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Evidence Against Solitons in Polyacetylene: Magnetic Measurements

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EPR and dc conductivity measurements in pristine and acceptor-doped *cis*-$(\mathrm{CH})_x$ and pristine *trans*-$(\mathrm{CH})_x$ are reported. At dopant concentrations of 0.7% and 0.9% AsF_5, the *cis* isomer shows a Pauli susceptibility and a conductivity that seem to arise from randomly distributed, highly conducting regions—a sign of dopant aggregation. There in no need to invoke charged solitons. Comparison with previous experimental results suggests that they do not support the existence of charged solitons in the doped *trans* isomer; neutral solitons in the undoped *trans* isomer are also questioned.

Doped polyacetylene $[(\mathrm{CH})_x]$ has recently become a subject of considerable interest. Its electronic properties are roughly similar to those of a simple classical semiconductor: the dc conductivity σ increases rapidly with concentration at low dopant levels and shows an insulator-metal transition at some higher level.[1,2] The magnetic properties that have been reported[3,4] contrast remarkably with these. First, the spin susceptibility χ that was observed in pristine *trans*-$(\mathrm{CH})_x$ was Curie-like. Furthermore, χ did not appear to increase on light acceptor doping with AsF_5,[4] which increased σ by a factor of 10^5,[1] nor did it change on compensation with NH_3,[3] which decreased σ by a factor of 10^4.[1] This suggested[4] that the charge carriers in lightly doped material carry no spin. Second, although the spin concentration in pristine *trans*-$(\mathrm{CH})_x$ was estimated from χ to be only one spin per 3000 carbon atoms, the EPR absorption line was Lorentzian with a width of 1.43 G at 296 K. This suggested[3] that the spins are mobile.

Noting that there are two equivalent dimerizations for a *trans*-$(\mathrm{CH})_x$ molecule, differing only by the interchange of the shorter (double) and longer (single) bonds, Goldberg *et al.*[3] suggested that domains of both kinds could coexist in the polymeric chain and that the resulting domain walls (mathematically akin to "solitons" or

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"kinks") would constitute a kind of mobile elementary excitation of the chain that would be neutral but would carry spin $\frac{1}{2}$. In the presence of some charge-transferring dopants, these solitons could become charged by capturing an electron or hole and more of such charged solitons could be created; though charged, they would have no spin. Rice[5] and Su, Schrieffer, and Heeger[6] made detailed studies of models of *trans*-$(CH)_x$ that could exhibit such soliton excitations and concluded that the charged and neutral solitons would have approximately the same energy (about 0.4 eV above the middle of the dimerization gap), that the neutral solitons can capture an electron or hole in a state near midgap, that the charged solitons could have a lower energy than an electron at the bottom of the conduction band (or a hole at the top of the valence band), and that being mobile they could be trapped in the potential of the off-chain donor (or acceptor), could form impurity bands, etc. Thus there emerged the picture of a quenched concentration of neutral solitons *with* spin being responsible for χ in pristine *trans*-$(CH)_x$ and charged solitons *without* spin being responsible for σ in the lightly doped material.

Because of the novelty of both the spin and charge carriers, we have tried to investigate these soliton mechanisms further by performing conductivity and EPR measurements on pristine and AsF_5-doped samples of the other isomer, *cis*-$(CH)_x$. This isomer offers two advantages: (1) The susceptibility of the undoped *cis*-$(CH)_x$ is much smaller than that of undoped *trans*-$(CH)_x$, and so the effects of doping are much more easily distinguished from the background. (2) If doping *cis*-$(CH)_x$ at our levels produces nearly complete isomerization,[7] then we shall be dealing with a doped *trans* isomer that is less imperfect than that in which the doping *followed* isomerization. We infer this from the conductivity at maximum doping which is three times larger in doped *cis*-$(CH)_x$ than in doped *trans*-$(CH)_x$. In this Letter, we give evidence that *cis*-$(CH)_x$, with sufficient doping, exhibits impurity-band or metallic conduction and a Pauli-like susceptibility that require no assumption of solitons. From a comparison of EPR linewidths in earlier samples[4] of *trans*-$(CH)_x$ and a new sample having one-sixth the earlier defect concentration, we raise questions about the line narrowing mechanism and the homogeneity of defect distribution in that isomer. With these findings in mind, and mindful of the strong possibility that our doped *cis*-$(CH)_x$ is largely isomerized to *trans*-$(CH)_x$, we reconsider those experimental results for *trans*-$(CH)_x$ from which the existence of the solitons was inferred. We conclude that the apparent lack of susceptibility associated with the charge carriers introduced by doping may be only a question of sensitivity, not evidence for spinless charged solitons, and that the small EPR linewidth is not convincing evidence for mobile, neutral, spin-carrying solitons. We also present evidence that in $(CH)_x$ doped with $\gtrsim 0.7\%$ AsF_5, the carriers aggregate into metallic regions.

Polyacetylene films were prepared at −78 °C according to the general procedure of Ito, Shirakawa, and Ikeda.[8] The films as prepared were predominantly *cis*-$(CH)_x$ and could be converted to essentially all *trans*-$(CH)_x$ by heating *in vacuo* at 200 °C for one hour.

The introduction of 0.007 and 0.009 AsF_5 molecules per carbon atom was accomplished by exposure of the pristine films to AsF_5 vapor at a pressure of ~ 0.1 Torr. After doping, all samples were pumped at ~ 10^{-5} to 10^{-6} Torr dynamic vacuum for at least 1 hour before use. The dopant concentration was determined by weight uptake in reference samples exposed simultaneously.

The spin susceptibilities were obtained by doubly integrating (typically over 14 linewidths) the derivative of the EPR absorption corresponding to $g = 2.0026$. The spin resonance measurements were performed at 10 GHz. The absolute magnitudes of the spin susceptibilities were calibrated against the susceptibility of a sample of CdSe containing Mn^{++}, which in turn was calibrated against the known susceptibility of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ). The dc conductivity was determined from conventional four-probe measurements.

Table I summarizes the spin susceptibilities and conductivities at room temperature of pristine and AsF_5-doped *cis*-$(CH)_x$ and of *trans*-$(CH)_x$ prepared as described above and as reported by Chiang *et al.*[1] and Weinberger *et al.*[4] It is seen that the AsF_5 doping increases not only the conductivity of *cis*-$(CH)_x$, by eight orders of magnitude, but also the spin susceptibility, *by one order of magnitude* (to 2.7×10^{-7} emu/mole-carbon), in contrast to comparable doping of *trans*-$(CH)_x$, where the data appear to show no change.[4] No effect of doping on the g shift was observed from which we conclude (as did Weinberger *et al.*[4]) that the spin susceptibility comes from the polyacetylene chains and not from AsF_5^- or related ions. Although a 0.9% AsF_5 concentration should

TABLE I. Spin susceptibility and dc conductivity of polyacetylene materials at 293 K.

Material	χ (10^{-7} emu/mole-carbon)	σ (Ω^{-1} cm^{-1})
pristine *cis*-$(CH)_x$	0.275 ± 0.005	3×10^{-9}
pristine *trans*-$(CH)_x$[a]	2.1 ± 0.1	2.5×10^{-6}
pristine *trans*-$(CH)_x$	~12[b]	1×10^{-5}[c]
cis-$[CH(AsF_5)_{0.009}]_x$	2.75 ± 0.05	5×10^{-1}

[a] Our sample.

[b] Ref. 4.

[c] Ref. 1.

produce ~10^{-2} carriers per carbon atom, if we assume complete charge transfer, the observed susceptibility is only 1/100 that expected from such a concentration of *noninteracting* spins at room temperature, nor is the temperature dependence Curie-like, as seen in Fig. 1. In fact, for $T > 35$ K, $\chi(T)$ is only weakly temperature dependent. Below 35 K, $\chi(T)$ begins to rise with decreasing T. The small fraction of charge carriers contributing to χ *might* be taken as evidence that most of the holes created by doping form charged nonmagnetic solitons, as was suggested[3] for doped *trans*-$(CH)_x$, only 1% of the holes going into nonsoliton states and hence carrying spin. However, the susceptibility of these holes would be either Curie-like or activated, depending on their position relative to the Fermi level, and neither of these is observed. The more traditional view, of a degenerate Fermi gas of spin-carrying holes, is in better agreement with a weakly temperature-dependent χ. However, for this concentration of dopant, apparently not all the states are so extended as to be doubly occupied and contribute to the Pauli susceptibility. A few localized electrons could account for the low-temperature behavior, which is qualitatively similar to that seen (Fig. 1) in undoped *cis*- and *trans*-$(CH)_x$.

The interpretation of the spin susceptibility of doped *cis*-$(CH)_x$ as being the Pauli susceptibility of an impurity band is not quantitatively unreasonable either; a crude estimate of the width of such a band obtained from the magnitude of χ is ~2 eV, which, if realistic, would imply a merging with the valence band.

As one would expect from the band nature of the susceptibility, the conductivity is not activated, as can be seen in Fig. 2, where we compare experimental results with analytic curves of the

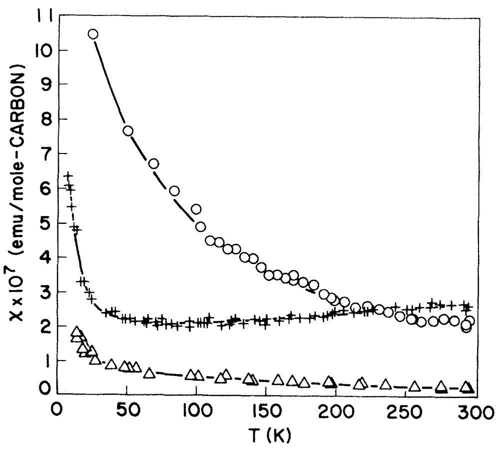

FIG. 1. Temperature dependence of spin susceptibility of polyacetylene. Plusses, *cis* isomer with 0.9% AsF_5; triangles, *cis* isomer, undoped; circles, *trans* isomer, undoped.

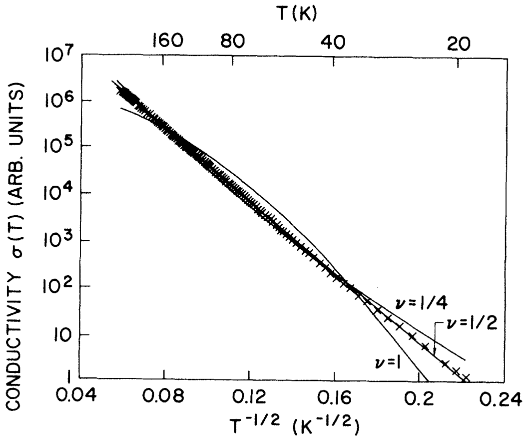

FIG. 2. Measured temperature dependence of dc conductivity of *cis*-polyacetylene doped with 0.9% AsF_5 (crosses) compared with model behaviors having the form $\sigma(T) = \sigma_0 \exp[-(T_0/T)^\nu]$, $\nu = \frac{1}{4}$, $\frac{1}{2}$, and 1. For each ν, σ_0 and T_0 are chosen to give the best fit.

form $\sigma_0 \exp[-(T_0/T)^\nu]$ for $\nu = 1$ (activated conduction), $\nu = \frac{1}{2}$ (proposed form for one-dimensional (1D) variable-range hopping[9] and also for tunneling between metallic droplets[10]), $\nu = \frac{1}{4}$ (3D variable-range hopping). The fit with $\nu = \frac{1}{2}$ is clearly the best. There is some important evidence for random metalliclike droplets and therefore for very inhomogeneous doping. $\chi(T)$ in the 0.7% sample is about $\frac{2}{3}$ that in the 0.9% sample, in contrast to what one expects under homogeneous doping, viz., an effective bandwidth that increases on doping and a χ_{Pauli} that most likely decreases.

The picture that emerges for doped *cis*-$(\mathrm{CH})_x$ from both the magnetic and transport data is that of charge carriers carrying spin, most of them delocalizing to form an impurity band with a Pauli susceptibility and a conductivity that involves either variable-range hopping or tunneling between random metallic droplets. A few charges are localized to give an observable Curie-like susceptibility at low temperatures. None of the experimental findings indicates a need for mobile solitons in this material, and if the material is indeed the *cis* isomer, they should not exist on theoretical grounds.

Whatever the microscopic nature of the doped *cis*-$(\mathrm{CH})_x$ is, the experimental findings in this Letter have important implications for the suggestions made for *trans*-$(\mathrm{CH})_x$, viz., that in the doped material σ is due to charged but spinless solitons. The experimental basis for this suggestion was the observation[4] that AsF_5 doping at concentrations below the semiconductor-metal transition increases σ significantly but does not increase χ. Because of the doped *cis*-$(\mathrm{CH})_x$ experiments, we believe this to be just a question of sensitivity: If, in *trans*-$(\mathrm{CH})_x$, χ increased on doping by no more than in *cis*-$(\mathrm{CH})_x$, viz., by 2.4×10^{-7} emu/mole-carbon, the increase would be undetectable against the background χ of the undoped sample, 1.2×10^{-6} emu/mole-carbon, in view of the scatter of the data and the uncertainties attendant on the large diamagnetic correction required in static susceptibility measurements.[4]

Let us now consider just what doped *cis*-$(\mathrm{CH})_x$ really is. If doping *cis*-$(\mathrm{CH})_x$ at these concentrations indeed promotes nearly complete isomerization, then we have a form of doped *trans*-$(\mathrm{CH})_x$ with almost identical σ but lower χ than the usual doped *trans*-$(\mathrm{CH})_x$. Since we do not require charged, nonmagnetic solitons for the doped *cis*-$(\mathrm{CH})_x$, the comparably doped *trans*-$(\mathrm{CH})_x$, with an even larger susceptibility but a similar σ, should not require them either. If the isomerization is nearly complete and appreciable regions of *cis*-$(\mathrm{CH})_x$ might remain, then in such regions, if there were any quenched solitons, they would not be mobile and could not give rise to conductivity. Thus solitons are not needed in *trans*-$(\mathrm{CH})_x$ to explain either an absence of spin susceptibility associated with the charge carriers or the magnitude of the conductivity.

Consider now the second suggestion of neutral solitons in pristine *trans*-$(\mathrm{CH})_x$ as the source of χ, the experimental basis for which was the narrow Lorentzian line showing no hyperfine broadening in samples with very low (if homogeneous) spin concentration and negligibly small conductivity.[3] However, the linewidth seems to be correlated with spin concentration. In our samples of *trans*-$(\mathrm{CH})_x$, where we have found $\chi \simeq (2.1 \pm 0.1) \times 10^{-7}$ emu/mole-carbon (about $\frac{1}{6}$ of the value of Weinberger *et al.*[4] of 1.2×10^{-6} emu/mole-carbon), the linewidth (3 G at 293 K is more than twice their value[4] (1.43 G at 293 K). If the spins in pristine *trans*-$(\mathrm{CH})_x$ are homogeneously distributed with a concentration of only one spin per 18 000 carbon atoms, then this dependence must be explained.

To summarize: (1) We have shown that doped *cis*-$(\mathrm{CH})_x$ has some kind of degenerate-band conduction and a related Pauli susceptibility, and that there is no need to invoke charged-soliton conduction in that material. (2) On the basis of these *cis*-$(\mathrm{CH})_x$ results, we suggest that the failure to see spin susceptibility associated with charge carriers in doped *trans*-$(\mathrm{CH})_x$ is only a matter of experimental sensitivity, not of spinless charge carriers. (3) If the doping drives the *cis* isomer *trans*, the arguments given are even stronger. (4) Two kinds of experimental results are given to argue that at $\geq 0.7\%$ AsF_5 doping, the doping is very inhomogeneous and there are highly conducting droplets. (5) The decrease of linewidth with increasing spin concentration in pristine *trans*-$(\mathrm{CH})_x$ argues for strongly inhomogeneous spin distributions which could exhibit exchange as well as motional narrowing, thereby weakening the argument for neutral solitons in the *trans* isomer.

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Symmetry of Donor-Related Centers Responsible for Persistent Photoconductivity in $Al_xGa_{1-x}As$

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We report on the attenuation of ballistic phonons generated in bulk GaAs and propagating through epitaxial layers of $Al_xGa_{1-x}As$ containing up to 10^{18} Sn or Te donors per cubic centimeter. The latter donors are known to form a complex with an unidentified defect (DX center) whose occupation is changed by photoexcitation. The symmetry of the ionized DX center is shown to be trigonal in the case of Sn and most likely orthorhombic in the case of Te donors.

The phenomenon of low-temperature, persistent impurity photoconductivity in compound semiconductors has attracted considerable recent attention. Most recently this phenomenon has been observed[1-3] in well-controlled, uniformly doped samples of the semiconductor $Al_xGa_{1-x}As$, and a large-lattice-relaxation model[1] to explain the results has been invoked. For the case of $Al_xGa_{1-x}As$ it involves a non-effective-mass-like donor complex labeled a "DX" center. The unoccupied DX center is believed to be resonant with the conduction band, yet sufficiently localized to produce a large lattice relaxation. Even though a large number of recent measurements[1,2,4] have given considerable support to this model, no microscopic information on the nature and symmetry of this important class of defects exists. A novel and direct method of determining such information is through the study of absorption of beams of ballistic phonons of well-defined propagation direction and polarization. The results of such studies on Sn- and Te-related donor centers in $Al_xGa_{1-x}As$ are reported here. The highly anisotropic nature of the attenuation provides compelling evidence for a (111) axial distortion in the case of Sn and a (110) distortion in the case of Te DX centers and the existence of donor-related resonant states in the conduction band of GaAs. Both of these features, as we shall see, are crucial to the model of large-lattice-relaxation DX centers in AlGaAs.

In the top of Fig. 1, we show a simple configuration-coordinate diagram proposed by Lang and co-workers[1] for DX centers in $Al_xGa_{1-x}As$. Curves *C* and *D* correspond to vibrations of the unoccupied and occupied defect. The physical significance of the large-lattice-relaxation limit is that the defect level is above the conduction-band minimum in the $Q = Q_{\text{empty}}$ configuration, but when energy is supplied to distort the local environment of the defect to $Q = Q_{\text{full}}$ the level drops deep into the gap. The net energy gained in the process, E_0, is small (~ 0.1 eV) and is the defect activation energy as measured thermally (e.g., Hall effect). The optical activation energy is, however, large (~ 1.5 eV) since such transitions

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