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Heterogeneous model for conduction in carbon nanotubes

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We point out a remarkable similarity between the resistivity behavior observed recently in single-wall carbon nanotubes and that of highly conducting polymers, in particular the change in sign of the resistivity temperature dependence from metallic to nonmetallic as the temperature is lowered. In analogy to the conducting polymers, we show that a good description of this resistivity behavior is given by a simple model of metallic conduction in aligned nanotubes with hopping or tunneling through small electrical barriers, e.g., tangled regions, inter-rope or intertube contacts, or tubule defects. The model predicts that thermoelectric power in the nanotubes is likely to show metallic behavior down to lower temperatures than resistivity. [S0163-1829(98)05803-2]

A landmark in research on carbon nanotubes was reached very recently with the observation by Fischer *et al.*[1] of a metallic sign for the temperature dependence of the resistivity ρ (i.e., $d\rho/dT>0$) for crystalline ''ropes'' or bundles of diameter 10–20 nm consisting of single-wall nanotubes,[2] consistent with the predicted metallic state for achiral single-wall nanotubes having the ''armchair'' configuration.[3,4] However, a fully metallic temperature dependence has not so far been observed: There is always a reversion to a nonmetallic temperature dependence $d\rho/dT<0$ at lower temperatures. The crossover temperature T^* between the metallic and nonmetallic temperature dependence varied from 35 K for a single well-ordered rope to approximately 250 K for a rope with tangled regions.[1] In the case of multiwall nanotube bundles[5,6] or films,[7] the temperature dependence of resistivity remains nonmetallic up to the limit of measurements at 300 K.

The resistance of individual carbon nanotubes has also been investigated recently. It was found for individual multiwall tubes[8–10] (apart from one sample showing a sharp resistance change[8]) that $d\rho/dT<0$, as for multiwall nanotube bundles. Measurements at ambient temperature[11] emphasized that structural defects (e.g., associated with tube curvature) cause substantial increases in resistivity. Very recent data for individual single-wall nanotubes[12] at extremely low temperatures (in the millikelvin range) indicate conduction through discrete electron states that are coherent over at least 140 nm.

In this paper, we focus on the observations[1] of the crossover from a metallic to nonmetallic sign for resistivity at temperatures between 35 K and 250 K. We point out the remarkable similarity to the behavior of conducting polymers, and show that the nanotube behavior is well accounted for by a heterogeneous conduction model similar to that used[13] for the polymers.

The resistivities of the carbon nanotubes showing metallic sign in their temperature dependence are compared in Fig. 1 to typical behavior for highly conducting polymers. The temperature dependence for the rope consisting of straight well-ordered segments interspersed with 1–2 μm tangled regions has $T^*\sim 250$ K and a strong increase of resistivity at lower temperatures.[1] As clearly seen in Fig. 1, this behavior resembles closely that for a polymer blend[14] with 40% polyaniline dispersed in the nonconducting polymer PMMA.

The resistivities of unoriented bulk samples, or ''mats,''

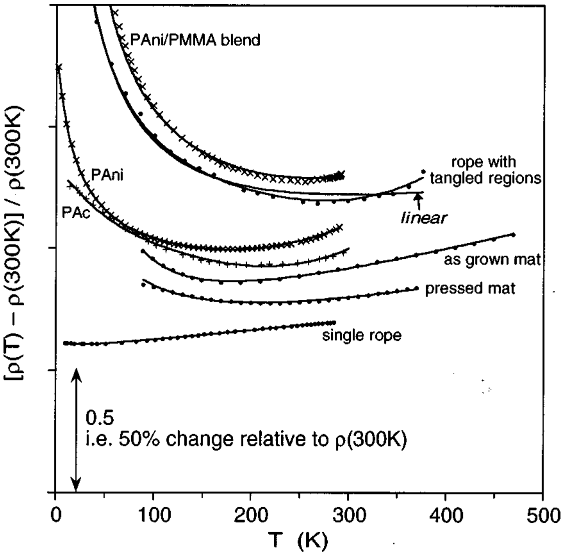

FIG. 1. Comparison of the temperature dependence of the normalized resistivity of single-wall nanotubes (●) reported by Fischer *et al.* (Ref. 1) with that of three typical conducting polymers ($\times,+$): $FeCl_3$-doped polyacetylene (PAc) (Ref. 15), CSA-doped polyaniline (PAni) (Ref. 16), and a 40% PAni/60% PMMA blend (Ref. 14). The lines are fits to Eq. (3) for heterogeneous conduction with a linear metallic term for the nanotubes (labeled ''linear'' for the rope with tangled regions), and to Eq. (2) with a highly anisotropic metallic term (Ref. 14) for the polymers and the rope with tangled regions, as discussed in the text. For clarity, the different data sets are displaced by steps of 0.1 in the vertical direction, and not all data points are shown.

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of long tangled ropes have $T^* \sim 200$ K and a smaller increase at low temperatures, for both as-grown and lightly pressed mats. This resembles the behavior seen in highly conducting polyacetylene[15,13] and polyaniline.[16,14] The most metal-like nanotube sample, the single low-defect rope, shows only a very small increase in resistivity at low temperatures with $T^* \sim 35$ K, and so the temperature dependence appears considerably more metallic than in any of the conducting polymers.

The magnitude of the single-wall nanotube resistivities near room temperature ranges from around 0.1 mΩ cm for the single rope to approximately 6 mΩ cm for the as-grown mat (the extremely low densities of the mats increase their resistivities[1]). Approximate values for the room temperature resistivities of the conducting polymers are 0.01 mΩ cm for the polyacetylene sample,[15] 4.4 mΩ cm for polyaniline,[16] and 100 mΩ cm for the PAni/PMMA blend.[14] For these nanotubes and even more for the polymers, the same generic pattern of resistivity temperature dependence is seen over a wide range of resistivity magnitudes and types of material. Fischer *et al.*[1] point out that for the nanotubes, the crossover phenomenon appears to be a general feature of electron transport in the ropes, as it is for a wide range of conducting polymers (we note that polypyrrole does not show such a crossover in sign of the temperature dependence below room temperature,[14] although a reduction in $d\rho/dT$ occurs in some samples as the temperature increases towards 300 K, which could be a precursor to a sign change at higher temperatures).

We suggest that the striking generic similarity between the temperature dependence of the nanotube and polymer resistivities arises from a similar feature in the conduction mechanism, namely, the presence of good conducting regions separated by barriers to conduction. The importance of heterogeneity was recognized for the earliest conducting polymers,[17] and still holds true for the latest and most highly conducting samples: Their resistivity has been found to be described very well by a heterogeneous model involving regions of highly anisotropic metallic conduction separated by ''barrier'' regions, as indicated by the fits to the polymer data illustrated in Fig. 1.[13,14] The general characteristic of a heterogeneous model of this kind is a crossover from a nonmetallic to metallic resistivity temperature dependence. The metallic resistance increases with temperature, while the barrier resistance decreases as temperature (and so thermal energy) increases. This leads naturally to a crossover at some temperature T^*, depending on the relative significance of the barriers, without a temperature-induced phase transition, and with no qualitative change in the nature of conduction at T^*. In the case of polyacetylene, the observation of a remarkably linear thermopower from low temperatures to well above T^* virtually rules out[13] the alternative explanation of the crossover as due to delocalization of carriers near T^*, or some other change in the nature of the electronic states, because thermopower is highly sensitive to electronic structure near the Fermi level and would show an effect at T^* in that case.

An analogous heterogeneous picture of this type seems particularly appropriate for the individual rope with low-defect rope segments separated by tangled regions that was measured by Fischer *et al.*,[1] and also for the mats of tangled ropes in which inter-rope contacts are likely to act as barriers [scanning electron microscope (SEM) and transmission electron microscope (TEM) images of these materials are shown in Fig. 1 of Ref. 2]. The qualitative similarity of the resistivities for all their samples emphasized by Fischer *et al.*[1] means that the model may also be appropriate for the high-conductivity low-defect rope with the least disorder. Fischer *et al.*[1] speculate that localization of carriers occurs in the nanotubes. In our model, localization could occur first at specific locations (at various sorts of defect), the localized-carrier segment then acting as a barrier separating conducting metallic regions. Thus we envisage that as well as inter-rope or intertube contacts, the barriers implied by our interpretation could be pentagon/heptagon defects or other defects in which tube sections with different electronic structures meet.[18]

For conduction along nanotube ropes consisting of aligned tubules of similar type, with metallic regions separated by disordered barrier regions, we write the resistivity, in analogy to our previous model for conducting polymers, as[19]

$$\rho(T)=\sum_i \frac{L_i A}{L A_i}\rho_i(T), \tag{1}$$

where L and A are the total effective length and cross-sectional area of the sample, L_i is the length of the path consisting of material i with intrinsic resistivity $\rho_i(T)$, and A_i is the effective cross-sectional area for conduction in each region. For example, $i=1$ would correspond to the metallic regions and $i=2$ to barrier regions in the simplest model. For mats of nanotube ropes, the resistivity would need to be averaged over the ropes in varying directions, with additional barriers at the inter-rope contacts. For a single rope of equivalent well-aligned weakly coupled tubules with defects localized on individual tubules, a similar expression might apply with $A_i = p a_i$, where p is the number of tubules in the rope, each with an effective cross-section a_i (a similar fibrillar model is discussed in our earlier paper[19]).

It is found that a wide range of conductivity data for conducting polymers is well described (except for localization effects near liquid helium temperatures) by the general expression[13,14]

$$\rho(T)=\rho_m \exp(-T_m/T)+\rho_t \exp[T_c/(T+T_s)], \tag{2}$$

where ρ_m, T_m, ρ_t, T_c, and T_s are constants [the geometric factors in Eq. (1) are incorporated in ρ_m and ρ_t]. This is illustrated by the fits for polyacetylene and polyaniline in Fig. 1 (see earlier papers for details[13,14]). The first term represents a highly anisotropic metallic term corresponding to conduction along the polymer chain direction where phonons of energy $k_B T_m$ that have wave vectors $2k_F$ spanning the Fermi surface are required to backscatter carriers.[20] The second term corresponds to fluctuation-induced tunneling between metallic regions separated by thin barriers.[21] For the PAni/PMMA blend in Fig. 1, for which the conductivity $\sigma \to 0$ as $T \to 0$, the fit is to the metallic term plus the expression $\exp(-T_0/T)^{1/2}$ for tunneling between mesoscopic metallic islands,[14] but the difference in shape between these two tunneling terms is small except at low temperatures.

The data[1] for the carbon nanotube rope with tangled regions also follow Eq. (2) well, as shown by the unlabeled fit in Fig. 1. The tunneling parameter values are $T_c = 65$ K and $T_s = 42$ K (with $T_m \sim 2000$ K), which are of the same order of magnitude as for the polymers.[13] The metallic term contributes only about 5% of the resistivity at room temperature (but leads to $d\rho/dT > 0$ because of its strong increase at higher temperatures).

The data for the other three nanotube samples are better described (see Fig. 1) using the standard linear metallic resistivity in place of the highly anisotropic metallic resistivity term:

$$\rho(T) = AT + \rho_t \exp[T_c/(T+T_s)], \qquad (3)$$

where A is a constant. It is clear from Fig. 1 that the linear metallic term is also only a small fraction of the total room temperature resistivity. The limited regimes with $d\rho/dT < 0$ and the fact that metallic resistivity would not be expected to be linear at lower temperatures[1] mean that unique values of the tunneling parameter pairs (T_c, T_s) cannot be determined, but clearly the same generic expression as for the polymers can account for the resistivity upturns at lower temperatures. This greater tendency to linearity of the high-temperature resistivity in the nanotubes does represent a difference from the polymers; it could be related to a stronger carrier backscattering effect by phonons along the one-dimensional polymer chains compared to the wrapped two-dimensional graphite sheets of the nanotubes, even though the nanotube diameter is only 1.38 nm.[2]

In Fig. 2, we show the measured conductivities of multiwall nanotubes as well as single-wall nanotubes (conductivity is plotted rather than resistivity to show the behavior at low temperatures more clearly). The data of Langer *et al.*[6] for multiwall bundles are similar to that for the single-wall rope of Fischer *et al.*[1] from 200 K down to 10 K, and also similar to the temperature dependence of some conducting polymers. From the data in Fig. 2, it is difficult to establish a consistent pattern for the multiwall nanotube data for either bundles or individual tubes. Below 20 K, both sharp decreases in conductivity[5,9] and plateaus[6,10] are seen for bundles and individual tubes. However, two features stand out. First, the conductivity (except for the very low conductivity NT4 sample[8]) does not appear to extrapolate to zero as $T \to 0$, suggesting that metallic conduction could play a role even at low temperatures in the multiwall nanotubes despite the lack of metallic sign for the conductivity temperature dependence. Second, as for the single-wall tubes, there appears to be more of a tendency to linear variations with temperature than for conducting polymers, although the temperature dependence is nonmetallic in the multiwall case.

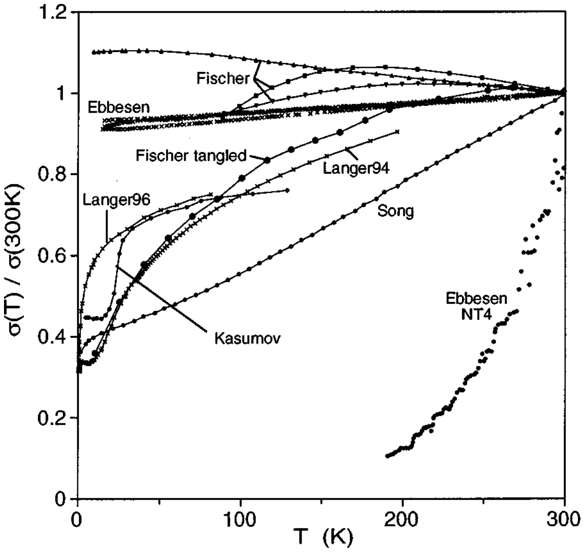

FIG. 2. Normalized conductivity of multiwall carbon nanotube bundles from Ref. 5 (Song) and Ref. 6 (Langer94), and of individual multiwall tubes from Ref. 9 (Langer96), Ref. 8 (Ebbesen), and Ref. 10 (Kasumov). For comparison, data for the single-wall nanotube ropes from Ref. 1 (Fischer) are also shown. Data not extending up to 300 K is normalized to 0.75 at 100 K or at 80 K (Langer96). The lines simply join data points.

Other properties may assist in clarifying the conduction process. Because localization near defects is a possible cause of the barriers to conduction in our model, magnetoconductance may well show localization effects at low temperatures. The absolute size of these localization effects in the total conductivity would be larger than in uniformly disordered systems, since they would be enhanced as the conductivity is enhanced by the presence of the conducting metallic regions according to Eq. (1).[19] Unusually large localization effects of this sort have been seen at very low temperatures in highly conducting polymers.[13] This heterogeneous localization near imperfections can explain why localization effects are seen in materials such as highly conducting polyacetylene with a lower resistivity than would normally be expected for localization. It also gives a more robust and general explanation for a combination of metallic and nonmetallic conduction features than a uniform localization model.

A property that could be of particular interest is the thermopower. Since the barriers we have postulated are electrical rather than thermal barriers, and the thermopower for series connections is weighted in favor of regions where most of the temperature gradient occurs, we would expect the thermopower to be more metallic than the conductivity in our picture, as observed for conducting polymers.[19,13]

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[1] J. E. Fisher, H. Dai, A. Thess, R. Lee, N. M. Hanjani, D. L. Dehaas, and R. E. Smalley, Phys. Rev. B **55**, R4921 (1997).

[2] A. Thess, R. Lee, P. Nikolev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tománek, J. E. Fischer, and R. E. Smalley, Science **273**, 483 (1996).

[3] J. W. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. **68**, 631 (1992).

[4] N. Hamada, S.-I. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).

[5] S. N. Song, X. K. Wang, R. P. H. Chang, and J. B. Ketterson, Phys. Rev. Lett. **72**, 697 (1994).

[6] L. Langer, L. Stockman, J. P. Heremans, V. Bayot, C. H. Olk, C. Van Haesendonck, Y. Bruynseraede, and J.-P. Issi, J. Mater. Res. **9**, 927 (1994).

[7] W. de Heer, W. S. Bacsa,A. Châtelain, T. Gerfin, R. Humphrey-Baker, L. Forro, and D. Ugarte, Nature (London) **268**, 845 (1995).

[8] T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio, Nature (London) **382**, 54 (1996).

[9] L. Langer, V. Bayot, E. Grivei, J.-P. Issi, J. P. Heremans, C. H. Olk, L. Stockman, C. Van Haesendonck, and Y. Bruynseraede, Phys. Rev. Lett. **76**, 479 (1996).

[10] A. Yu. Kasumov, I. I. Khodos, P. M. Ajayan, and C. Colliex, Europhys. Lett. **34**, 429 (1996).

[11] H. Dai, E. W. Wong, and C. M. Lieber, Science **272**, 523 (1996).

[12] S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs, and C. Dekker, Nature (London) **386**, 474 (1997).

[13] A. B. Kaiser, Synth. Met. **45**, 183 (1991).

[14] A. B. Kaiser, C.-J. Liu, P. W. Gilberd, B. Chapman, N. T. Kemp, B. Wessling, A. C. Partridge, W. T. Smith, and J. S. Shapiro, Synth. Met. **84**, 699 (1997).

[15] J. Tsukamoto, Adv. Phys. **41**, 509 (1992).

[16] C. O. Yoon, M. Reghu, D. Moses, A. J. Heeger, and Y. Cao, Synth. Met. **63**, 47 (1994).

[17] Y. W. Park, A. J. Heeger, M. A. Druy, and A. G. MacDiarmid, J. Chem. Phys. **73**, 946 (1980).

[18] C. L. Kane and E. J. Mele, Phys. Rev. Lett. **78**, 1932 (1997).

[19] A. B. Kaiser, Phys. Rev. B **40**, 2806 (1989).

[20] L. Pietronero, Synth. Met. **8**, 225 (1983).

[21] P. Sheng, Phys. Rev. B **21**, 2180 (1980).