Thermoelectric power behavior in carbon nanotubule bundles from 4.2 to 300 K

Mingliang Tian, Fanqing Li, Lin Chen, and Zhiqiang Mao
Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, Anhui, People's Republic of China

Yuheng Zhang
Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, Anhui, People's Republic of China and Chinese Center of Advanced Science and Technology (CCAST), Beijing 10080, People's Republic of China

(Received 3 October 1997)

Thermoelectric power (TEP) properties of carbon nanotubule bundles were measured in the range 4.2–300 K. It was found that the TEP is positive over the whole temperature range, and increases with the increase of temperature. Above 30 K it can be well described by a formula $S(\mu V)=0.181T-(61.8+0.092T)e^{-308.3/T}$, which is derived based on a two-band model. This result supports the theoretical prediction for both kinds of nanotube bundles, metallic and semiconducting. Below about 30 K, the fitting curve clearly deviates from the experimental data, which may indicate some possible changes of electronic structures, an electron weak localization effect, for example. [S0163-1829(98)00324-5]

The studies of electronic structures of fullerene nanotubes have attracted much attention due to their extraordinary nature.[1] For example, band structure calculations predict that fullerene nanotubes can exhibit some striking variations in their electronic structures from metallic to semiconducting depending on the diameter of the tube and the degree of helical arrangement.[2–8] Theoretical studies of these features are advancing and are predicted to have significant potential for applications to electronic devices.[3,9] However, support from experiments is still deficient, mainly because of the difficulties in isolating single tubes with almost molecular dimensions and attaching electrical contacts to their ends. As far as we are aware, experimental studies so far performed on nanotubule films or so-called single tubes, including dc conductivity,[10,11] Hall effect and magnetoresistance,[12,13] static magnetic susceptibility,[14] and optical reflectivity,[15] have not provided information about semiconducting tubes; these studies support that nanotubule films or bundles are rather good conductors with some anisotropy or semimetals above 50 K. Below about 50 K, a localization of carriers on tubes or a spin-dependent hopping mechanism might be involved.

In order to investigate the electronic properties of nanotubes, we reported a preliminary thermoelectric power (TEP) experimental result for nanotubes above 85 K.[16] In that report we could not achieve TEP results below 85 K due to the limitations of our experimental equipment. As is well-known, the physical properties of nanotubes at lower temperatures are more attractive due to a possible change of dimensionalities from three to two dimensions (2D) near about 50 K. In this paper, we improved our experimental system, and extended our measurements to 4.2 K. This system can be controlled by a computer automatically using a LABVIEW program, and the voltage difference between the two terminals of the bundle was measured by a Keithley 182 nanovoltmeter. The system was strictly calibrated using a high-purity lead Pb standard sample.

Fullerene nanotube bundles used in this work were prepared using the normal carbon arc plasma method.[1] The deposition which built up on the end of the cathode was composed of an inner soft black core and an outer gray hard shell. The structural characterization of the black inner core of the deposit was carefully characterized by scanning electron microscopy (SEM) and by high-resolution electron microscopy (HREM). It was revealed that the inner black core contains many aligned carbon bundles with ~mm scale in length as shown in Fig. 1(a). Figure 1(b) shows one of these carbon bundles. Inside the carbon bundle, a lot of nanotubes with a diameter of about 20 nm on average are contained. Figure 1(c) shows one of the HREM pictures of these nanotubes. The nanotubes have a multiwall structure and are dominant in the bundles.

Figure 2(a) shows the result of TEP measured in a carbon nanotubule bundle in the range 4.2–300 K. The TEP is posi-

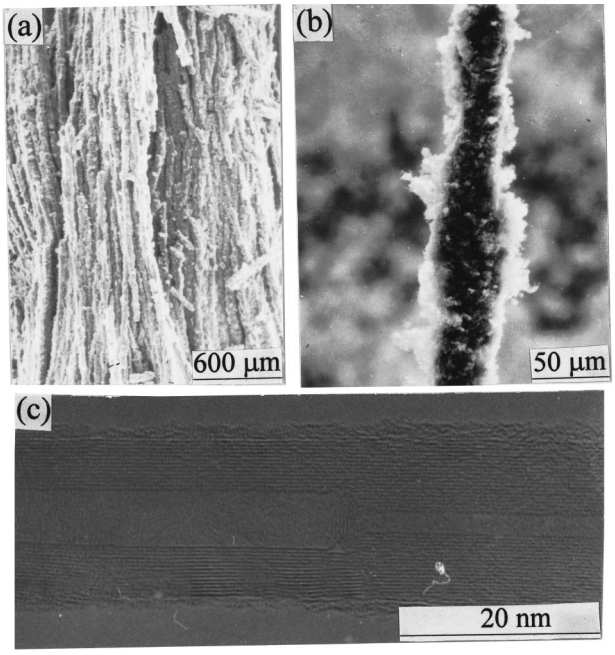

FIG. 1. (a) The SEM picture for the inner core of the deposit; (b) the SEM picture for a single carbon bundle; (c) one of the HREM pictures of nanotubes inside the bundle; the multishell structure can be clearly seen.

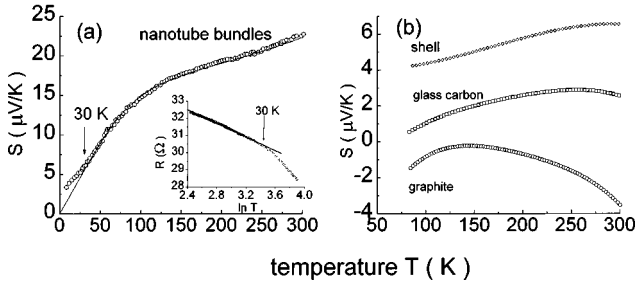

FIG. 2. (a) The temperature dependence of thermoelectric power for nanotubule bundle in range 4.2–300 K; the solid curve is the fitting data given by the formula $S=0.181T-(61.8+0.092T)e^{-308.3/T}$ derived based on a two-band model; the inset is the temperature dependence of resistivity below 50 K; (b) the thermoelectric power versus temperature T for HOPG, the glass carbon, and outer hard shell of the deposit in range 80–300 K.

tive over the whole range and increases with temperature. Figure 2(b) shows the temperature dependence of the TEP in highly oriented pyrolytic graphite (HOPG), the commercial glass carbon rod used in this work, and the outer gray hard shell of the deposit in the range 80–300 K. Obviously, the TEP behavior in the carbon nanotubule bundle is quite different from that in HOPG, the outer shell of the deposit, and the glass carbon. In the nanotubule bundles, the TEP was strongly enhanced and reaches an order of about $+22\ \mu$V/K at 300 K, far larger than that in the HOPG, glass carbon, and the shell of the deposit. Based on the fact that the sign of the TEP of the nanotubule bundle is always positive, this may imply that the majority carriers in the nanotubule bundles should be P type, and the hole carriers are dominant. This result is in good agreement with the Hall coefficient measurement reported by Song *et al.*[12] and by Baumgartner *et al.*,[13] where the observed Hall coefficients are also positive over the entire temperature range.

From Fig. 2(a), it is worth noting that the obtained temperature dependence of the TEP behavior cannot be simply explained by a single-band model for a metal or a nondegenerate semiconductor. In Ref. 16, we analyzed the TEP data above 85 K using the two-band model, where the TEP was considered to be mainly dominated by the contributions of metallic band carriers and semiconducting band carriers. The total TEP can be expressed as

$$S=AT+(B\Delta+CT)e^{-\Delta/T}, \tag{1}$$

where A, B, and C are constants, and Δ is the thermally activated energy for the semiconducting tubes. The first term AT, where $A=-\pi^2k^2/2eE_F$,[17] denotes the contributions of metallic tubes (where E_F, k, and e are, respectively, the Fermi energy, Boltsmann constant, and the value of electron charge), while the other terms are the contributions of semiconductive tubes. Taking Eq. (1) to fit our experimental data here, the constant parameters can be, respectively, given as $A=0.181\ \mu\text{V/K}^2$, $B=-0.2\ \mu\text{V/K}^2$, $C=-0.092\ \mu\text{V/K}^2$, and $\Delta=308.3$ K. The final expression for the TEP of the carbon nanotubule bundle can be described by $S(\mu\text{V})=0.181T-(61.8+0.092T)e^{-308.3/T}$. The fit data is plotted in Fig. 2(a) as a solid curve. It is seen that above about 30 K the calculated values of S are in good agreement with the experimental data, the TEP property is dominated by the first term with a positive sign contributed by the hole carriers from metallic nanotubes, and the negative terms are contributed by the electron carriers from semiconducting tubes.

From parameter A, we can approximately estimate the Fermi energy of the valence band of the metallic tubes and get $E_F=-0.2$ eV. The minus sign means that the conduction of the metallic tubes results from the holes of the valence bands. If assuming the effective mass of a hole carrier on the Fermi surface is $m^*=0.06m_0$ (m_0 is the static electron mass),[18] yielding a Fermi velocity $V_F=(2E_F/m^*)^{1/2}\approx10^8$ cm/s, which is in good agreement with that estimated by Song *et al.*, who used Hall measurement[12] (they neglect the Hall scattering factor and use $R=1/ne$ and carrier density $n\approx10^{18}$ cm^3, yielding $V_F\sim10^8$ cm/s). Using the parameter Δ, the energy gap $E_g=2\Delta$ for the semiconductor tubes is estimated to be about 53 meV. These values are in good agreement with our previous preliminary report,[16] although the magnitudes of the TEP are, to some extent, larger than those reported previously. The estimated values for the energy gap, Fermi energy, and Fermi velocity are almost the same as the previous report based on the two-band model, the differences in the magnitudes of the TEP for both measurements may result from the differences in the nanotubule samples used.

In this paper, we want to emphasize that below about 30 K the fitting curve according to the above two-band model clearly deviates from the experimental data; such a slight deviation below about 30 K is in good agreement with the measurement of resistivity, where, at lower temperatures $T<30$ K, the resistivity showed a linear dependence with $\ln T$, i.e., $R=37.3-1.99\ln T$, as shown in the inset of Fig. 2(a). Such a temperature-dependent behavior of resistivity with $\ln T$ was usually considered to be a possible signature of two-dimensional weak localization of carriers in a metal.[19] Therefore, the deviation of the fitting curve near 30 K may be an indication of some changes of the transport mechanism, possibly related to the localization effect of carriers in the metallic nanotubes since a possible 2D-3D crossover of dimensionalities should occur near that temperature as reported by Song *et al.*,[12] at lower temperatures the electronic structure is essentially two dimensional in character. As far as we know, the TEP behavior for the 2D localized system is not very clear. A quantitative explanation at present is rather difficult and further clarification needs to be done in more detail in future work.

On the other hand, we also noted that for the nanotubes no large negative phonon-drag minimum near about 40 K, which usually appears in HOPG, was observed.[20] As is well known, a nanotube can be visualized as a graphite sheet rolled up in a helical fashion about the tube axis. They act as a collection of microcrystals of HOPG's of different sizes.[1,21] The disappearance of such a phonon-drag effect in nanotubes indicates that the electronic structures in nanotubes are indeed remarkably different from HOPG and closely related to their special structures. The electron-phonon interactions below 40 K are very weak in nanotubule materials, and the carrier-carrier interactions may play a dominant role, which leads to a possible weak localization effect of carriers.

In summary, we report TEP measurements on carbon

nanotubule bundles from 4.2 to 300 K. The results can be well described by a two-band model above 30 K. They provide experimental evidence that both kinds of nanotubes in the bundles, i.e., metallic tubes with a highly mobile carrier velocity and semiconducting tubes with a narrow energy gap, coexisted, a conclusion which coincides with the theoretical predictions. Below about 30 K a deviation of the fitting curve was observed, which may be an indication of some changes of transport mechanisms, possibly related to the weak localization of carriers in the nanotubes.

[1] S. Iijima, T. Ichihashi, and Y. Ando, Nature (London) **356**, 776 (1992); S. Iijima, *ibid.* **354**, 56 (1991).
[2] N. Hamada, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).
[3] R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett. **60**, 2204 (1992); Phys. Rev. B **46**, 1804 (1992); J. Appl. Phys. **73**, 494 (1993).
[4] C. T. White, D. H. Robertson, and J. W. Mintmire, Phys. Rev. B **47**, 5458 (1993).
[5] S. Ishihara and S. Itoh, Phys. Rev. B **48**, 5643 (1993).
[6] M. S. Dresselhaus, G. Dresselhaus, and R. Saito, Phys. Rev. B **45**, 6234 (1992).
[7] J. W. Mintmire, D. H. Robertson, and C. T. White, J. Phys. Chem. Solids **54**, 1835 (1993); J. W. Mintmire, S. I. Dunlap, and C. T. White, Phys. Rev. Lett. **68**, 631 (1992).
[8] H. Yorikawa and S. Muramatsu, Phys. Rev. B **50**, 12 203 (1994).
[9] L. Chico, V. H. Crespi, L. X. Benedict, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **76**, 971 (1996).
[10] A. Yu. Kasumov, I. I. Khodos, P. M. Ajayan, and C. Colliex, Europhys. Lett. **34**, 429 (1996).
[11] L. Langer, V. Bayot, E. Grivei, J. P. Issi, J. P. Heremans, C. H. Olk, L. Stockman, C. Van Haesendock, and Y. Bruynseraede, Phys. Rev. Lett. **76**, 479 (1996).
[12] S. N. Song, X. K. Wang, R. P. H. Chang, and J. B. Ketteson, Phys. Rev. Lett. **72**, 697 (1994).
[13] G. Baumgartner, M. Carrard, L. Zuppiroli, W. Bacsa, Walt A. de Heer, and L. Forro, Phys. Rev. B **55**, 6704 (1997).
[14] O. Chauvet, L. Forro, W. Bacsa, and D. Ugarte, Science **270**, 1179 (1995).
[15] F. Bommeli, L. Degiorgi, P. Wachter, W. S. Bacsa, W. A. de Heer, and L. Forro, Solid State Commun. **99**, 513 (1996).
[16] M. L. Tian, L. Chen, F. Q. Li, R. P. Wang, Z. Q. Mao, Y. H. Zhang, and H. Sekine, J. Appl. Phys. **82**, 3164 (1997).
[17] D. K. C. MacDonald, *Thermoelectricity: An Introduction to the Principles* (Wiley, New York, 1962).
[18] R. C. Tatar and S. Rabii, Phys. Rev. B **25**, 4126 (1982).
[19] P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).
[20] C. Ayache, A. de Combariett, and J. P. Jay-Gerin, Phys. Rev. B **21**, 2462 (1980).
[21] H. Hiura, T. W. Ebbesen, K. Tanigaki, and H. Takahashi, Chem. Phys. Lett. **202**, 509 (1993).