Electron spin resonance and microwave resistivity of single-wall carbon nanotubes

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We compare the thermal variations of ESR, dc, and microwave resistivity of unoriented bulk single wall carbon nanotube samples. We conclude that the ''metallic'' high-T behavior ($d\rho/dT > 0$) is an intrinsic property of the bulk material, and that the system remains metallic even at low temperature where $d\rho/dT < 0$. The spin susceptibility is also independent of T, and a long mean free path implies transport predominantly along the tube axes in bulk material. [S0163-1829(97)08440-3]

Nonchiral single-wall carbon nanotubes (SWNT) with an armchair wrapping[1] $[N,N]$ are attracting great interest, as they are predicted by band theory to be intrinsically metallic.[2,3] Laser ablation of graphite targets doped with Co and Ni produces samples in which [10,10] SWNT are predominant.[4] In this process, the SWNT self-organize into crystalline ropes consisting of tubes close-packed on a two-dimensional (2D) triangular lattice.[1] The conducting behavior of both unoriented bulk material and oriented single ropes has been experimentally confirmed.[1,5,6] An explanation for the linear resistivity ρ versus T behavior observed at high temperature has been proposed, in which the dominant process is electron backscattering by low-energy twists of the tube.[6] Measurements of the temperature dependence of ρ agree qualitatively with this prediction down to a sample-dependent crossover temperature T^* below which $d\rho/dT$ becomes negative.

Here we report experiments performed on unoriented bulk material using electron spin resonance, microwave and dc resistivity measurements. In the high-temperature regime, all our results are consistent with the reported metallic behavior, and establish that the observed resistivity is intrinsic to the bulk material. By estimating transport parameters from the ESR data and comparing with $\rho(T)$, we also show that the system remains metallic below T^* despite the sign change in $d\rho/dT$, ruling out a metal-insulator transition.[7] ESR spectra are also characteristic of a metal at all temperatures; the integrated ESR intensity is independent of temperature, consistent with the (small) constant Pauli spin susceptibility expected for intrinsically metallic carbon nanotubes.[2,3]

Experiments were performed on samples containing 70–90% SWNT with a narrow diameter distribution,[1,8] vacuum annealed at 1000 °C to remove fullerenes. We used a Bruker ESP 300 ESR spectrometer equipped with an NMR gaussmeter and an HP 9000 computer for data handling facilities. Microwave resistivity ρ_{ac} was measured using a home-built apparatus based on the resonant cavity perturbation method at 10 GHz.[9] Differences in the passband D and resonant frequency shift S of the TE(011) cavity (quality factor 22000), determined with and without the sample in place at an electric field antinode, allow the determination of ρ_{ac} for a long cylindrical sample (length $\gg$ radius).[9] Absolute values of ρ_{ac} were obtained by determining the depolarization factor n, controlled by the geometry of the sample[10], and the filling factor $a = V_s/V_a$, the ratio of sample to cavity volumes. For a metal, the magnitude of S should be close to a/n. We tested this relation for samples of different lengths (1 to 2 mm), cut in thin sheets about 0.1 mm thick. For all samples the calculated ratio a/n lies in the range 1/2 to 1/3 the experimentally measured frequency shift, indicating that the unoriented bulk material is metallic. If the skin depth is larger than the smallest sample dimension then $\rho_{ac} \propto D$.[11]

The measured room-temperature resistivities range from 10 to 40 mΩ cm for different samples, consistent with previously reported values.[5,6] More importantly, for a given sample $\rho_{ac} = \rho_{dc}$ to within experimental error. The thermal variations are also the same. Figure 1 shows the thermal behavior of normalized (directionally averaged) resistivity measured at dc with 2 contacts and at 10 GHz (contactless) on the same sample. These results show that the measured resistivity is intrinsic to the bulk material, the equality of ρ_{ac} and ρ_{dc} indicating that there is no effect of random electron hopping between conducting grains.[12] This in turn suggests a large diffusion-limited mean free path. From the absolute value of ρ_{ac} we estimate the skin depth of the unoriented bulk material $\delta = c/(2\pi\omega\sigma)^{1/2} \sim 50$ μm. Similar experiments were performed on pressed pellets; resistivities were comparable (about 10 mΩ cm) and we found similarly good agreement between dc and microwave results.[13] Skin effects were observed with a sample thickness of 0.2 mm but not for 0.1 or 0.05 mm, consistent with the skin depth estimated above.[14]

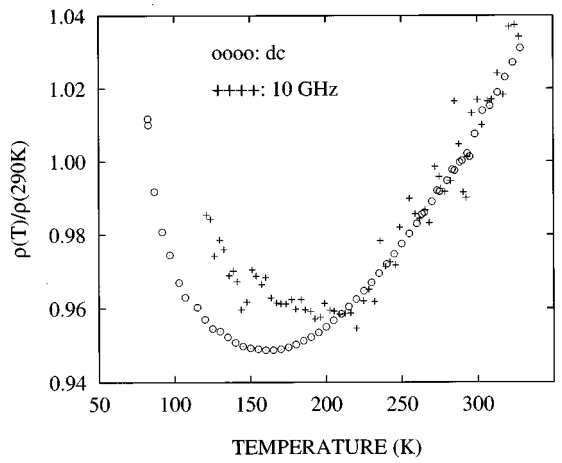

FIG. 1. Thermal variation of the normalized resistivity of the bulk material measured by direct current (open circles) and at 10 GHz (+++++++).

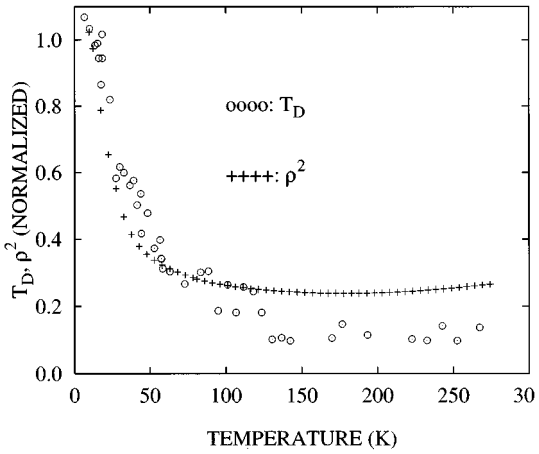

FIG. 3. Temperature dependence of the diffusion time (open circles) and ρ_{dc}^2 (+++++++), both normalized at 10 K.

Residual Co and Ni catalyst particles are responsible for a very broad ESR line near $g=2$, which obscures the expected conduction electron response from the SWNT. A very weak and narrow signal is observed within the main broad line. Approximating the catalyst-derived signal as a cubic baseline and subtracting it out reveals a narrow, strongly asymmetric SWNT line with a Landé factor $g=2.002\pm0.001$ and linewidth $\sim$25 G. To confirm that this narrow line is associated with SWNT, we vacuum-annealed a sample at 1500 °C to remove the remaining Co and Ni. The x-ray peaks characteristic of Co and Ni disappeared after this treatment,[1] as did the broad ESR component, leaving only the narrow asymmetric line with $\Delta H=26$ G. This is characteristic of a metal for which δ is smaller than the conducting particles.[15] The 1500 °C anneal also reduces the intensities of the 2D lattice reflections, suggesting either that the ropes are separating into isolated SWNT or that tubes are being destroyed. In any event we limit further discussion to the samples annealed at the lower T.

The narrow ESR component (Fig. 2) remains Dysonian at all temperatures in the range 4–300 K. The amplitude asymmetry of the absorption derivative A/B ($\sim$4 at 100 K) is related to the ratio T_D/T_2, where T_D is the time for an electron to diffuse through the skin depth and $T_2=1/\gamma\Delta H$ is the spin relaxation time ($=T_1$ for metals). In the framework of Feher and Kip,[16] knowledge of A/B, ΔH, and the density of conduction electrons N in the metal allows the determination of transport properties. Unfortunately we do not have a good estimate of N since as many as 50% of the SWNT may be chiral and nonmetallic.[4] On the other hand, knowing A/B and ΔH provides values for T_D and T_2. Assuming that all the conduction electrons have the same velocity v and that the mean free path Λ is small compared to the (classical) skin depth, then[16] $T_D=(3/2)(\delta^2/v\Lambda)$. Writing Λ and δ as functions of the resistivity, $\Lambda=m^*v/Ne^2\rho$ and $\delta^2=c^2\rho/2\pi\omega$, we obtain

$$T_D=\frac{3Ne^2c^2\rho^2}{2\pi\omega m^*v^2}. \tag{1}$$

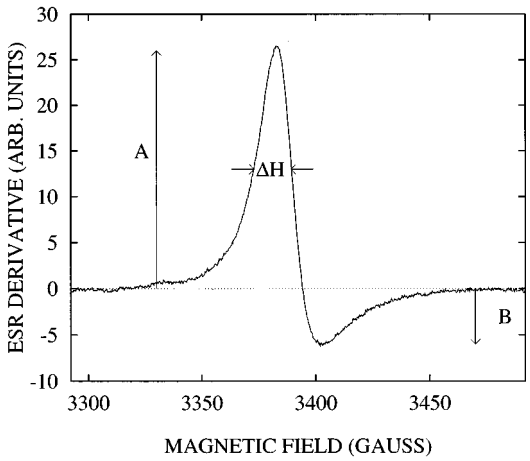

FIG. 2. ESR spectrum of as-grown bulk (low density) SWNT recorded at 100 K.

The temperature dependence of T_D is shown in Fig. 3 and compared to the square of the dc resistivity in the same temperature range. The very good agreement shows that ESR and resistivity are probing the same electrons. The fact that the ESR line remains Dysonian down to low temperature indicates that the upturn in the resistivity is not due to a metal-insulator transition. The room temperature value for $T_D\sim10^{-9}$ sec, combined with $\delta\sim50$ μm and an estimated Fermi velocity 8×10^7 cm/sec,[3] leads to a mean free path $\Lambda\sim5$ μm, in good agreement with the 3 μm estimate from dc measurements on an isolated SWNT.[18] While crude, this estimate suggests that conduction occurs mainly along the tube axes in the bulk material, at least at high temperature, consistent with the twiston model.[6]

The as-grown bulk material is very porous, consisting of long entangled ropes and as much as 90% free volume. Upon pressing the sample into a dense pellet, the ESR line shape remains Dysonian but with asymmetry reduced at 300 K from 8 to 1.6, as shown in Fig. 4. This indicates that pressing has reduced the size of conducting particles to a value comparable to δ. As a consequence the apparent ΔH approaches

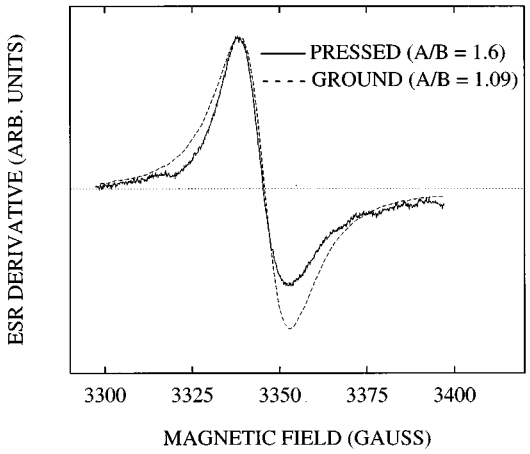

FIG. 4. 300 K ESR spectra for the same material as in Fig. 1, after pressing into a pellet (solid curve) and grinding into a fine powder (dashed curve).

the value that would obtain in the limit of a symmetric Lorentzian[17] (particle size $<\delta$). To test this effect, we reduced the size further by mechanical grinding and observed a nearly symmetric line with $A/B=1.09$ (Fig. 4) and the same peak-to-peak width as the pressed sample. The full width of the first integral of this ''symmetrized'' line is 22 G, whence $T_2=5.2\times10^{-9}$ sec. For the as-grown material $\Delta H=25$ G and $A/B=8-9$, thus $T_2=2.7\times10^{-9}$ sec. This small discrepancy is likely due to small differences in ρ induced by the grinding process. In general the results are fully consistent with Dyson's theory;[15,16] although the intensity and line shape are affected by diffusion through the skin depth, the observed width of a Dysonian line remains close to $1/\gamma T_2$.

The area under a Lorentzian is proportional to the product of peak height and (width)^2, which for a symmetric ESR line becomes proportional to the spin susceptibility. Assuming that the line shape does not vary with T, we show in Fig. 5 that the ESR intensity is quite independent of T and thus N is constant. This again allows us to rule out a metal-insulator transition (e.g., localization) as the origin of the change in $\rho(T)$ slope from positive to negative at low T, and further

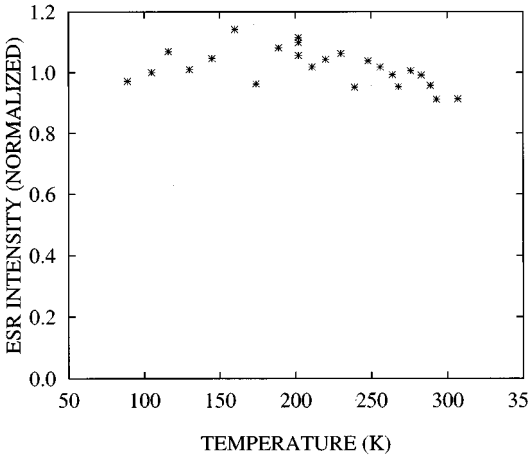

FIG. 5. Normalized temperature dependence of the ESR intensity (proportional to the spin susceptibility) for a ground sample.

confirms our observation that the as-grown material remains metallic in the bulk, even at low T.

From the present experiments, and particularly the 10-GHz resistivity measurements, unoriented bulk SWNT material behaves as a homogeneous system. This means that, despite the finite length of rope segments, there must be pathways for conduction electrons to diffuse over macroscopic distances. High-resolution electron microscope lattice images reveal several kinds of defects—ropes that split and recombine, rotational ''twins,'' etc.[1,19]—while rope ends are generally not observed. Evidently the perfect segments are sufficiently long (and the effects of interparticle resistance sufficiently benign) that the physics of single-rope (1D) transport above T^* (e.g., intratube backscattering *via* twistons) is preserved in unoriented bulk material.

The mechanism governing the low-T upturn in resistivity has yet to be identified. Several possibilities may be considered: (1) incipient condensation to a SDW or CDW ground state,[7,20] (2) onset of strong backscattering from quenched disorder (e.g., twists, fluctuations in intertube hopping), and (3) coherent effects of intertube hopping leading to a suppression of $N(E_F)$ and the opening of a pseugogap.[21] The results presented here indicate that the upturn in ρ is more likely associated with an increased scattering rate rather than a reduction in carrier density; this we believe allows us to rule out mechanism 1, an intrinsically 1D effect. On the other hand, there are indications that intertube and/or interparticle coupling may be implicated in the negative $d\rho/dT$ behavior below T^*. Light mechanical force shifts T^* slightly to higher temperature,[5] as if the prefactor weighting the low- T process were growing with respect to the high- T one.[7] Pressing into a dense pellet shifts T^* to well above 300 K,[13] completely suppressing the high-T intratube scattering. Intercalation has the opposite effect;[22] $d\rho/dT$ remains positive down to the 7-K experimental limit in a potassium-doped bulk sample while ρ overall is reduced by about a factor of 40 due to charge transfer.[23] This reduces the prefactor of the high-T resistivity, which *per se* would cause T^* to increase. Here it seems more likely that intercalation dilates the rope lattice, reducing the intertube coupling and suppressing the low- T mechanism. Pressure-dependent measurements should help to clarify the origin of the excess low-T resistivity.

The above results are distinctly different from observations on multiwall carbon nanotubes.[24,25] The observation of Dysonian lines at all temperatures shows that the system remains highly metallic down to low temperatures, the measured resistivity being intrinsic to the bulk material. Therefore the sign change in $d\rho/dT$ at T^* cannot be assigned to a metal-insulator transition, ruling out the few mechanisms invoked to explain a hypothetical low-temperature insulating state. It indicates more probably an increase of the contribution of interrope resistivity.

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