Electrical conductivity of I_2-doped polyacetylene

M. Audenaert, G. Gusman, and R. Deltour
Université Libre de Bruxelles, Physique des Solides (CP 233), Bd. du Triomphe, B-1050 Bruxelles, Belgium
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Experimental results on electrical conductivity for iodine-doped polyacetylene at concentrations above 1% molar ratio are presented. In conjunction with Park's data on the thermoelectric power for the same system these results support its microscopic description as an assembly of three-dimensional amorphous semiconducting islands separated by potential barriers.

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Polyacetylene, as some recent studies have shown, has the ability to form highly conductive derivatives by the reaction of the pure polymer film with vapors of different materials (I_2, Br_2, AsF_5).[1,2] Although the AsF_5-doped polymer obviously shows a metal-like behavior, as was suggested by electrical conductivity, thermopower, and ESR measurements,[3-9] the situation seems to be a little more complicated for iodine-doped polyacetylene films. For this material, even for the highest doped systems, the electrical conductivity does not reach a miximal value below 300 K (Ref. 3) and the thermoelectric power measurements show an absence of linearity versus temperature.[5]

In this work, we present some careful new experimental measurements of the conductivity versus temperature in the temperature range $1\ \mathrm{K} < T < 300\ \mathrm{K}$ on iodine-doped polyacetylene films for various iodine concentrations. The results have been analyzed statistically by computer techniques and fully interpreted on the basis of a three-dimensional disordered semiconductor model for the iodine-doped samples.

The polyacetylene films were prepared by polymerization of acetylene gas on Ziegler-Natta catalysts as described by Shirakawa *et al.*,[10] then isomerized to the *trans* form by heating them to 180 °C for one hour under an inert argon atmosphere to prevent oxydation of the films. Doping was achieved by exposing the films to iodine vapors at room temperature. The iodine concentration was measured by weight uptake. Only samples doped at iodine concentrations higher than one percent (molar ratio) were studied, e.g., in the concentration range where doped polyacetylene is usually assumed to be metallic. The dc-conductivity measurements were carried out using the four-probe method. The electrodes were painted on the surface of the films using Electrodag +502.

Two types of behavior were observed; both will be described by the same model hereafter. The first type of behavior is illustrated in Fig. 1, where we have plotted the logarithm of the conductivity normalized to the room-temperature conductivity as a function of $T^{-1/4}$, respectively, for a 3% and a 29% (molar ratio) doped sample. For both samples a deviation from linearity occurs at a temperature which is higher for the 3% doped sample (~100 K) than for the 29% doped sample (~20 K). This type of behavior can be readily well understood on the basis of a model of highly conducting "islands" (although atomically disordered with localized electron wave functions) separated by potential barriers.

This is almost similar to the model developed by Sheng[11] where the highly conducting regions were assumed to be metallic. The expression derived by Sheng for the fluctuation-induced-tunneling resistance of the junctions between the highly conducting regions is given by

$$R_j(T) = R_{j0} \exp\left(\frac{T_1}{T}\epsilon^2 + \frac{T_1}{T_0}\varphi(\epsilon)\right), \tag{1}$$

where T_0 and T_1 are two parameters representing,

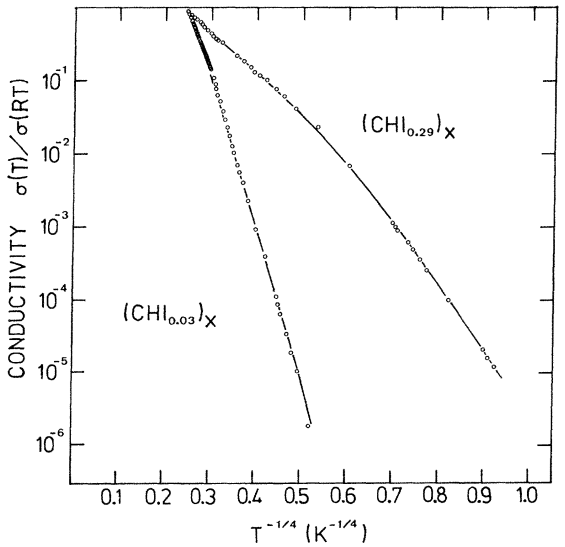

FIG. 1. Logarithm of the electrical conductivity normalized to room-temperature conductivity versus $T^{-1/4}$ for $(CHI_{0.03})_x$ and $(CHI_{0.29})_x$.

respectively, the temperature below which the resistance becomes temperature independent corresponding to a pure elastic tunneling mechanism and the temperature above which the conduction mechanism across the junctions is purely thermally activated. The function $\varphi(\epsilon)$, where ϵ is a reduced electrical field and temperature-dependent parameter, contains another parameter λ that governs the shape of the image-force-corrected rectangular potential barrier in Sheng's theory.

In our case the intrinsic resistance of the conducting regions is attributed to the electrical transport in a three-dimensional disordered semiconductor, i.e., in an amorphous isotropic semiconductor where

$$R_i(T) = R_{i0} \exp\left(\frac{B}{T^{1/4}}\right) . \tag{2}$$

The total resistance can then be written as the sum

$$R(T) = R_i(T) + R_j(T) . \tag{3}$$

This relation has been found to fit very well our experimental data for the above-mentioned samples as illustrated by the full curves drawn in Fig. 1. The different values of the parameters T_1, T_0, and B for both samples are given in Table I. An independent confirmation of the validity of the model has been obtained by the analysis of the experimental data for the thermoelectric power as a function of temperature obtained by Park *et al.*[5] These data concern a 22% (molar ratio) iodine-doped sample of transpolyacetylene. The thermoelectric power is expressed by

$$S = -\frac{\pi^2}{3}\frac{k_B^2}{e} T \left(\frac{\partial}{\partial E} \ln\sigma(E)\right)_{E=E_F} . \tag{4}$$

According to this model, we can write

$$\sigma(E) = \frac{R_0}{R_{i0}\exp[B(E)/T^{1/4}] + R_{j0}\exp[(T_1/T)\epsilon^2 + (T_1/T_0)\varphi(\epsilon)]} , \tag{5}$$

where R_0 is a geometrical correcting factor and $B(E)$ is given by

$$B(E) = 2.1\left(\frac{\alpha^3}{k_B N(E)}\right)^{1/4} , \tag{6}$$

TABLE I. Values of the parameters obtained from formulas (1), (2), and (3) for $(CHI_{0.03})_x$ and $(CHI_{0.29})_x$.

Iodine concentration y	T_1 (K)	T_0 (K)	λ	B ($K^{1/4}$)
0.03	448	22.8	0.065	52.9
0.29	88	4.3	0.050	12.8

where, according to Mott,[12] α is the inverse spatial extension of the localized wave function. Combining this relation with (3) gives for the thermoelectric power

$$S = -\frac{T}{A' f(T) + 1}\left(B' - C' T^{-1/4}\right), \tag{7}$$

where

$$f(T) = \frac{\exp[T_1/T)\epsilon^2 + (T_1/T_0)\varphi(\epsilon)]}{\exp[B(E_F)/T^{1/4}]} \tag{8}$$

and A', B', C' are given by

$$A' = \frac{R_{j0}}{R_{i0}} \tag{9}$$

$$B' \sim \frac{1}{R_{i0}}\frac{dR_{i0}}{dE}\bigg|_{E=E_F} , \tag{10}$$

$$C' \sim 0.5\left(\frac{\alpha^3}{k_B N(E)}\right)^{1/4} \frac{1}{N(E)}\frac{dN(E)}{dE}\bigg|_{E=E_F} . \tag{11}$$

In Fig. 2 we see the remarkably good fit of expression (6) for the experimental data of S versus temperature measured by Park *et al.* taking $B = 14$ $K^{1/4}$, $T_1 = 150$ K, $T_0 = 13.6$ K whose values are quite reasonable for a 22% (molar ratio) iodine-doped film.

The other type of behavior for the conductivity of the I_2-doped samples appears in Fig. 3 which shows the data for 11% and 19% molar ratio doped samples, respectively, and where we have again plotted the normalized conductivity versus $T^{-1/4}$. Here we are concerned with "purely" three-dimensional disordered semiconductors. The best fit is a linear one.

When we compare the values of B of Table II to

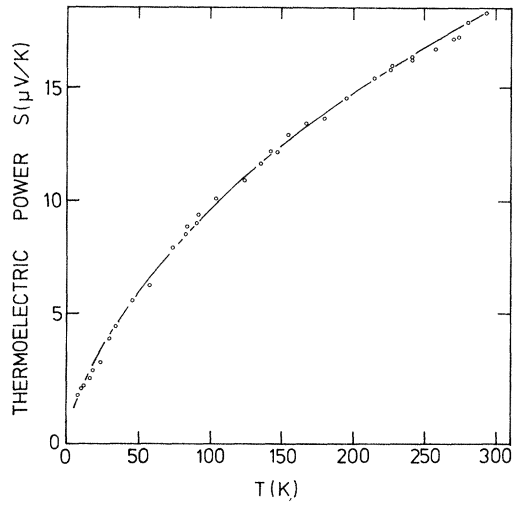

FIG. 2. Thermoelectric power of $(CHI_{0.22})_x$ vs T from the data of Park *et al.*

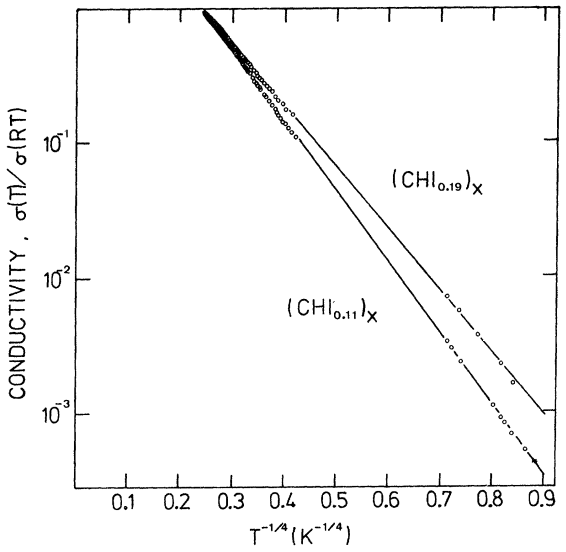

FIG. 3. Logarithm of the electrical conductivity normalized to room-temperature conductivity versus $T^{-1/4}$ for $(CHI_{0.11})_x$ and $(CHI_{0.19})_x$.

those of Table I, we see that even though the iodine concentration can be higher for the samples where a tunneling barrier mechanism is limiting the conductivity as compared to the I_2 concentration for samples showing a pure three-dimensional disordered semiconducting behavior, the values of B of the former are not smaller.

It seems that at the same time the barriers appear, the density of states into the conducting regions drops. It is likely that this may be due to different kinds of textures of the pristine polyacetylene rather than to inhomogeneous doping; indeed the technique of doping remained the same for all samples. Some defects altering the ideal structure of the polycrystalline fibriles could presumably be induced during the preparation of the polymer. The barrier parameters will be doping dependent as is shown in Table I, because a certain amount of iodine will be trapped in these defects. Epstein also mentioned two kinds of behaviors for iodine-doped polyacetylene.[13] However, we never did observe any kind of two-dimensional metallic behavior.

TABLE II. Values of the parameter B of formula (2) for $(CHI_{0.11})_x$ and $(CHI_{0.19})_x$.

Iodine concentration y	B ($K^{1/4}$)
0.11	12.18
0.19	10.56

As a conclusion, we have shown from our conductivity measurements that iodine-doped polyacetylene for dopant concentrations above 1% molar ratio, rather than being metallic, can be described by a three-dimensional disordered semiconductor model even if the conductivity is limited by the presence of potential barriers in some samples. The same analysis applied to the thermoelectric power measurements of Park *et al.* is in agreement with this model.

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