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Title: Transport in strongly disordered multiwalled carbon nanotubes

Year: 2004

Version: Final published version

Please cite the original version:

Tarkiainen, R. & Ahlskog, M. & Zyuzin, A. & Hakonen, Pertti J. & Paalanen, M. 2004. Transport in strongly disordered multiwalled carbon nanotubes. Physical Review B. Volume 69, Issue 3. 033402/1-4. ISSN 1098-0121 (printed). DOI: 10.1103/physrevb.69.033402

Transport in strongly disordered multiwalled carbon nanotubes

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(Received 28 July 2003; revised manuscript received 17 October 2003; published 7 January 2004)

We have studied magnetic field and temperature dependence of electron transport in chemical vapor deposition synthesized highly resistive multiwalled carbon nanotubes. The analysis of the weak-localization magnetoresistance according to electron-electron interaction theories leads to very small mean free paths, $\ell < 10$ nm. At lowest temperatures the sheet resistance is near $R_K = h/e^2$. Both of these observations suggest that our samples are close to the strong-localization limit.

DOI: 10.1103/PhysRevB.69.033402 PACS number(s): 73.63.Fg

In order to realize future nanotube electronics, it is not only necessary to thoroughly understand the underlying transport phenomena, but also to be able to fabricate devices possessing the desirable qualities. While the latter goal is still distant, the transport in single-walled nanotubes (SWNTs) is already understood quite well.[1] It has been experimentally verified that SWNTs are either metallic or semiconducting depending on their chirality. The metallic tubes are one-dimensional quantum wires, where the transport is coherent over hundreds of nanometers. With multiwalled carbon nanotubes (MWNTs) the situation is more complicated, due to, for example, variation among differently synthesized nanotube materials. Room temperature ballistic transport has been reported in MWNTs contacted by dipping into Hg,[2] with resistivity less than 100 Ω/μm. However, in the typical configuration with MWNTs on an insulating substrate, diffusive transport behavior is mainly observed, with a length dependent resistance on the order of 10 kΩ/μm.[3] In a number of experiments on individual nanotubes at low temperatures, interference effects are found to be significant,[4–7] either in 1D or 2D depending on the electron mean free path.

In this paper, we report electron transport measurements of strongly disordered MWNTs as a function of magnetic field and temperature. The MWNTs were synthesized by catalytic decomposition of acetylene, as described by Hernadi *et al*.[8] There is a striking difference between the chemical vapor deposition (CVD) synthesized material used in this study and the arc-discharge grown tubes, used in most of the previous transport experiments. Our atomic force microscopy (AFM) studies reveal that the curvature of the CVD tubes [see Fig. 1(b) in Ref. 9] is intrinsic, due to a high concentration of structural defects. The arc-discharge grown tubes are straight and are known to have better quality and mechanical properties.[10] We find that in our CVD grown tubes the electron mean free path ℓ and phase coherence length L_ϕ are very short. In fact, ℓ turns out to be so short that our nanotube samples are near the strong-localization regime.

For electrical transport measurements, the individual tubes (see Table I) were contacted by 2–4 electrodes. In order to obtain low ohmic contacts, the samples were oxidized in air (300–400°C, 10 min) after deposition of the tubes onto the SiO_2 substrate. After the oxidation, no change in the diameter and shape of the tubes was visible in AFM images. Next, electrodes were fabricated using standard e-beam lithography. Defining the contact resistance as $R_C = (R_{2t} - R_{4t})/2$, where R_{4t} is the four-terminal and R_{2t} the two-terminal resistance, we obtain $R_C \approx 0.4$–2 kΩ and resistivity $\rho = 30$–70 kΩ/μm for our multiterminal samples (4 and 5). On the contrary, contacting tubes without the oxidation step gives unpredictable results, the room temperature resistance extending from 50 kΩ to megaohms. The role of oxidation remains unclear: It may clean the nanotube of amorphous carbon, but may also increase the number of defects. However, the transport behavior was similar in a few cases with no oxidation step and yet relatively small R_C.

The magnetoresistance was measured on two samples (4 and 6) at magnetic fields of 0–6.7 T, perpendicular to the plane of substrate. The resistance was found to decrease with increasing magnetic field, as shown in Fig. 1(a) for sample 4. The measured field dependence was found consistent with two-dimensional weak-localization theory,[11] and phase coherence lengths were extracted. The change of conductance is given by

$$\Delta G(B) = \frac{N_v w_{\mathrm{eff}}}{L} \frac{e^2}{\pi h} \left[\psi\left(\frac{1}{2} + \frac{\ell_B^2}{4L_\phi^2} \right) + \ln\left(\frac{4L_\phi^2}{\ell_B^2} \right) \right], \quad (1)$$

where $\ell_B^2 = \hbar/eB$, N_v is the number of separate valleys on the Fermi surface,[12] and w_{eff} is the effective width of the tube, which takes into account the variation of the perpendicular component of the magnetic field due to the curvature of the nanotube. Equation (1) gives $L_\phi \approx 18$ nm at 10 K, consistent with the nanotube perimeter 90 nm. The other, ringlike sample 6, gives even shorter L_ϕ on the order of 10 nm. Similar results were obtained earlier in Ref. 4, while an order of magnitude larger values were reported in Ref. 5. The difference in $L_\phi = \sqrt{D\tau_\phi}$ may be attributed to the larger resistivity of our samples. While there is no direct measurement of the diffusion constant D, we may argue that the mean free path ℓ in our samples must be larger than the lattice spacing a, and to keep the weak-localization picture consistent, it is necessary that $\ell < L_\phi$. Using these limits and Fermi velocity $v_F = 8 \cdot 10^5$ m/s,[13] we obtain $D = v_F \ell/2 = 1$–50 cm^2/s, which is an order of magnitude less than in Ref. 5. In the inelastic electron-electron (e-e) scattering picture, τ_ϕ also tends to decrease with increasing resistivity [see, e.g., Eq. (2)], and thus we can understand the order of magnitude of L_ϕ. In Eq. (1), w_{eff} was used as a second fitting parameter. The fit gives a reasonable value $w_{\mathrm{eff}} \approx 60$ nm, approximately twice the nanotube diameter 29 nm.

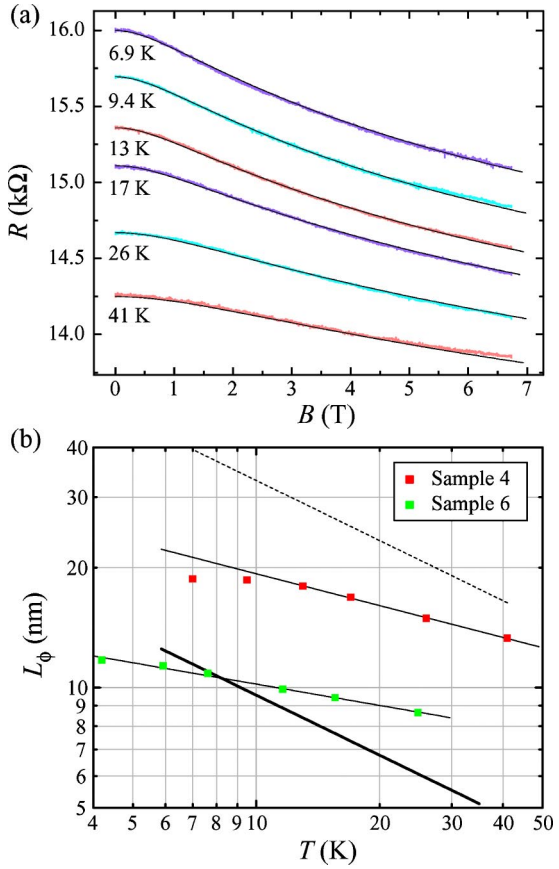

FIG. 1. (Color online) (a) Resistance of sample 4 vs magnetic field at a few different temperatures. Best fits, obtained using the two-dimensional weak-localization theory, are displayed by the black solid lines. (b) The dephasing length obtained from the above fit, and results of similar analysis for sample 6. Power-law fits of $L_\phi \propto T^{-p/2}$ give $p=0.53$ and 0.36 for samples 4 and 6, respectively. The thick solid line is the crossover between weak and strong localization in the *e-e* scattering picture. The dashed line is the contribution of the two-dimensional *e-e* scattering [Eq. (2)] for sample 4 assuming $D=2.5$ cm^2/s and $R_\square=3.35$ kΩ.

As a conclusion, both the coherence length $L_\phi < \pi\Phi < L$ and mean free path ℓ are surprisingly short, and our system is two dimensional for electron diffusion and interference effects.

TABLE I. *Sample parameters*. Φ is the nanotube diameter, estimated by the height of the tubes in AFM images, and L_{total}, L, and L_C are the total length of the nanotube, length of the section between the contacts, and length in touch with the electrodes, respectively. Resistances at 300 K are given.

	Φ (nm)	L_{total} (μm)	L(μm)	L_C(μm)	R_{300K}(kΩ)
1	29	1.8	0.50	0.17/0.20	16.5
2	20	2.6	0.29	0.14/0.17	22
3	24	4.63	1.18	0.29/0.5 . . . 1.9	62
4	29	2.14	0.38	0.25/0.26	16
5	16	3.92	0.29	0.18/0.18	15.8
6	16	3.1	1.48/1.21[a]	0.19/0.22	67

[a]A ringlike nanotube connecting the electrodes twice.

The dephasing length is weakly temperature dependent and a power-law fit $L_\phi \propto T^{-p/2}$ shown in Fig. 1(b) gives $p=0.53\pm0.09$ and 0.36 ± 0.07 for samples 4 and 6, respectively. This dependence is weaker than expected for *e-e* scattering mechanism which gives $p=2/3$ in one-dimensional and $p=1$ in two-dimensional samples. The sample dimensionality for the *e-e* interaction effects depends on the thermal length $L_T=\sqrt{\hbar D/(k_B T)}$. Using the above estimate for D, we find our samples two dimensional relative to the interaction effects, except for lowest temperatures below 0.2–10 K. According to *e-e* interaction theory in two dimensions[14]

$$\frac{1}{\tau_\phi} = \frac{k_B T R_\square e^2}{2\pi\hbar^2} \ln\left(\frac{\pi\hbar}{e^2 R_\square}\right). \tag{2}$$

The theoretical prediction for $L_\phi=\sqrt{D\tau_\phi}$ is sketched in Fig. 1(b) as a broken line in case of sample 4. In Eq. (2), the measured value of $R_\square=3.35$ kΩ at $T\sim20$ K was employed. At high enough square resistances $R_\square \gtrsim (1/2e)(h/e^2)$ Eq. (2) breaks down, and higher-order corrections will become significant. In the *e-e* scattering theory, L_ϕ becomes short and comparable to L_T when the borderline between weak- and strong-localization regimes is approached, and the quasiparticle picture of the Fermi-liquid theory breaks down. At the borderline $k_F\ell\sim1$, and the diffusion constant $D\sim v_F a/2 \simeq 1$ cm^2/s, where a is the lattice constant and a lower limit for the mean free path. Therefore we obtain that the *e-e* interaction theory is applicable only if $L_\phi \gtrsim (\frac{1}{2} v_F a\hbar/k_B T)^{1/2}$. This borderline is plotted as thick solid line in Fig. 1(b). Because one of our samples is actually below this border, higher-order corrections to the *e-e* interaction theory are necessary.

There are also other possible reasons for the apparent saturation of $L_\phi(T)$, such as magnetic impurities, two-level systems (also causing $1/f$ noise), external noise, etc. Because our nanotube material was synthesized using catalytic method, it is not unlikely that some magnetic impurities remain (in our case Co). Also such impurities are less likely in arc-discharge grown nanotubes, where longer dephasing times were observed.[5] Using the Nagaoka-Suhl formula, we can estimate from L_ϕ that the required amount of impurities is at least 200 ppm. In nanotubes there are some electronic two-level systems, which demonstrate themselves as fluctuations between two resistance values. They as well as external noise may cause dephasing.[15,16] In any case, our results are well in line with L_ϕ's measured by some other groups.[4,17]

In Fig. 2, our measured dephasing rate is compared to the prediction of the *e-e* interaction theory,[14] taking into account an additional dephasing mechanism, which for simplicity is assumed to be independent of temperature. The inverse square of L_ϕ is plotted as a function of T, and theoretical curves in both 1D and 2D have been fitted to the data using D as an adjustable parameter. This type of plot clearly shows that to account for the data, it is necessary to include the additional dephasing mechanism, which is employed as a second fitting parameter: $1/L^2_{\phi,meas}=1/L^2_{\phi 0}+1/(D\tau_\phi)$. The fits give quite small diffusion constants, corresponding to $\ell = dD/v_F = 0.6$ nm in 2D and 0.2 nm in 1D (d is the dimen-

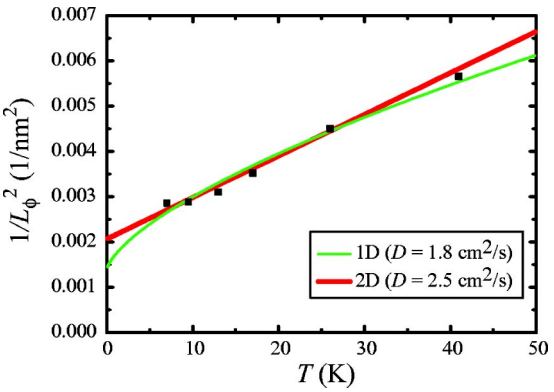

FIG. 2. (Color online) Comparison of $1/L^2_{\phi,meas}$ with theoretical models (sample 4). It is assumed that $1/L^2_{\phi,meas}=1/L^2_{\phi 0}+1/(D\tau_\phi)$, with two fitting parameters: the diffusion constant D and a temperature-independent scattering term characterized by length $L_{\phi 0}$. We obtain $L_{\phi 0}=22$ nm (27 nm) in 2D (1D).

sionality of the sample). For the second parameter we obtain $L_{\phi 0}=22$ nm (27 nm) in 2D (1D). We note that a fit to the recent theory by Golubev and Zaikin[18] nearly coincides with the two-dimansional curve in Fig. 2, provided that in addition to the diffusion coefficient D, an integration cutoff $\omega_c \sim(1/100)v_F/\ell$ is taken as the second fitting parameter in their two-dimensional formulas.

The zero-bias resistance of all measured samples is found to decrease monotonically, with roughly logarithmic temperature dependence down to the lowest temperatures [Fig. 3(a)]. All curves have more or less apparent knee around 10 K, with weaker temperature dependence above it, and exponential increase sets in near room temperature. Conductance decrease towards lower temperatures is typical for nanotubes,[4,5] and it has been related to electron interaction and interference effects.

Figure 3(b) shows the square conductances of the same samples. It has been assumed that only one layer is conducting, which was suggested by Bachtold *et al.*,[6] and should hold at low enough T. Assuming more than one conducting layers would lead to unacceptably low conductances for diffusive electron-transport picture. The small values of $G_\square \gtrsim 2e^2/h$ are also consistent with the estimated small ℓ values. It turns out that in all our samples, where data have been recorded at low temperatures, the prefactor of the $\ln T$ dependence is roughly given by a universal number

$$\Delta G = G(T) - G_0 = S_{\rm exp}\frac{\Phi}{L}\frac{e^2}{h}\ln(T/T_0), \qquad (3)$$

where $S_{\rm exp}\approx 1.3$ at 10–100 K increasing to $S_{\rm exp}\approx 2.0$ at lower T. The experimental slope, measured in two-terminal configuration, should be corrected by the ratio of the contact and nanotube resistances. If the contacts are one tenth of the nanotube resistance, the correct prefactor is about 20% larger than the measured one. Taking this correction into account we obtain $S_{\rm exp}=1.6\pm 0.4$ at 10–100 K and $S_{\rm exp}=2.4\pm 0.3$ at lower T.

In a two dimensional disordered electronic system, both weak-localization and interaction corrections give rise to logarithmic corrections. The corrections sum up to give[19]

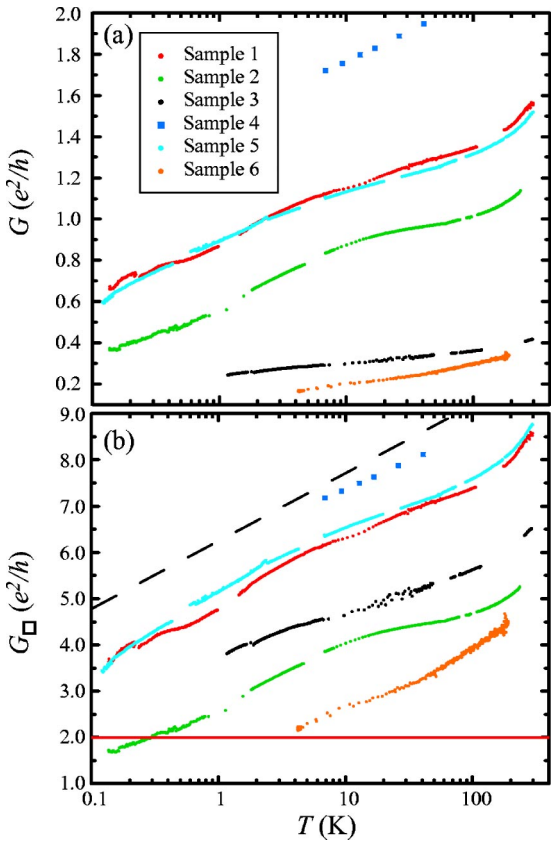

FIG. 3. (Color online) (a) Zero-bias conductance vs temperature for some of our samples. All curves are roughly logarithmic. (b) The square conductance assuming one conducting layer. At low temperatures the conductivity has roughly universal slope close to $2(e^2/h)$ (plotted as dashed line). The solid horizontal line indicates the regime where the strong localization sets in.

$$S_{\rm theory}=N_v p+1+(4N_v^2-1)\left[1-\frac{\ln(1+F_0^\sigma)}{F_0^\sigma}\right]. \qquad (4)$$

Here F_0^σ is the e-e interaction parameter related to the exchange interaction: if $F_0^\sigma<0$ the spins tend to align, leading to ferromagnetic transition at $F_0^\sigma=-1$. In nanotubes $N_{\rm v}=2$, and for sample 4, with $S_{\rm exp}\approx 1.7$ and $p=0.53$ at 4–40 K we obtain $F_0^\sigma\approx -0.05$. However, in case of short-range impurity potentials leading to strong intervalley scattering, we may have $N_{\rm v}=1$ and $F_0^\sigma\approx 0.09$. Sample 6 gives similar values. We conclude that even though the conductivity correction is quite large, it is still consistent with the theory. The positive magnetoresistance, due to e-e interaction and proportional to F_0^σ,[11] is negligible, less than 10% of the weak-localization magnetoresistance in the temperature range of our measurements.

The conductivity correction due to e-e interactions is expected to follow the two dimensional theory down to 0.2–10 K. The low T increase in $S_{\rm exp}$ is somewhat mysterious. Saturation of L_ϕ at lowest T would lead to a decrease of the slope instead of increase. In the work of Langer *et al.*,[4] a complete saturation of resistance was observed around 0.3 K. The lack of saturation in our data gives further evidence that the in-

teraction effects make up a considerable part of the observed $\ln T$ dependence. Most of our samples are so short, that clear one-dimensional effects are not likely to occur ($L \approx 5 \times \pi\Phi$). At lowest temperatures, small Coulomb effect will appear due to the presence of finite contact resistances, causing a small additional correction to the results.[20] Our data do not show any indications of variable range hopping as seen by Kang *et al.* in millimeter-long bundles of MWNTs.[21]

The observed logarithmic behavior is characteristic to some other models too. In a zero-dimensional coherent conductor Coulomb interactions give rise to a logarithmic decrease of conductance at low enough temperatures.[22] This model cannot be applied as such to our samples owing to their small D, but, by considering an array of independent coherent scatterers, a rather good agreement with the low-temperature data can be obtained: $S = 2\pi/3$.[23]

Similar conductance suppression appears in a strong tunneling single electron transistor (SET),[24] a resistor-tunnel junction system at high-temperature limit,[25] and in an array of many tunnel junctions.[26] Logarithmic decrease of conductivity applies also to a granular metal, with strong coupling between grains, at relatively high temperatures,[27] and Kondo effect, if magnetic impurities are present. However, these corrections are small compared to the dominant interaction and weak-localization effects.

We have studied electrical transport of diffusive carbon nanotubes. The measured $G(T,B)$ was found to be consistent with two dimensional weak-localization theory over $T \simeq 4-40$ K, though the logarithmic temperature dependence was found to extend even below 4 K. The 2D analysis of our magnetoresistance data gave a diffusion constant of $D = 2.5$ cm^2/s, barely above the theoretical lower limit of $D = 1$ cm^2/s. Thus, $k_F\ell$ is relatively small in our samples, which may lead to the breakdown of theoretical models that are first order in $(k_F\ell)^{-1}$. The closeness to the strong-localization regime may also be one of the reasons behind the weaker than expected temperature dependence of L_ϕ.

We would like to thank B. Altshuler, B. Spivak, and A. Zaikin for interesting discussions, and A. Fonseca and J. B. Nagy for the nanotube material. This work was supported by the Academy of Finland and by the Large Scale Installation Program ULTI-3 (Grant No. HPRI-1999-CT-00050) of the European Union.

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