Electrical conductivity of heavily doped polyacetylene at ultralow temperatures

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The electrical conductivity of heavily doped polyacetylene, $(CH)_x$, has been measured from room temperature down to 0.4 mK and in magnetic fields from 0 to 290 Oe. Below 30 mK the resistance increases logarithmically with decreasing temperature, and decreases roughly logarithmically with increasing magnetic field. The results are compared to recent localization and interaction models of electron transport in systems of reduced dimensionality.

Linear polyacetylene is the simplest conjugated polymer, consisting of a chain of carbon atoms, along which π electrons overlap and form a quasi-one-dimensional energy band. Interest in this semiconducting polymer has been stimulated by the successful demonstration of doping; the room-temperature electrical conductivity of $(CH)_x$ films can be varied over 12 orders of magnitude. The qualitative changes in electrical and optical properties at dopant concentrations above a few percent have been interpreted as a semiconductor-metal transition.[1] Recent evidence[2,3] suggests that the energy gap closes in heavily doped $(CH)_x$, leading to metallic behavior. Transport,[4] optical,[2] and magnetic resonance[5] experiments indicate highly anisotropic, i.e., quasi-one-dimensional (1D), behavior. Since the metallic state has been established at ordinary temperatures, we have cooled heavily doped $(CH)_x$ to ultralow temperatures to test its behavior in an entirely new regime. Below 30 mK we find a logarithmically increasing resistance and a strong magnetic field dependence.

Samples were prepared from stretch-oriented ($l/l_0 = 2.8$) $(CH)_x$ films heavily doped with AsF_5 (9.7 mol%), and had dimensions $10 \times 2 \times 0.05$ mm^3. The conductivity was measured along the stretched direction using standard low-frequency ac four-probe techniques. Current and voltage leads were attached by gold-plated BeCu spring-loaded contacts. The room-temperature conductivity of a test sample prepared at the same time as, and identical to, the sample whose properties are shown in Figs. 1 and 2, was 3180 $(\Omega\,\mathrm{cm})^{-1}$. Samples were cooled by direct immersion in liquid ^{3}He contained in the sample chamber of a nuclear demagnetization cryostat in which several other experiments were being performed simultaneously. The ^{3}He pressure was nominally 0.8 bars.

Thermometry depended on the temperature regime. Above 1 K we used a commerical carbon-glass thermometer. Below 20 mK we used the nuclear susceptibility of Pt measured by pulsed NMR. Intermediate temperatures, as well as low temperatures,

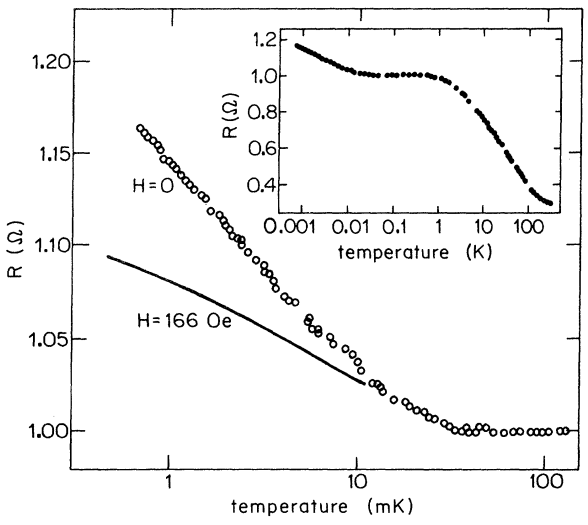

FIG. 1. Electrical resistance at low temperatures in zero magnetic field (data points) and with $H = 166$ Oe (solid curve). The inset shows the zero-field resistance over the entire temperature range from 300 K to 0.4 mK.

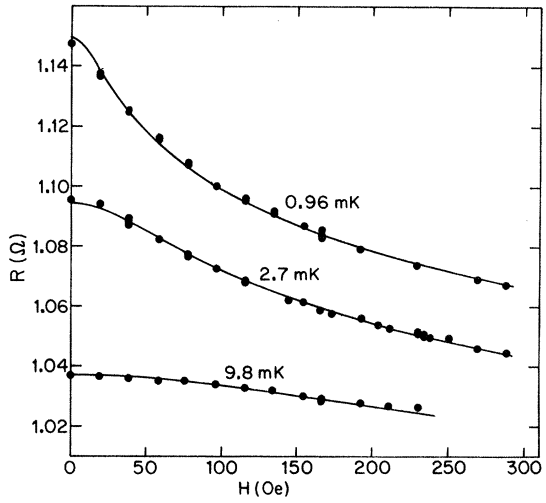

FIG. 2. Magnetic field dependence at three different temperatures. Note that as temperature increases, the magnetoresistance decreases along with the excess resistance over the plateau value. The solid curves are the functional fit described in the text.

were measured by the electronic susceptibility and internal field shift of quinolinium tetracyanoquinodimethanide [Qn(TCNQ)$_2$].[6] Despite well-known problems of thermal contact at ultralow temperatures, we are confident that measured temperatures equal sample temperatures because of the low power dissipation in the polyacetylene sample itself and the fact that the surface-to-volume ratio of polyacetylene is an order of magnitude larger than any traditional metal sinter used for thermal contact.[7]

The temperature dependence of the resistance in zero magnetic field ($H \lesssim 0.1$ Oe) is shown in the inset to Fig. 1 for the entire temperature range of the experiment. We suggest below that the observed temperature dependence arises from two distinguishable sources, one of which is responsible for the high-temperature variation and saturation at a plateau resistance below 1 K. This plateau resistance has been observed previously.[8] The essential new result on which we have concentrated is the slowly increasing resistance below 30 mK shown in the main part of Fig. 1.

As temperature decreases below 30 mK the resistance slowly begins to increase until below about 7 mK it varies logarithmically in T quite accurately. The data in Fig. 1 were taken with applied electric fields less than 200 nV/cm. We checked for an electric field dependence and found none for $E < 50$ μV/cm, at which point our thermometer began to warm, and we terminated the measurement. We also checked for a pressure dependence by increasing the ^{3}He pressure to 24 bars, but found no variation greater than 0.1%. All of the data presented here were taken at a frequency of 620 Hz, though a cursory check over the range 50 Hz to 1.2 kHz revealed no frequency dependence.

In an earlier series of measurements[9] on a different sample of polyacetylene we also observed a logarithmic temperature dependence for $T < 17$ mK. While that sample was not studied as thoroughly as the present one above 17 mK (owing to a lack of an appropriate thermometer), it does demonstrate that the logarithmic behavior is not unique to a particular sample.

We have also applied a magnetic field up to 290 Oe along the direction of average current flow. [However, because of the tangled structure of the $(CH)_x$ fibrils, the current flow in a particular fibril can be in any direction relative to the applied magnetic field.] The temperature dependence in an applied field of 166 Oe is shown as the solid curve in Fig. 1. Note that the curve is not straight so that the temperature dependence cannot be described as logarithmic with a field-dependent prefactor.

To determine the field dependence we held the sample at a constant temperature and varied the magnetic field from zero to 290 Oe. The data from a series of such experiments are shown in Fig. 2. We have tried to fit these data to a number of simple functions, only one of which has been at all successful:

$$R(T,H) = R_0(T)\{1 - \alpha \ln[(k_B T)^2 + \beta(g\mu_B H)^2]\} \ . \tag{1}$$

The solid curves shown in Fig. 2 are calculated from Eq. (1) measuring energy in units of mK and using $g = 2$, $\alpha = 0.0130$, $\beta = 0.149$, and $R_0(T)$ a temperature-dependent factor. $R_0(T)$ can be extracted from the zero-field data of Fig. 1 and turns out to depend logarithmically on T below 8 mK, $R_0(T) \simeq 1.145 - 0.02 \ln T$ (mK). The logarithmic zero-field temperature dependence comes approximately equally from the explicit logarithm in Eq. (1) and the implicit logarithm in $R_0(T)$.

An interesting point regarding these data is that at no point does the resistance in a field become smaller than the "plateau resistance" seen above 30 mK. Above 40 mK, a careful examination revealed no magnetoresistance (± 0.002 Ω) over our entire field range.

A useful characterization of our data is the asymptotic field and temperature dependences of the resistance. We define the coefficients S_T and S_H by

$$\begin{aligned} R(T,H_0) &= \text{const} - S_T \ln T, \quad k_B T >> g\mu_B H_0 \ , \\ R(T_0,H) &= \text{const} - S_H \ln H \ , \quad k_B T << g\mu_B H_0 \ . \end{aligned} \tag{2}$$

For our sample $S_T = 0.0501$ Ω. The ratio S_T/S_H is slightly temperature dependent, but is always near 2.

The logarithmic zero-field temperature dependence is reminiscent of the Kondo effect, though its magnitude appears too large. The small Curie-law contribution to the magnetic susceptibility in heavily doped $(CH)_x$ implies a magnetic impurity content of no greater than a few ppm.[10] Thus the magnitude of the logarithmic increase is $\sim 10^2$ Ω cm/mol%, i.e., more than six orders of magnitude greater than typically found in Kondo systems. Moreover, in ordinary Kondo materials the field and temperature dependences of the resistance are given quite accurately by the simple phenomenological equation $\delta R \propto \ln(T^2 + H^2 + \Theta^2)$, where Θ is a constant.[11] When this function is fitted to our data there are severe, systematic deviations. Lastly, if this idea were correct, then the ratio S_T/S_H defined in the previous paragraph would be identically unity instead of 2 as required by the data.

Transport[4] and optical[2] studies have resulted in the conclusion that dc transport is limited by interfibril contacts and that the heavily doped polymer can be described as metallic strands separated by thin potential barriers. At high temperatures ($T > 0.1$ K) the measured resistance is dominated by the interfibril contacts, and can be understood in terms of fluctuation-induced tunneling[12] across interfibril contacts, a model to which the data fit very well. In particular, the extended temperature-independent plateau below 1 K is a direct result of this tunneling mechanism.

The logarithmic increase in resistance at low temperature may arise from an increase in the intrinsic resistance of the metallic fibrils, from a change of behavior of the complex series-parallel network of fibrils as a whole, or from an unexpected modification to the tunneling characteristics of the interfibril contacts. Either of the first two sources could be manifestations of electron localization in $(CH)_x$. Current theories of electron transport in lower dimensionalities[13,14] maintain that one- and two-dimensional metals are not metallic in the classical sense. Impurities and disorder are expected to lead to localized wave functions, rather than residual resistivity, so that such systems do not remain conductive down to absolute zero.

The structure of polyacetylene samples consists of C–H units connected into chains. These chains are bundled into fibrils 100–200 Å in diameter and a few thousand Å long. These fibrils are interconnected in a quasirandom fashion to form bulk samples. Owing to this complicated morphology of $(CH)_x$, we cannot *a priori* predict the localization mode. Furthermore, the localization mode depends on the inelastic scattering rate for which theoretical estimates are known to be unreliable.

At least four possible localization modes can be envisioned. They are (1) 1D localization along a single chain; (2) 1D localization within a single fibril but across many chains; (3) localization across several interconnected fibrils; and (4) localization across the entire 50-μm thickness of our sample. If we use the inelastic scattering rate deduced in other materials[15] as a guide, then possibility (4) is ruled out. Possibility (2) appears unlikely because the resistance of a single fibril is too small.

A logarithmic temperature dependence is associated in current theoretical models[13,14] with 2D behavior. If possibility (1) is correct then the models in 1D predict a power-law behavior, which is inconsistent with the data unless we assume that the complex series-parallel network of chains and contacts obscures the intrinsic chain resistance. If possibility (3) is correct, then the logarithmic behavior may indicate the nature of the interconnectedness of the fibrils. Possibilities (1) and (3) may be distinguished by a measurement of the intrinsic fibril conductivity (as in Refs. 2 and 5) at low temperatures.

There are two points regarding our data which are especially relevant to a theoretical interpretation. First, the increasing resistance at low temperatures is clearly distinct from the plateau resistance above 30 mK which is independent of temperature over nearly two decades. Second, the excess resistance (and only the excess resistance) is substantially suppressed by a (relatively small) magnetic field. Qualitatively, this negative magnetoresistance is expected in the localization model[13] but not in the interaction model.[14]

Very recently we have discovered that the ultralow-temperature excess resistance and magnetoresistance also exist in unstretched $(CH)_x$, even though there is no plateau in resistance between 30 mK and 1 K.

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