Hall effect and magnetoresistance of carbon nanotube films

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(Received 6 March 1996)

We report Hall coefficient (R_H) and magnetoresistance ($\Delta\rho/\rho$) measurements on thin films of aligned carbon nanotubes. R_H is positive in the whole temperature range (1.7–300 K) showing the predominance of hole transport in the electronic conduction. The upper limit of the carrier concentration is 1.6×10^{19} cm^{-3}. The resistance of the thin-film samples is governed mainly by the loose tube-tube contacts and this shows up in the $\Delta\rho/\rho<0$ at low fields, suggesting a noncoherent transport between the nanotubes. [S0163-1829(97)03311-0]

Years after the discovery of carbon nanotubes,[1] many basic questions remain. For example, in what respect do these one-dimensional-like conducting objects differ from graphite? What is the dimensionality of the electronic states? What is the conduction mechanism? What is the carrier density, etc.? Theoretical studies of these features are advancing, but support from experiments is deficient, mainly because of the difficulties manipulating these nanoscopic objects.

A year or so ago a simple method was elaborated for partially purifying and aligning carbon nanotubes.[2] This technique has resulted in partially horizontally or vertically aligned carbon nanotube films on various substrates, enabling bulk measurements on reasonably well-defined, reproducible samples. Recently, it was shown that these films of nanotubes are excellent candidates for electron-emitting devices,[3] so their characterization is essential for steps toward applications. Static susceptibility and electron-spin resonance (ESR) measurements have shown substantial anisotropy in magnetic properties.[4] Furthermore, the spin susceptibility of the conduction electrons of the nanotubes recorded by ESR shows a Pauli temperature-independent behavior in the 50–300 K range. The Elliott relation enables one to deduce the resistive scattering rate (τ_R^{-1}) and its temperature dependence from the ESR linewidth and g factor. It was shown that the intrinsic resistivity of the nanotubes has a temperature dependence characteristic for metals,[4] and its upper limit at room temperature (taking the free-electron mass) is 1 mΩ cm. On the other hand, two- or three-point resistivity measurements on a single nanotube give stronger or weaker but always nonmetallic temperature dependence.[5–7]

In this paper we report Hall-effect and transverse magnetoresistance measurements on thin films of aligned carbon nanotubes. The Hall coefficient (R_H) gives an upper limit of 1.6×10^{19} cm^{-3} for the carrier density. The negative magnetoresistance shows that the transport between the metallic nanotubes is hoppinglike. At very low temperatures a positive contribution to the magnetoresistance suggests either a localization of the carriers on the tubes when the cyclotron radius matches the tube radius, or a spin-dependent hopping mechanism.

The nanotubes were synthesized by the usual arc-discharge method, and thin films of oriented nanotubes were prepared as described in Ref. 2. Following the nomenclature of Ref. 2, there are films with β orientation, where the long axis of the nanotubes are perpendicular to the surface of the substrate (usually Teflon). Starting from this geometry the α orientation can be obtained by laying down the nanotubes mechanically onto the substrate and aligning them unidirectionally. The thickness of the β films is $\sim$1–3 μm (the length of the nanotubes) while that of the α films can be varied from 0.5 μm (still uniform) up to 10 μm. For thick films some misalignment of the deep layers is observed. The thickness of the samples is measured with scanning electron microscopy (SEM) and/or profilometer. A typical SEM picture of the thin films is shown in Fig. 1.

The resistivity was measured in a standard four probe configuration with silver paste contacts. The resistance was linear in the range of the applied currents (1–1000 μA). The Hall effect was performed in a five-probe configuration in fields up to 12 T.

Figure 2 shows the temperature dependence of the resistance for the α and β configurations. For the α case the resistance was measured along and perpendicular to the nanotubes. Some fluctuation in the absolute values is observed; however, $\alpha_\parallel$ is always lower than $\alpha_\perp$ and β. However, the close values of the resistances suggests that the intrinsic resistance and temperature dependence of the nanotubes do not show up, but the intertube hops because the ''loose'' contacts between the tubes rule the resistivity curves. The barrier between the tubes is small, since at high temperatures the resistivity curve is not activated—these bar-

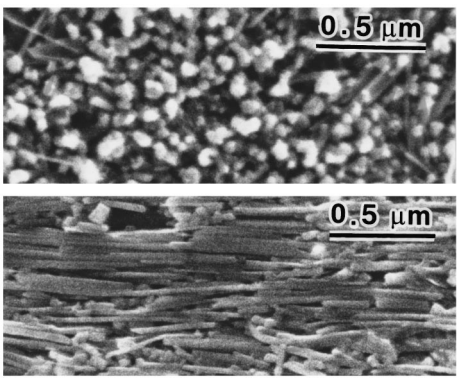

FIG. 1. Scanning electron microscopic images of the β (the long axis of the tubes is perpendicular to the substrate) and α (the long axis of the tubes is parallel to the substrate) configurations, upper and lower panels, respectively.

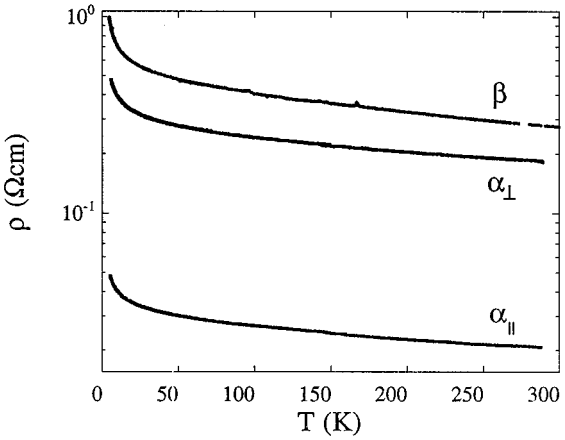

FIG. 2. Bulk resistivity vs temperature of the thin films of nanotubes. The $\alpha_\parallel$ and $\alpha_\perp$ labels denote current flow along and perpendicularly to the long axis of the nanotubes, respectively, in the α configuration. β shows the perpendicular current flow to the tube axis in the β configuration.

riers act almost like strong elastic scatterers, which limit the mean free path of the charge carriers. A simple description of the resistances for the $\alpha_\parallel$ and $\alpha_\perp$ configurations could be the following:

$$R_\parallel = (R_\parallel)_0 + n_\parallel \gamma \exp(-k_B T/\Delta), \tag{1a}$$

$$R_\perp = (R_\perp)_0 + n_\perp \gamma \exp(-k_B T/\Delta), \tag{1b}$$

where $(R_\parallel)_0$ and $(R_\perp)_0$ are the intrinsic resistances parallel and perpendicular to the nanotubes, respectively; $n_\parallel$ and $n_\perp$ are the number of longitudinal and transverse hops through the intertube barriers Δ, respectively; and γ has the dimension of resistance. In the high-temperature limit $T \gg \Delta$, $R_\parallel/R_\perp$ should measure $(R_\parallel)_0/(R_\perp)_0$, while at low temperatures $T < \Delta$ should give $n_\parallel/n_\perp$, which is proportional to the aspect ratio of the tubes ($\sim$1000). From the curves in Fig. 1, it is clear that the anisotropy does not exceed 10–15 even at the lowest temperatures, so transverse hops must occur before the carrier gets to the end of the tubes.

A detailed study of the temperature dependence of the resistivity on an extended temperature scale (30 mK–300 K, not shown here) enabled us to describe the transport mechanism independently from the particular orientation of the tubes in respect to the current flow.[8] The description which we found the more compatible with the data is the thermal fluctuation induced tunneling model of Sheng,[9] which describes the conducting properties of mesoscopic conducting objects which are separated by small energy barriers. A fit of the data within this model yields that the barrier height between the tubes is 10 meV, i.e., less than $k_B T$ for $T > 100$ K.

Evidence of incoherent charge transport at low temperatures is seen in magnetoresistance, as well. Figures 3(a) and 3(b) show the transverse magnetoresistance $(\rho(B)-\rho(0))/\rho(0) \equiv \Delta\rho/\rho$ as a function of the magnetic field (B) at fixed temperatures for $\alpha_\parallel$ and β configurations. Except at very low temperatures, $\Delta\rho/\rho$ is always negative. The negative magnetoresistance is usually encountered in systems where phase coherence between different conducting paths is destroyed in the magnetic field. One such case is a localized system in

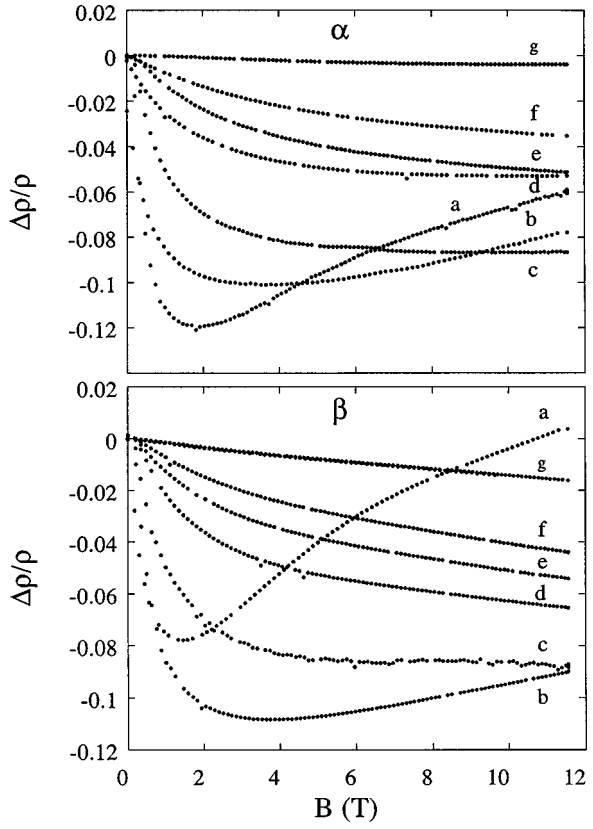

FIG. 3. Magnetic-field dependence of the magnetoresistance of the α (precisely $\alpha_\parallel$, upper panel) and β (lower panel) configurations at fixed temperatures: (a) 1.7 K, (b) 4.2 K, (c) 10 K, (d) 30 K, (e) 70 K, (f) 100 K, and (g) 180 K.

which the transport occurs via variable-range hopping. In these cases the negative magnetoresistance is due to the modification of the quantum interference between many possible hopping paths in the magnetic field.[10,11] Careful experimental work performed by Faran and Ovadyahu[12] on In_2O_{3-x}, varying in a wide range the magnetic and electrical fields, temperature, and disorder, have confirmed the theoretical calculations. The negative magnetoresistance scales with the magnetic flux SB threading through the area of the coherent loop $S = (L_{\rm hop})^{3/2}(l_{\rm loc})^{1/2}$, where $L_{\rm hop}$ and $l_{\rm loc}$ are the hopping and localization lengths, respectively. Since in most of the hopping models $L_{\rm hop}$ decreases with temperature, the magnetoresistance decreases, as well. Furthermore, when the magnetic field is such that SB is comparable to ϕ_0 (where ϕ_0 is the flux quantum), $\Delta\rho/\rho$ saturates. All these findings are in qualitative agreement with the magnetoresistance data of the thin films of nanotubes. In the thermal-fluctuation-induced tunneling model of Sheng,[9] the variable-range hopping is not present, nevertheless one can find phase coherent loops of equivalent paths. The surface of these loops might decrease as more and more backflow is induced with temperature. This in turn decreases the negative magnetoresistance, as observed.

The formation of Landau levels in disordered graphite was also invoked to explain the negative magnetoresistance observed at low temperatures.[13] Briefly, this is due to the enhancement of the density of states when the Fermi level falls into a partially filled Landau level. It is unlikely that in

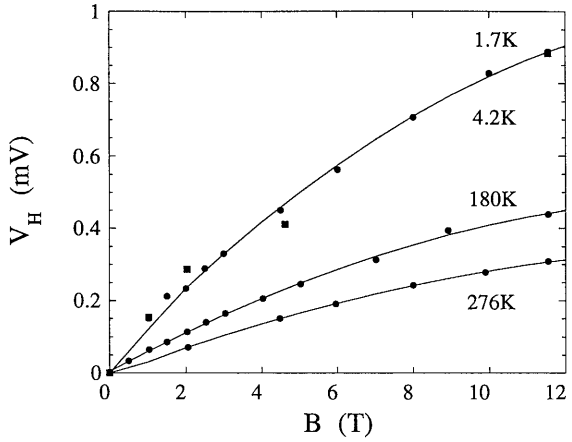

FIG. 4. Magnetic-field dependence of Hall voltage at selected temperatures of a β-aligned film.

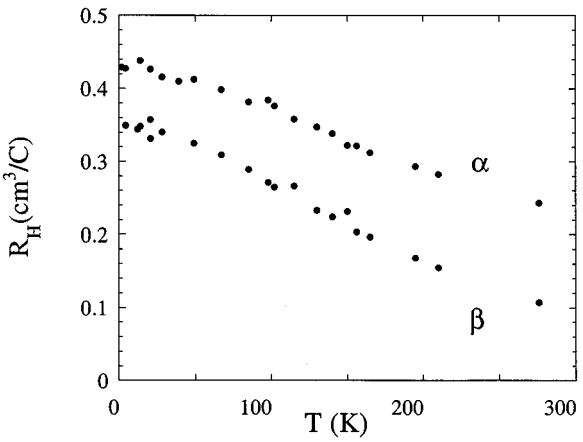

FIG. 5. Temperature dependence of the Hall coefficient for the α and β-aligned films.

our thin films of nanotubes the negative magnetoresistance is caused by the same effect, since it is present at temperatures as high as 230 K. We believe that the suppression of the phase interference in forward scattering[10] is at the origin of the $\Delta\rho/\rho<0$ in our case.

The high-field positive contribution to the magnetoresistance is usually attributed to spin effects or shrinkage of the orbits in strongly localized systems. This latter mechanism would give an exponentially increasing magnetoresistance, which is not the case here. A positive contribution could also result when the cyclotron orbit matches the radius of the nanotube and a localization of the carrier on the tube is expected. The fact that the positive contribution in the β configurations is stronger (B is along the tube) than in the $\alpha_{\parallel}$ case tends to support this idea. However, taking $v_F \approx 10^7$ cm/s and an average radius of 10 nm of the nanotubes, one would need a light carrier mass ($m^* \leqslant m_0/40$) in order to match the orbital frequency on the nanotube with the cyclotron frequency at $\sim$2 T.

The saturating tendency of the positive component in $\Delta\rho/\rho$ at 1.7 K resembles very much the magnetoresistance data of Frydman and Ovadyahu[14] obtained in In_2O_{3-x}, and the spin-dependent hopping mechanism of Kurobe and Kamimura[15] was applied to explain the data. The ingredients of this model are strong on-site Coulomb correlations, and unoccupied singly and double occupied localized states near the Fermi level. The magnetic field aligns the spins which renders more difficult the hopping between these states due to spin exchange, and the magnetoresistance increases until all the spins are aligned. This explanation implies that on the nanotubes, which are metallic at high temperatures, all the states become localized at low temperatures. This is not unlikely due to the low carrier density and probably strong Coulomb interactions, and the presence of structural defects. ESR data suggested such a metal-insulator transition in the 20–50 K range, however, more work is needed to confirm this scenario.

In the systems, where the transport is governed by hopping conduction, the Hall effect is usually anomalous. For example, in the assembly of small metallic particles where the transport is charging energy limited, in disordered conducting polymers with polaron formation, or in amorphous semiconductors where the conduction is in the mobility edge. In all these cases the Hall effect arises from the interference between direct and indirect hopping paths of the charge carriers. Depending on the sign and magnitude of the transfer integral, both the sign and magnitude of the Hall coefficient can be anomalous. In that respect, it is not possible to deduce a carrier density from R_H.

However, our assembly of nanotubes is not a classical hopping system, at least not at high temperatures. The carriers are easily activated across the barriers by k_BT, and actually the tube-tube contacts act more like strong elastic scatterers. Within this picture it is justified to speak about ''regular'' Hall effect in thin films of carbon nanotubes.

As it is shown in Fig. 4, the Hall voltage is nonlinear in magnetic field, it shows a tendency toward saturation with increasing B. The shape of the V_H versus B curves does not change with temperature.[16] At low fields ($B<2$ T), we deduce a Hall coefficient as plotted in Fig. 5 as a function of temperature. The difference between $R_H(T)$ for the α and β films is not significant, it might come from the difference in the effective thickness of the films. The variation of factor of $\sim$4 from room temperature to 1.7 K, is probably not due to the change in n, but, like in graphite, rather shows the significance of two types of carriers with mobilities having different temperature dependencies. We can attribute an effective carrier density $n_{\rm eff}=(n_e\mu_e+n_h\mu_h)^2/(n_e\mu_e-n_h\mu_h)$ to the Hall coefficient. In this case we do not have enough independent measurements to extract the electron and hole concentrations and their respective mobilities. We can suppose that, at low temperature, when R_H saturates, the hole carriers become predominant, and their density is 1.6×10^{19} cm^{-3}. This number corroborates with the carrier density deduced from the plasma frequency of carbon nanotubes measured by optical reflectivity.[17] The low spin susceptibility[4] gives also the same magnitude for the carrier density.

In conclusion, films of aligned nanotubes are rather good conductors with some anisotropy in transport properties for different alignment configurations. Magnetoresistance shows that the major contribution to the bulk resistivity of the films comes from intertube contacts or intertube hopping. The overall field and temperature dependence of the Hall coefficient and magnetoresistance relates the thin films of nanotubes with turbostatic graphite. In order to extract the characteristics of the individual nanotubes, local probes like high-frequency conductivities, optical and NMR measurements are needed.

[1] S. Ijima, Nature **354**, 56 (1991).
[2] Walt A. de Heer, W. S. Bacsa, A. Châtelain, T. Gerfin, R. Humphrey-Baker, L. Fooró, and D. Ugarte, Science **268**, 845 (1995).
[3] W. A. de Heer, A. Chatelain, and D. Ugarte, Science **270**, 1179 (1995).
[4] O. Chauvet, L. Forró, W. Bacsa, D. Ugarte, B. Doudin, and W. de Heer, Phys. Rev. B **52**, R6963 (1995).
[5] dc resistivity measurements by Langer *et al.*, Phys. Rev. Lett. **76**, 479 (1996) on a single nanotube, show the nonmetallic temperature dependence of the resistivity, which might come from defects or the influence of the contact resistances.
[6] A. Y. Kasumov, I. I. Khodos, P. M. Ajayan, and C. Coliex, Europhys. Lett. **34**, 429 (1996).
[7] Hongjie Dai, Eric. W. Wong, and Charles M. Lieber, Science **272**, 523 (1996).
[8] L. Forró, G. Baumgartner, W. A. de Heer, L. Zuppiroli, and G. Remenyi, in *Proceedings of the 6th International Conference on Hopping and Related Phenomena, Jerusalem*, 1995, edited by O. Millo and Z. Ovadyahu (Racah Institute of Physics, Jerusalem, 1995), p. 392.
[9] P. Sheng, Phys. Rev. B **21**, 2180 (1980).
[10] V. I. Nguyen, E. Z. Spivak, and B. Schklovskii, Pis'ma Zh. Eksp. Teor. **41**, 35 (1985) [JETP Lett. **41**, 42 (1985)].
[11] U. Sivan, O. Entin-Wohlman, and Y. Imry, Phys. Rev. Lett. **60**, 1566 (1988).
[12] O. Faran and Z. Ovadyahu, Phys. Rev. B **38**, 5457 (1988).
[13] K. Yazawa, J. Phys. Soc. Jpn. **26**, 1407 (1969).
[14] A. Frydman and Z. Ovadyahu, Solid State Commun. **94**, 745 (1995).
[15] A. Kurobe and H. Kamimura, J. Phys. Soc. Jpn. **51**, 1904 (1982).
[16] The Hall voltage measurements by S. N. Song *et al.*, Phys. Rev. Lett. **72**, 697 (1994), show a much stronger field dependence than ours, but their single bundle nanotube is a less-defined sample, which might contain many graphitic particles, impurities, etc.
[17] F. Bommeli, L. Degiorgi, P. Wachter, W. Bacsa, Walt A. de Heer, and L. Forró, Solid State Commun. **99**, 513 (1996).