy, whereas the polysusceptibility ($\chi_p$) is determined by the density of states at $E_F$. Thus, since $\sigma$ and $\chi_p$ may be decoupled, the small $\chi_p$ reported in this paper need not be inconsistent with the variable range hopping mechanism.

## ACKNOWLEDGMENTS

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