RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 15 15 APRIL 1993-I

Temperature dependence of the electrical conductivity of potassium-doped polyacetylene as a function of pressure and magnetic field

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(Received 29 December 1992)

The effects of pressure and magnetic field on the electrical conductivity (σ) of oriented polyacetylene highly doped to the metallic state with potassium, K-$(CH)_x$, has been investigated. The conductivity at 10 kbar is greater than that at ambient pressure by a factor of two, and the temperature dependence is substantially weaker. The power-law temperature dependence of conductivity at ambient pressure, $\sigma(T) \propto T^{0.57}$, implies that K-$(CH)_x$ is in the critical regime near the metal-insulator boundary. At 10 kbar, $\sigma(T)$ becomes nearly temperature independent at low temperatures, consistent with pressure driving the system toward a transition into the metallic state. At ambient pressure, it is possible to localize the wave functions of the states near the Fermi level by an external magnetic field; at high fields $\sigma(T)$ crosses over from the power-law to the $\exp(-T^{-1/4})$ dependence characteristic of variable range hopping between localized states. Thus, increased pressure tends to delocalize the electronic wave functions, whereas high magnetic fields tend to localize the electronic wave functions.

INTRODUCTION

Although transport measurements have been reported for n-doped polyacetylene,[1,2] $(CH)_x$, prepared by the Shirakawa method[3] (density ≈ 0.7), relatively little is known about the properties of n-doped $(CH)_x$ prepared by the nonsolvent method[4] (density ≈ 1.15; i.e., close to the density inferred from the crystal structure), whereas p-doped $(CH)_x$ has been studied extensively in both cases.[5] Since the size of the counterions used for n doping (e.g., alkali-metal ions) is much smaller than those used for p doping (e.g., I_3^-), the interchain separation in the metallic state is smaller for n doping. Hence, one might anticipate that the interchain electron transfer matrix elements would be larger in n-doped materials. Since hydrostatic pressure will result in even stronger interchain coupling, three-dimensional metallic behavior might be achievable in n-doped metallic $(CH)_x$ at high pressures. On the other hand, application of high magnetic fields tends to localize the electronic wave functions.[6] Thus, for disordered systems near the metal-insulator boundary, the combination of high pressure and high magnetic field enables a study of the transition from insulator to metal.

The power-law temperature dependence of the electrical conductivity (σ) of oriented polyacetylene highly doped with potassium, K-$(CH)_x$, $\sigma(T) \propto T^{0.57}$, implies that at ambient pressure K-$(CH)_x$ is in the critical regime near the metal-insulator (MI) boundary. We have, therefore, used high pressure and high magnetic fields to investigate the electrical conductivity near the MI boundary. The conductivity at 10 kbar is greater than that at ambient pressure by a factor of 2, and the temperature dependence is substantially weaker. At 10 kbar, $\sigma(T)$ becomes temperature independent at low temperatures, demonstrating that pressure induces the transition into the metallic state. At ambient pressure, it is possible to localize the wave functions of the states near the Fermi level by an external magnetic field (H); at high fields, $\sigma(T)$ crosses over from the power law to $\exp(-T^{-1/4})$, characteristic of variable range hopping between localized states. Thus, increased pressure tends to *delocalize* the electronic wave functions, whereas high magnetic fields tend to *localize* the electronic wave functions.

EXPERIMENT

Polyacetylene films were prepared according to the nonsolvent method described by Akagi *et al.*[4] The samples were plasticized and tensile drawn to 7–10 times their original length; typical thicknesses were in the range 7–25 μm.[7] The oriented polyacetylene samples were doped by exposure to 0.005M solution of potassium naphthalide in tetrahydrofuran (THF).[8] *In situ* conductivity measurements were carried out using miniature four-terminal pressure contacts to monitor the conductivity while doping; the samples were removed from the doping solutions when the conductivity reached its maximum value. After doping, the same sample with the pressure contact assembly intact is inserted into a Teflon cell for high-pressure conductivity measurements.[9,10] Since K-$(CH)_x$ is extremely air sensitive, contamination is avoided by using the doping solution itself, or high-purity hexane, as the pressure transmitting medium.

More than 60 samples were prepared for the low-temperature studies; room-temperature conductivities were reproducible to within about a factor of 2. The temperature dependence was measured for eight samples (two under pressure). The power-law temperature dependence ($\sigma \propto T^n$) was reproducible with n between 0.5 and 0.6.

High-pressure conductivity measurements were carried out in a self-clamped beryllium-copper cell. After pressurizing, the cell was clamped at room temperature and then cooled to 1.3 K in a cryostat containing a superconducting magnet (0–10 T). Four-terminal direct current conductivity and high-pressure magnetoresistance measurements, up to 8 T, were carried out using a computer-controlled measuring system. Temperature was measured with a calibrated platinum resistor (300 to 40 K) or a calibrated carbon-glass resistor (40 to 1.2 K). To avoid sample heating at low temperatures, the current source was adjusted at each temperature so that the power dissipated into the sample was less than 1 μW.

RESULTS AND DISCUSSION

Previous conductivity measurements on K-$(CH)_x$, prepared by the Shirakawa method, yielded a maximum conductivity of 220 S/cm at room temperature.[1] The maximum conductivities reported for K-$(CH)_x$ prepared by the nonsolvent method and doped via the high-temperature vapor-phase method are 260 and 4300 S/cm for nonoriented and oriented films, respectively.[11] In the present work, using oriented $(CH)_x$ prepared by the nonsolvent method and doped by exposure to potassium naphthalide in THF, it was possible to achieve conductivities of 4000 S/cm.

As shown in the inset of Fig. 1, the conductivity of K-$(CH)_x$ increases steadily with pressure reaching a maximum at 10 kbar. The initial increase in conductivity is as anticipated; the increase results from enhanced interchain coupling and improved interchain hopping of charge carriers at high pressures. The origin of the decrease in conductivity about 10 kbar is less clear. The maximum in $\sigma(P)$ at 10 kbar is reversible and therefore appears to be an intrinsic feature (for example, it does not originate from an irreversible pressure-induced crosslinking reaction). Structural studies above and below the maximum will be required to obtain a better understanding of the origin of the maximum in $\sigma(P)$.

A wide range of functional forms has been explored for characterizing the temperature dependence of conductivity of K-$(CH)_x$ in its various forms,[1,2,11] including the $\exp[-T^{-1/4}]$ dependence characteristic of variable range hopping and the $\exp[T/T_0+T]$ derived within the Sheng model.[12] We find, however, that a power-law dependence, $\sigma(T) \propto T^{0.57}$, is the best fit for K-$(CH)_x$, as shown in Fig. 1. The exponent varies slightly for different samples, depending on the extent of disorder present in the material. The sample-to-sample variation correlates with the value of $\rho(300\ \mathrm{K})$ and with the ratio $\rho(1.2\ \mathrm{K})/\rho(300\ \mathrm{K})$; samples with lower (higher) $\rho(300\ \mathrm{K})$

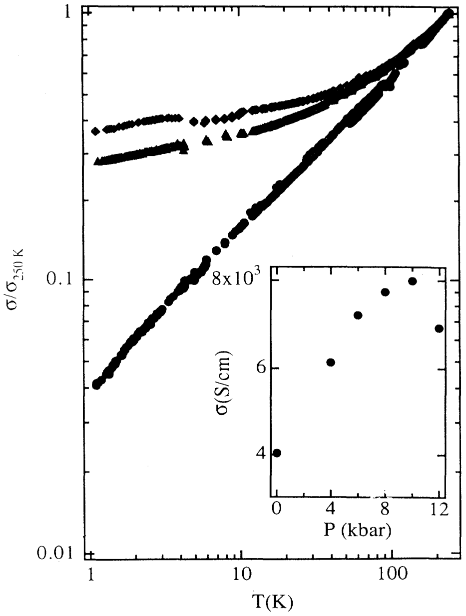

FIG. 1. Log-log plot of the conductivity vs temperature showing the power-law dependence of the normalized conductivity for K-$(CH)_x$ at ambient pressure. At 8 and 10.5 kbar, the conductivity becomes nearly temperature independent at low temperatures. The inset shows the conductivity vs pressure.

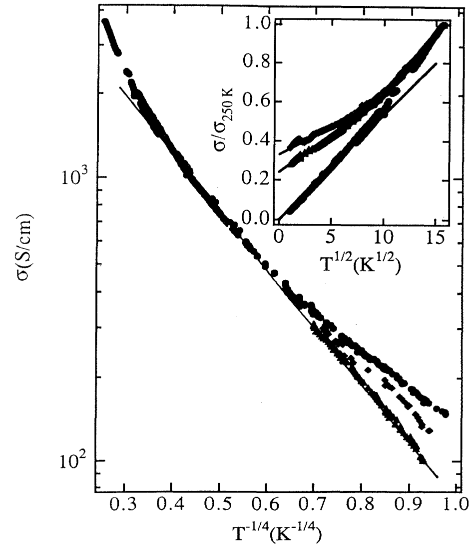

FIG. 2. $\ln\sigma(T)$ vs $T^{-1/4}$ for K-$(CH)_x$ at $H=0$, 4, and 8 T (at ambient pressure). The inset shows the normalized conductivity vs $T^{1/2}$ using the same data.

and smaller (larger) $\rho(1.2\text{ K})/\rho(300\text{ K})$ give slightly smaller (larger) exponent.

A $T^{1/2}$ dependence of conductivity $[\sigma=\sigma(0)+CT^{1/2}]$, typical of disordered systems with strong electron-electron correlations in three dimensions[6] was previously reported for K-$(\mathrm{CH})_x$.[2] However, for our data the $T^{1/2}$ fit is not satisfactory above 20 K, as shown in the inset of Fig. 2.

For a three-dimensional conductor in the metallic regime, but very close to the MI transition, the correlation length (L_c) is large and has a power-law dependence on $\delta=[(E_F-E_c)/E_c]\ll 1$, $L_c\approx a\delta^{1/\eta}$, where, a is a microscopic length, η is the critical exponent, E_F is the Fermi energy, and E_c is the mobility edge.[13] In this critical region, Larkin and Khmelnitskii found that the resistivity ($\rho=1/\sigma$) is not activated, but follows a power law as a function of temperature,[13]

$$p(T)\approx(e^2p_F/\hbar^2)(k_BT/E_F)^{-1/\eta}\ , \qquad (1)$$

where p_F is the Fermi momentum, e is the electron charge, and $1<\eta<3$.

This power-law dependence for $\rho(T)$ is universal and requires only that the disordered system be close to the MI transition, i.e., in the critical region where $\delta\ll 1$. The power-law temperature dependence has been observed in polyacetylene, in polypyrrole,[14] and in the emeraldine salt form of polyaniline prepared with surfactant counterions.[15]

The temperature dependence of conductivity of K-$(\mathrm{CH})_x$ changes drastically when the samples are at high pressure. As shown in Fig. 1, the conductivity ratio $\sigma(250\text{ K})/\sigma(1.3\text{ K})$ for K-$(\mathrm{CH})_x$ at ambient pressure is 25 whereas at 10 kbar the ratio is reduced to only 2.8. The *temperature-independent* conductivity observed at 10 kbar for temperatures below 4.2 K indicates that pressure shifts the material out of the critical regime of MI transition toward the metallic state. This is consistent with the increased magnitude of the conductivity at high pressure and with expectations based on increased interchain coupling. The larger interchain bandwidth delocalizes the electrons near the Fermi level and thereby shifts the mobility edge away from E_F, thus making a better metal. This shows that metallic transport in doped oriented $(\mathrm{CH})_x$ is still limited by the interchain transfer interaction.

Khmelnitskii and Larkin used scaling arguments to demonstrate that in the metallic region near the MI transition, the mobility edge can be shifted by an external magnetic field (H).[16] When the magnetic length $L_H=(\hbar c/eH)^{1/2}$ becomes comparable to L_c, the shift in E_c is proportional to $(L_H/L_c)^{1/\eta}$, where $\hbar$ is Planck's constant and c is the velocity of light. Because of this ability to shift E_c by an external magnetic field, one can envision a crossover from the metallic behavior with power-law dependence for $\rho(T)$ in zero field to insulating behavior with variable range hopping among localized states for $L_H/L_c\le 1$. This type of behavior has been reported for the emeraldine salt form of polyaniline doped with camphor-sulfonic acid.[15]

The magnetic-field dependence of the conductivity of K-$(\mathrm{CH})_x$, at ambient pressure, is shown in Fig. 3. At $H=0$, the power-law fit is excellent, $\sigma(T)\propto T^{0.57}$; at $H=8$ T, however, $\sigma(T)$ deviates strongly from the power law at low temperatures. The magnetic-field dependence of conductivity above 4.2 K is not very significant.

When the same data are plotted in Fig. 2 as $\ln\sigma$ vs $T^{-1/4}$, the magnetic-field-induced transition from power-law dependence (characteristic of transport at the MI boundary) to variable range hopping (VRH) (charac-

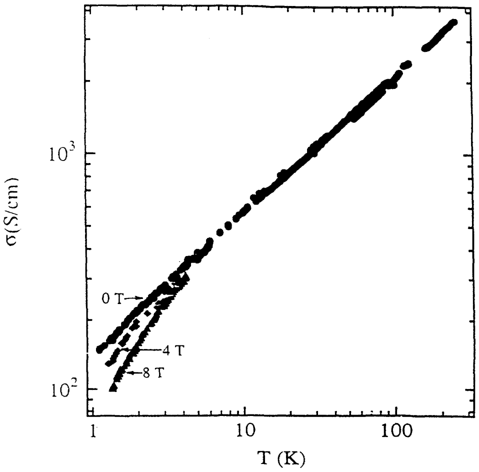

FIG. 3. Log-log plot of the conductivity vs temperature showing the power-law dependence of the normalized conductivity for K-$(\mathrm{CH})_x$ at ambient pressure and at $H=0$; at $H=4$ and 8 T (at ambient pressure) the temperature dependence is stronger (see Fig. 2).

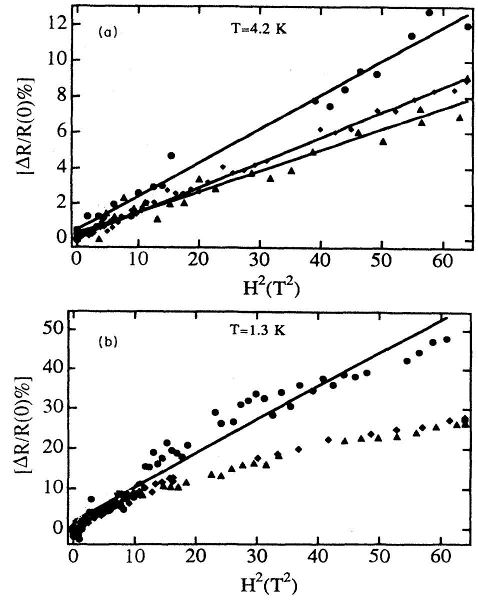

FIG. 4. (a) Magnetoresistance vs H^2 for K-$(\mathrm{CH})_x$ at ambient pressure (dots), at 8 kbar (diamonds), and at 10 kbar (triangles) at 4.2 K. (b) Magnetoresistance vs H^2 for K-$(\mathrm{CH})_x$ at ambient pressure (dots), at 8 kbar (diamonds), and at 10 kbar (triangles) at 1.3 K.

teristic of transport through localized states near E_F) is clearly evident.[17] The linear dependence of $\ln\sigma$ vs $T^{-1/4}$ at 8 T is shown in Fig. 2; at 4 T and at $H=0$, however, the low-temperature conductivity data deviate from the VRH dependence (as expected from the excellent power-law fit shown in Fig. 1).

This magnetic-field-induced localization is expected to become important when $L_H/L_c \leq 1$. Since $L_H = 90$ Å at $H=8$ T, the condition $L_H/L_c \approx 1$ implies a localization length of comparable magnitude. For VRH in three dimensions,

$$\rho(T)=\rho_0 \exp[T_0/T]^{1/4} , \tag{2}$$

where

$$T_0 = 16/N(E_F)L_c^3 , \tag{3}$$

k_B is the Boltmann constant, and $N(E_F)$ is the density of states at the Fermi level. For fully doped $(CH)_x$, $N(E_F)$ is 4.1×10^{21} states/eV cm^3. The slope of the $H=8$ T data in Fig. 2 yields $T_0=57$ K. Substituting for $N(E_F)$ into Eq. (3) for T_0, we find $L_c=93$ Å. Indeed, the condition $L_H/L_c\approx 1$, necessary to observe the magnetic-field-induced localization (and associated shift in the mobility edge), is satisfied.

Because of the shift of E_F away from E_c at high pressure, the system has crossed into the metallic regime away from the critical region of the MI boundary. Consequently, at high pressure, the magnetoresistance is that of a disordered metal. The magnetoresistance data $\Delta\rho(H)/\rho(0)$ of K-$(CH)_x$ at ambient pressure, at 8 kbar, and at 10 kbar are linear in H^2 as shown in Fig. 4. At 1.3 K the H^2 fit is linear only at low fields, since at high fields, $\Delta\rho(H)/\rho(0)$ begins to saturate. At 10 kbar the magnetoresistance has decreased by a factor of 2. This substantial decrease is in agreement with the previous observation that, under pressure, K-$(CH)_x$ is in the metallic regime away from the critical region of the MI transition. Typically, in disordered metals the positive magnetoresistance is less than 10% at 1.3 K.[6,18] The comparatively large value (25% at 1.3 K) in K-$(CH)_x$ at 10 kbar, is possibly due to the large localization length ($L_c \approx 100$ Å) and the dependence of L_c on magnetic field.

CONCLUSION

The power-law temperature dependence of conductivity shows that heavily doped K-$(CH)_x$ is in the critical regime of the MI transition. Application of an external magnetic field causes a crossover from the Larkin-Khmelnitskii power-law dependence of the disordered metal in the critical regime to variable range hopping among localized states near the Fermi energy. This transition is suppressed at high pressure. At 10 kbar, the conductivity increases by a factor of 2, the ratio of $\sigma(250\ \mathrm{K})/\sigma(1.3\ \mathrm{K})$ decreases by a factor of 9, and the magnetoresistance at 1.3 K decreases by a factor of 2. These results show that pressure improves the interchain transport and thereby shifts K-$(CH)_x$ away from the critical regime of the MI transition into a marginally metallic state. Quite clearly, therefore, the magnitude of the electrical conductivity of "metallic" *n*-doped polyacetylene remains severely limited by disorder even at high pressures.

ACKNOWLEDGMENTS

This work was partially supported by the National Science Foundation through Grant No. NSF-DMR 91-00033, and partially supported by a research grant from the Electric Power Research Institute (EPRI).

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