

Non-Ohmic Behavior of *cis*-Polyacetylene Doped with AsF₅

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Detailed conductivity measurements on *cis*-(CH)_x doped with AsF₅ as a function of electric field for various temperatures are reported. For concentrations well below the semiconductor to metal transition, an exponential dependence of the resistance on the reciprocal of the electric field is observed. This result is consistent with a model of metallic domains embedded in a dielectric. It is their charging energy which determines both the temperature dependence and the field dependence of the conductivity. Non-Ohmic effects for concentrations above the transition are also discussed.

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Extensive interest in the conjugated organic polymer (CH)_x was generated by the demonstration that doping by AsF₅ or various halogens increases its conductivity by up to twelve orders of magnitude.¹ Because the alternation of C-C bond lengths of the pristine polymer gives rise to a gap in the middle of its π -electron band, the increase of conductivity was originally interpreted according to the traditional model for a doped semiconductor. Namely, that at low dopant concentrations, the carriers are trapped by dopants and the conductivity is activated, while at higher concentrations a Mott transition to impurity band conduction occurs. In this interpretation any gross carrier-density inhomogeneities were ignored. More recently, it has been recognized that since dimerization is a Peierls distortion, the change of electron concentration with doping can have two different consequences: It could result in the distortion becoming incommensurate but uniform, or it could result in the formation of charged domain walls between uniformly dimerized domains—so called π -phase kinks or charged solitons. These solitons were shown to be energetically favorable compared with band carriers in a uniformly dimerized polymer.³⁻⁶ While the transition from semiconducting state with soliton carriers to the high-conductivity state could be in principle a Mott transition, experimental evidence has been given to argue against it. Instead, it was suggested^{4,7,8} that the transition is a commensurate-incommensurate transition, which, however, was still seen as intrinsic to regions of relatively homogeneous carrier concentration. Recently,^{9,10} it was argued that the doping is so inhomogeneous as to lead to

formation of metallic clusters in [CH(AsF₅)_y]_x even for $y = 0.003$, well below the critical concentration for the semiconductor to metal transition which was claimed to be 0.01–0.02 from transport data¹¹ and larger than 0.02 from susceptibility data¹² Moreover, conductivity changes that have previously been interpreted as arising from a transition *within* the doped region were¹⁰ attributed to a change in the topology of these regions, i.e., the occurrence of a percolation threshold.

In this paper, we present detailed conductivity measurements on *cis*-(CH)_x doped with AsF₅ as a function of electric field (E) for various temperatures. For concentrations well below the semiconductor to metal transition, we observe an exponential dependence of the resistivity on $1/E$. These results are consistent with a picture of metallic domains embedded in a dielectric with the charging energy determining both the temperature dependence and the field dependence of the conductivity. This finding is in excellent agreement with previous suggestions^{9,10} for phase separation between the doped and undoped parts of the polymer and formation of metallic clusters in the doped parts.

Polyacetylene films were prepared at 195 K according to the general procedure of Ito, Shirakawa, and Ikeda.¹³ Doping was accomplished by exposure of pristine films to AsF₅ vapor at a pressure of ~ 0.1 Torr. After doping, all samples were pumped at $\sim 10^{-5}$ to 10^{-6} Torr dynamic vacuum for at least one hour before use. The dopant concentration was determined by weight uptake in reference samples exposed simultaneously and by microprobe measurements. The temperature dependence of the Ohmic conductivity was ob-

tained by a conventional four-probe technique. The field dependence of the conductivity was obtained in a two-probe configuration, with the 10-mm² contacts being applied with silver paste across the thickness of a 50- μ m polyacetylene film. In this configuration, fields up to 6×10^4 V/cm could be achieved. In order to minimize sample heating, the I - V characteristics were measured with a pulsed technique with typical pulse widths of 300 nsec and repetition rates of 5–50 Hz. It was verified for all the measurements that there was neither a heating effect during the pulse nor an average heating effect. In the two-probe configuration, the measured resistance is the contact resistance in series with the sample resistance. Therefore, the contribution, if any, of the contacts to the non-Ohmic behavior has to be determined. If the observed field dependence were caused by the contacts, it would indicate that the intrinsic sample resistivity is equal to or smaller than the two-probe resistivity extrapolated to the $E \rightarrow \infty$ limit. However, the intrinsic resistivity of the sample was measured by the four-probe technique and at least six orders of magnitude higher than the $E \rightarrow \infty$ extrapolation limit. The I - V curves were symmetrical with the field direction and Ohmic in the very low-field regime, thus eliminating the possibility of a diode formation as was observed¹⁴ in $(\text{CH})_x$ doped with I_2 .

The temperature dependence of resistance of $[\text{CH}(\text{AsF}_5)_{0.005}]_x$ is shown in Fig. 1. As was shown previously,⁹ a fit with the relationship

$$R_L = R_{L0} \exp(T_0/T)^{1/2} \quad (1)$$

is excellent. This particular dependence is expected^{15,16} for the resistivity of granular metals in the concentration regime in which isolated metallic particles are dispersed in a dielectric continuum. In the charge-carrier generation process, an electron has to be removed from a neutral metallic grain and placed on another neutral grain. Since every such a grain has a capacitance, the process of carrier generation requires a nonnegligible charging energy. Therefore, for low electric fields, namely, when the voltage drop between neighboring grains is smaller than the thermal energy, the carriers are thermally activated. For this regime, the expected temperature dependence of the resistance is given by (1) with T_0 determined by the charging energy and the barrier height. At high fields, the number of carriers deviates appreciably from the thermal

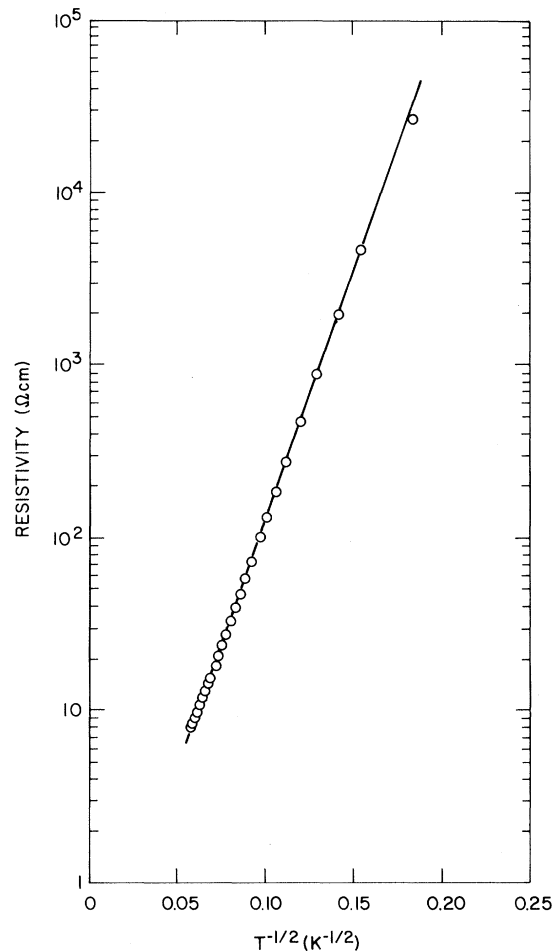


FIG. 1. Four-probe resistivity in the low-field regime as a function of $1/\sqrt{T}$ of $[\text{CH}(\text{AsF}_5)_{0.005}]_x$.

equilibrium value and the resistance is given by^{16,17}

$$R_H = R_{H0} \exp(E_0/E). \quad (2)$$

Thus the field dependence of the conductivity can test directly whether the metallic particles model is indeed applicable to doped $(\text{CH})_x$.

The field dependence of the resistivity of $[\text{CH}(\text{AsF}_5)_{0.005}]_x$ is shown in Fig. 2 for two different temperatures 4.2 and 77 K. At 4.2 K, the resistance (over at least three orders of magnitude) has an exponential dependence on $1/E$. As expected, at higher temperatures (77 K) the number of the thermally generated carriers is larger and, therefore, the fields required for the observation of the exponential field dependence would be larger. The high-field limit could not be reached at this temperature because of electrical breakdown. Therefore, the studies of the temperature

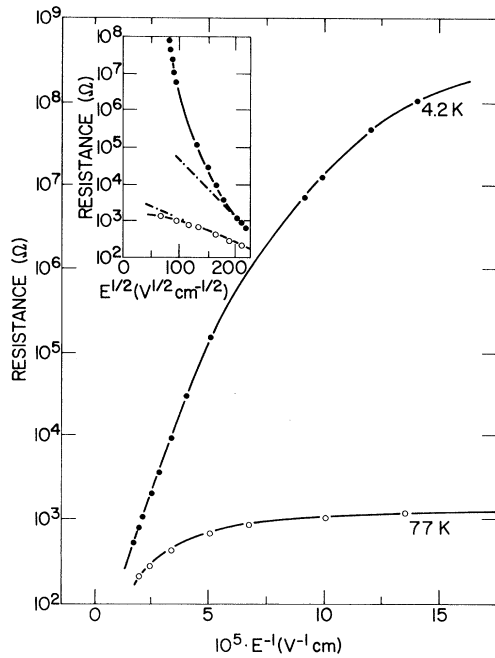


FIG. 2. Resistance as a function of $1/E$ of $[\text{CH}-(\text{AsF}_5)_{0.005}]_x$ at 4.2 and 77 K. The inset shows the field dependence in a Poole-Frenkel plot.

dependence of the field effect are limited to temperatures in which the thermal activation is negligible.

Figure 3 shows the field dependence of the resistance for four different temperatures in the temperature range 4.2–10 K. It is clearly seen that the field dependence follows Eq. (2) with a temperature-independent E_0 being 2×10^5 V/cm. By applying an analysis similar to that used for granular metals^{16,18} one can determine the average repeat distance of the metallic grains, w . As was shown,^{16,19} w can be determined in two independent ways: (a) E_0 and T_0 as determined by Eqs. (1) and (2) are related to w by

$$w \sim (k_B/4e)T_0/E_0. \quad (3)$$

(b) Field-generated carriers become important when the voltage drop across the barrier exceeds the thermal energy, namely, the crossover field E_c between Ohmic and non-Ohmic behavior will occur at

$$eE_c w = k_B T. \quad (4)$$

For 0.5% dopant concentration, w was determined by these *two independent* methods and was found to be approximately 60 Å. Similar values of w and E_0 were reported¹⁶ for the granular Ni-SiO₂

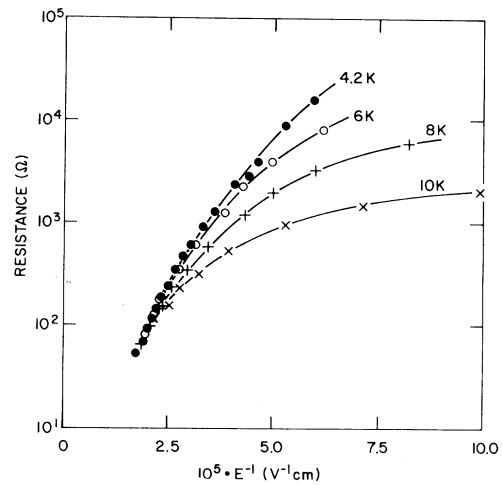


FIG. 3. Resistance as a function of $1/E$ of $[\text{CH}-(\text{AsF}_5)_{0.005}]_x$ for several temperatures below 10 K.

system for a Ni concentration regime below the percolation threshold. It should be noted though, that while the percolation threshold in granular metals is achieved when the volume fraction of the metal is about 50%, in doped polyacetylene it occurs for 1–2%,^{10,11} indicative that the volume fraction of the cluster is larger than that of AsF₅. Thus, our results on doped polyacetylene, for dopant concentrations below the percolation threshold, indicate existence of metallic domains with high tunneling barriers between them, analogous to granular metals. Measurements on concentrations above the percolation threshold show a much weaker field dependence indicating that barriers still do exist, but they are much reduced and that the conductivity can be understood both in terms of its temperature and field dependence by fluctuation-induced tunneling.²⁰ The physical reason for the existence of the barriers above the percolation threshold is most probably the microscopic structure of polyacetylene consisting of fibers 200 Å in diameter.¹³

Since the data presented in this paper were obtained with AsF₅ as dopant, the question that arises is whether the formation of aggregates during doping can be generalized to other dopants. Non-Ohmic behavior was also^{21,22} observed for (CH)_x doped with I₂, but it was much weaker than the effect reported here. There are, however, two basic differences between the experimental conditions: The upper limit of the field for the iodine-doped samples was 100 V/cm, about two orders of magnitude lower than the fields in the

exponential regime in our experiments, and the investigated samples were in the metallic regime. Therefore, more studies in overlapping regimes of field and concentrations should be performed before the aggregation effects of various dopants can be compared.

In conclusion, we have shown that for $[\text{CH}(\text{AsF}_5)_y]_x$, $y < 0.01$ there is an exponential $1/E$ dependence of the resistance on E . This experimental observation is in excellent agreement with the model suggested by detailed spin-susceptibility studies^{9,12} which indicated that a phase separation occurred between the doped and undoped parts of the polymer, the doped regimes being metallic. In the conductivity measurements, undoped regimes give rise to the high barriers, which are responsible for the exponential dependence of the resistance on $1/E$.

Weaker non-Ohmic effects observed for concentration above the percolation threshold still indicate existence of barriers, most probably related to the fibrous nature of polyacetylene.

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