Persistent Metallic Behavior of Thin Bismuth Whiskers

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(Received 21 December 1979)

The electrical resistance of Bi and Bi–6 at.% Sb whiskers has been measured. Sample diameters were as low as 140 nm, lengths as large as 1.5 mm, and residual resistances as high as 165 kΩ. Down to temperatures of 0.4 K, metallic behavior persists; the resistance R decreases with decreasing temperature T in contrast to other systems in which electron localization is invoked to explain negative dR/dT's.

PACS numbers: 72.15.Eb, 71.50.+t

Of late there has been considerable theoretical and experimental interest in one-dimensional Anderson localization. Theory[1-3] has predicted that in one-dimensional (1D) systems (i.e., wires) of sufficiently high impurity resistance all conduction-electron states should be localized. As a result, electrons can only transport electric current if they are provided with enough energy to hop from one localized state to another. At very low temperatures there are no phonons and no other available sources of hopping energy, so that in these systems the electrical conductivity should go to zero as the temperature goes to zero. Recent experiments[4-6] appear to support this localization. However, at present there is only qualitative agreement with theory and neither the samples nor the data can be considered definitive in the 1D regime.

The whiskers studied in the present work were grown by the "squeeze" technique[7] in vacuum at temperatures of about 200 °C and mounted on a straining device[8] shown schematically in Fig. 1. Samples were obtained one at a time by picking off likely whiskers with hand-held tweezers under a microscope. The sample whisker was laid onto four shaved copper wire contacts, Fig. 1, and silver painted in place. Two of the contacts were movable, allowing the whiskers to be either bent *in situ* as illustrated in the figure or pulled *in situ*. Sample lengths were measured between the two inner potential contacts to ± 15 μm with a calibrated microscope eyepiece. Displacements of the movable contacts were read off a linear differential transformer with a resolution of ± 30 nm. Both the sample and the straining device could be inserted in a conventional ^{3}He refrigerator[9] which could be pumped down to 0.4 K. Four-probe dc resistance measurements were made with battery-powered electronics in a screened room. Temperatures were measured with a calibrated germanium resistance thermometer located in the ^{3}He vapor about 1 cm from the sample.

Three different measurements were made on each whisker: (1) At room temperature the whisker was *pulled* and displacement Δl versus resistance R graphed to ensure that the sample was a single elastic whisker. The slope $dR/d(\Delta l)$ then also gave the crystallographic orientation. (2) At 4.2 K, the whisker was elastically *bent in situ* as illustrated in Fig. 1, and negative displacement versus resistance graphed to obtain the bending effect[10] which gives a lower bound on the phonon-limited electron mean free path. (3) The resistance of the slightly bent whisker was measured as a function of temperature down to our lowest temperatures in an effort to detect localized electron states.

In what follows we present results for whiskers grown from pure Bi and from Bi–6 at.% Sb. Figure 2 shows typical x-y recorder data for a Bi–6 at.% Sb whisker of diameter 170 nm, length 1.473 mm, and extrapolated zero-temperature residual

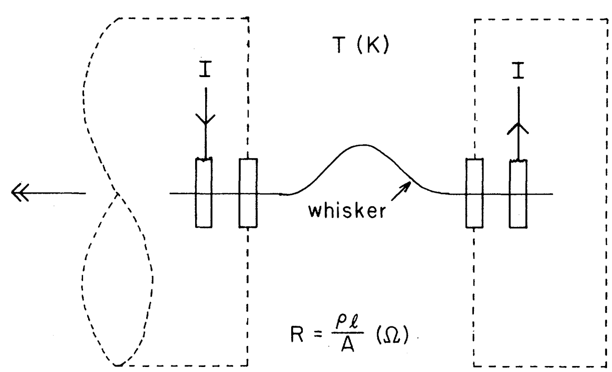

FIG. 1. The whisker-straining device. A whisker, shown bent, is silver painted on to shaved copper contacts epoxied on quartz holders. The movable pair of contacts connect through a long quartz rod to a micrometer-driven differential screw outside the cryostat. The fixed pair of contacts are epoxied on an equally long quartz tube concentric with the long quartz rod.

resistance 165.02 kΩ. The top curve is a room-temperature measurement of the displacement versus resistance, generally described as a strain-resistance curve. As the whisker is pulled it gradually straightens with no noticeable change in resistance till it is straight and starts to be strained; at which point its resistance smoothly and linearly decreases with increasing strain in a reversible, i.e., elastic, fashion. Those samples which were not elastic (i.e., reversible) were discarded, as were samples which, although otherwise perfect, reflected light unevenly. A special attempt was made to mount thin and long whiskers in an effort to satisfy (1) a sample resistance in excess of 10 kΩ, and (2) the empirical criteria of Ref. 4 of sample diameter less than 180 nm. The highest-residual-resistance whisker mounted had a residual resistance of 165.02 kΩ (Fig. 2) and the thinnest whisker mounted had a diameter of $\sqrt{A} = 140$ nm, where A is the cross-sectional area of the whisker determined from published bulk room-temperature resistivity and supported by scanning electron micrographs.

The bottom curve of Fig. 2 is a low-temperature measurement of the resistance versus temperature for the same (top curve) whisker. Note the downward trend in resistance with decreasing

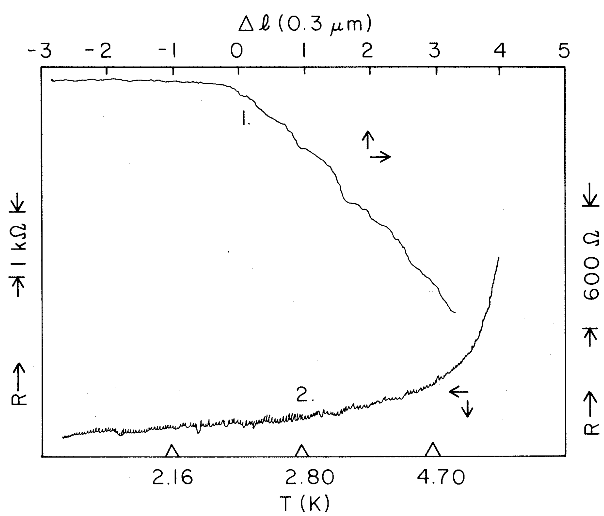

FIG. 2. Typical x-y recordings of (1) room-temperature displacement vs resistance (strain resistance curve). Top curve, Bi–6 at.% Sb whisker of length 1.473 mm, $R_{300} = 69.14$ kΩ, $R_{4.2} = 165.02$ kΩ, and diameter $\sqrt{A} = 170$ nm, where A is the cross-sectional area of the whisker. (2) Resistance vs temperature. Bottom curve, the same whisker. The top curve is evidence for a single elastic whisker and the bottom curve for continued mettallic behavior.

temperature, evidence of continued metallic behavior. Especial care was exercised to eliminate possible electric-field-induced conductivity by working at low currents and plotting I-V characteristics down to 5 pA. The I-V characteristics were linear from 5 pA to several microamperes. At higher currents, effects attributable to heating were clearly seen. Thus our currents, comparable to those used by Refs. 4 and 5, appear to have been low enough to have picked up localization effects had they existed.

In order for localization to be observable, the sample must be at a low enough temperature that the electron can diffuse a localization length before it is scattered inelastically. The scale of localization is set by the wire length that has $\lambda_l = 2\hbar/e^2 \cong 8$ kΩ and the inelastic diffusion length is set by $\lambda_T = (\lambda_e \lambda_1)^{1/2}$, where λ_e and λ_1 are the elastic and inelastic mean free paths. We now show that our Fig. 2 sample meets this criterion. For this sample $\lambda_l = 1.473$ mm/(166/8) $\cong 70$ μm. Our estimation of λ_e is 0.2 μm, set by the sample diameter and confirmed by Zhilyaev and Mezhov-Deglin's[11] value of $\rho\lambda = 1.4\times10^{-12}$ Ω m^2 and the sample residual resistivity of 3×10^{-6} Ω m. Estimating λ_i is more difficult. If we believe that the inelastic mean free path is the same as that in bulk Bi, then we can use Zhilyaev and Mezhov-Deglin's[11] value of the total mean free path, $\lambda_{\text{bulk}} = (19\times10^{-3}$ K^2 m$)/T^2$ as a lower bound. This gives $\lambda_{\text{bulk}} > 100$ mm at our lowest temperature (and extrapolates the bulk data from 1.3 to 0.4 K). We

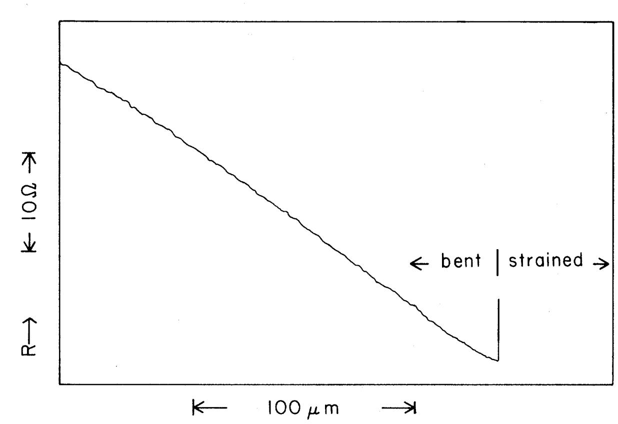

FIG. 3. Typical x-y recording of low-temperature negative displacement vs resistance (the bending effect) for a Bi whisker of length 1.2 mm, $R_{300} = 3.46$ kΩ, $R_{4.2} = 1.16$ kΩ, and diameter $\sqrt{A} = 600$ nm, where A is the cross-sectional area of the whisker. Such data are evidence (see text) for phonon-limited electron mean free paths $\geq 10^{-4}$ m.

can use the bending effect[10] (Fig. 3) to set a lower bound of 10^{-4} m on the total mean free path at 4.2 K. This is far too conservative since our least count does not allow us to detect $\lambda_{\rm bulk} > 10^{-4}$ m. Now if we set $\lambda_i \geq \lambda_{\rm bulk} = 100$ mm and $\lambda_e = 0.2$ μm we obtain $\lambda_T \cong 140$ μm $\cong 2\lambda_i$.

A second criterion for observing localization in our samples is that they are 1D, that is that the diameter, $d < \lambda_i$ or $d < \lambda_T$, both of which seem to be easily met by our samples, since, for example, 0.14 μm $\ll$ 70 μm $<$ 140 μm.

Figure 4 shows the averaged resistance versus temperature data for three different Bi–6 at.% Sb samples of different diameters. The temperature-dependent part of their resistances scale well for all three samples and can be described by an approximately linear temperature dependence. This reinforces our belief that the behavior illustrated by Fig. 2 is typical and that we do measure an intrinsic property of the whisker which thus far does not exhibit localization.

Why do we see no effects of localization? One might at first suspect that $\lambda_i \geq 100$ mm is an overestimate. But, if we examine previous experiments that have seen effects attributed to localization we find that in Dolan and Osheroff's[5] work if we assume $\lambda_T = \lambda_i$, $\lambda_i \cong 3\times10^{-2}$ m and similarly in Giordano *et al.*[4] $\lambda_i = 3.2\times10^{-3}$ m and Chaudhari and Habermeier[6] $\lambda_i = 2\times10^{-5}$ m. Thus $\lambda_i \geq 10^{-1}$ m in a pure sample is not unreasonable. It may be, however, that the experimental bulk value of λ_i is not relevant or is strongly affected by surface scattering (in the pure Bi samples there are 10^6 surface scatterings for each bulk phonon interaction). It may also be that surface scattering does not create enough disorder to cause localization. But then the simple criterion of maximum metallic resistance $R_c \cong 2\hbar/e^2$ is not so simple and further whiskers grown from Bi–6 at.% Sb also do not show localization effects. Note that it is not only the resistance increase at low temperatures that we fail to find, but neither do we find any deviations from Ohm's law.

Attempts to observe localization in thin wires have so far been somewhat ambiguous. Garland, Gully, and Tanner[12] found no effect in percolative mixtures of Ag particles in KCl. Dolan, Osheroff, and Tsui[13] found no effect in silicon metal-oxide-semiconductor field-effect transistors, and Dolan and Osheroff[5] find no 1D effect and deviations from Ohm's law in discontinuous metal films. Giordano, Gilson, and Prober[4] find a negative dR/dT in alloys of Au-Pd whose composition is in a range in which the bulk also shows a negative dR/dT. Chaudhari and Habermeier[6] also find a negative dR/dT in alloys of W-Re whose composition is delicately balanced such that the bulk dR/dT is nearly zero. By using Bi we can obtain the high resistivities necessary with a pure metal, avoiding some of the complications of other materials and allowing a comparison to the known properties of bulk materials. Unfortunately we do not find any evidence of localization.

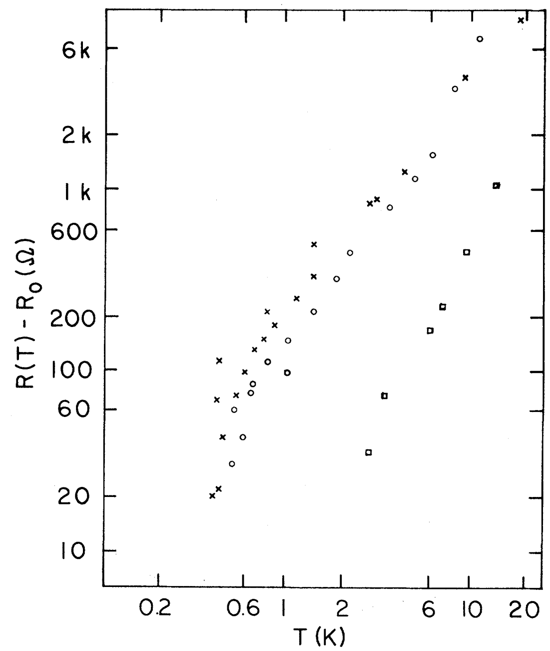

FIG. 4. Resistance vs temperature for three long and thin Bi–6 at.% Sb whiskers. Note the metallic behavior and the approximate low-temperature linear T dependence. The crosses, circles, and squares, respectively, denote whiskers characterized by diameters $\sqrt{A} = 140$ nm, 170 nm, and 210 nm, where A is the cross-sectional area of the whisker; lengths $L = 1.123$, 1.473, and 1.315 mm; and residual resistances $R_0 = 80.08$, 165.02, and 29.57 kΩ.

We would like to thank T. V. Ramakrishnan and M. D. Sherrill for several useful discussions and P. W. Anderson and D. J. Thouless for useful correspondence. We especially thank C. Leemann for growing the whiskers. This work was supported by the National Science Foundation through Grant No. DMR-78-12002.

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Momentum Dependence of Electronic Excitations in Polyacetylene

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Inelastic-electron-scattering experiments indicate that electronic excitations in polyacetylene, $(CH)_x$, are similar to those of a semiconductor with wide energy bands and an excitonic or indirect absorption edge. However, the measured bulk-plasmon energy increases linearly with momentum unlike that of known inorganic solids. Heavy doping with AsF_5 or iodine is found to result in an inhomogeneous mixture of metallic and insulating regions.

PACS numbers: 79.20.Kz, 71.35.+z

Polyacetylene, $(CH)_x$, is the first organic polymer for which the consequences of wide electronic energy bands appear to be significant.[1-4] But, the nature of its electronic structure is still controversial and both one-electron and many-particle theories have been advanced to explain the fundamental absorption edge.[1-4] Therefore, spectroscopies which probe the momentum dependence of electronic states and their excitations are crucial to an understanding of the electronic structure of $(CH)_x$. Here we report the first of such studies. Utilizing inelastic-electron-scattering spectroscopy we find that excitations in pure $(CH)_x$ can be described as those of a semiconductor with wide energy bands but that the fundamental absorption threshold is dominated by either indirect or excitonic effects. In addition, the present results suggest that the highly conducting state induced by heavy doping with AsF_5 or iodine is one in which the semiconducting band gap has been closed.

Thin-film samples of predominantly *trans*-$(CH)_x$ were prepared by standard techniques.[5-7] Heavy doping into the highly conducting state was accomplished by exposing the films to iodine vapor for 3 d or AsF_5 gas for 2 h at room temperature. While such procedures are known to produce samples of very high conductivity, the final stoichiometry or degree of homogeneity in doping are sample dependent.[7] Sample-dependent differences were observed in our experiments as differences in relative peak amplitudes. However, our conclusions are based on general features exhibited by all samples.

Energy-loss spectra of 80-keV electrons transmitted through the thin samples were measured with an energy-loss resolution of 0.11 eV and a momentum resolution of 0.055 $Å^{-1}$. Raw data at momentum $q = 0.1$ $Å^{-1}$ are given in Fig. 1. For better comparison with optical studies a Kramers-Kronig calculation was performed. Our results on unoriented films show only excitations known