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Chirality of internal metallic and semiconducting carbon nanotubes

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We have assigned the chirality of the internal tubes of double walled carbon nanotubes grown by catalytic chemical vapor deposition using the high sensitivity of the radial breathing (RB) mode in inelastic light-scattering experiments. The deduced chirality corresponds to several semiconducting and only two metallic internal tubes. The RB modes are systematically shifted to higher energies when compared to theoretical values. The difference between experimental and theoretical energies of the RB modes of metallic tubes and semiconducting tubes are discussed in terms of the reduced interlayer distance between the internal and the external tube and electronic resonance effects. We find several pairs of RB modes corresponding to different diameters of internal and external tubes.

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Carbon nanotubes have unique properties due to their low dimensionality.¹ Numerous potential applications depend critically not only on the control of their chirality, diameter, number of layers, and tube length, but also on the development of high yield and low cost synthesis techniques.² It has been recently shown that the catalytic chemical vapor deposition (CCVD) technique based on transition-metal oxides produces small diameter carbon nanotubes having one to four walls with high yield and low cost.² The electronic and optical properties of the tubes are linked to their chirality and they can be semiconducting as well as metallic.^{1,3–6} Metallic carbon nanotubes are considered to be model systems for one-dimensional electronic transport where strong electronic correlations lead to collective low-energy excitations.^{7,8} Recent experimental reports suggest the existence of superconductivity in bundles of single walled carbon nanotubes.⁹ Double walled carbon nanotubes (DWCNT) with an internal metallic tube and an insulating external tube could represent the ultimate one-dimensional carbon based conductor. For DWCNT the chirality of the external tube can in principle be determined by scanning probe techniques or by electron or x-ray diffraction.^{10,11} However, the determination of the chirality of the internal tube remains particularly challenging and has not been determined so far. The energy of the radial breathing (RB) mode in carbon nanotubes is inversely proportional to its diameter¹² which gives the possibility to find the diameter distribution using inelastic light scattering provided the scattering cross section does not vary strongly with the tube diameter. For tube diameters smaller than 1 nm, the sensitivity of the radial breathing mode (RB) to the diameter is particularly high and ranges between 220 and 470 cm⁻¹/nm for a tube diameter between 1.0 and 0.7 nm.¹² The chirality of the tubes can be explained by the fact that the honeycomb lattice can have different orientations with respect to the tube axis. For a given diameter range the number of different orientations possible for a honeycomb lattice is restricted to a finite number and can be found by the chiral vector specified by (n,m) .¹ The chiral vector connects equivalent points in the honeycomb lattice; its length de-

termines the tube circumference and its direction gives the orientation with respect to the tube axis. For smaller diameters the number of unit cells forming the circumference decreases and hence the number of tubes with different chirality within a given diameter range decreases. Combined with the higher sensitivity of the RB mode it becomes possible, provided the observed RB modes are sufficiently narrow, to identify from the position of the RB mode the chirality of the tube.

Carbon nanotubes were prepared by the catalytic chemical vapor deposition method (CCVD).² Selective reduction at 1000 °C in a methane-hydrogen (18% CH₄) atmosphere of a solid solution of a transition-metal oxide and an insulating oxide (Mg_{0.95}Co_{0.05}O) led to the formation of small diameter carbon nanotubes with one to four walls. After the reaction, the unreacted Co and MgO were dissolved in dilute (3.7%) hydrochloric acid and carbon nanotubes were recovered. High-resolution electron microscopy images showed the presence of individual and bundles of nanotubes of diameters ranging from 0.6 to 3 nm. Most of them were single or double walled and were >100 μm in length. Chemical analysis showed that the sample contained 95 vol % of carbon.

We have selected a sample with mostly single and double walled tubes as verified by high-resolution electron microscopy¹³ with a significant fraction of internal tubes with diameters smaller than 1 nm and we have examined the inelastic light spectrum of tubes along a single tube bundle. The tubes agglomerate to networks of bundles or ropes when deposited on a silica surface from a suspension.^{2,14} We find that the packing of ropes depends on the diameter of the single and double walled tubes. The bundles have a variable diameter due to the fact that they consist of tubes with different diameter and can on some locations consist of only a few tubes or one single tube. We have dispersed the tubes on a bilayer substrate to enhance the light-scattering signal due to the enlarged local field.¹⁵ This enhancement technique has the advantage that it is not based on electronic resonance which can modify the spectra. We have used a micro-Raman

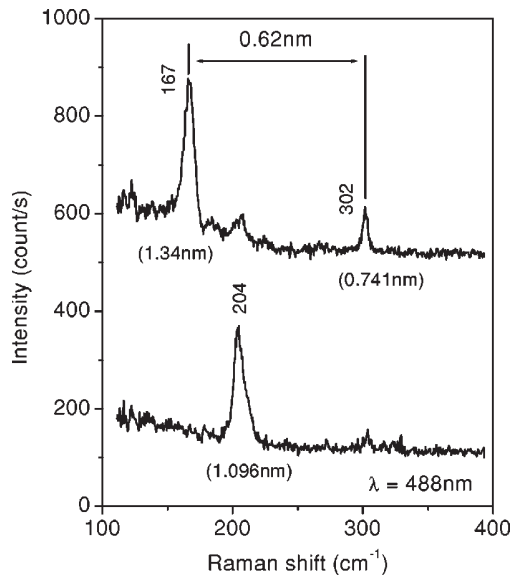


FIG. 1. Room-temperature Raman spectra of RB modes on two location of the sample. The spectrum at the bottom is assigned to mostly single walled tubes and the spectrum at the top can be assigned to mostly double walled carbon nanotubes.

spectrometer (DILOR XY, objective $\times 100$, spot size: $0.7 \mu\text{m}$) with a microdisplacement stage to record successive spectra in steps of $0.5 \mu\text{m}$ along a single tube bundle.

Raman scattering from vibrational modes of single wall carbon nanotubes have been reported earlier and have provided valuable structural and electronic information.^{16–18} Strong in-plane covalent bonds and weak interplanar interaction result in several in-plane modes in the range $1560\text{--}1600 \text{ cm}^{-1}$, a disorder induced band in the range $1300\text{--}1400 \text{ cm}^{-1}$, and out-of-plane (radial) modes at $<400 \text{ cm}^{-1}$. The mode with the highest intensity at low energy is the radial breathing mode with symmetry A_{1g} . Modes of symmetry E_{2g} at low energy have not been observed so far due to their presumably low intensity.¹⁹ Single wall CNT's grown by other techniques such as the pulsed laser evaporation²⁰ or the electric arc technique²¹ have a typical diameter of 1.35 nm and a RB mode at 157 cm^{-1} . We present here inelastic light spectra from DWCNT grown by the CCVD method with a significant fraction of tubes with small internal diameter tubes and RB modes between 150 and 370 cm^{-1} . While the electronic structure depends on tube diameter and chirality, the light scattering resonance is expected to follow the changes in the electronic structure of the tube. We have selected the 488-nm line of the argon laser which is in resonance with metallic single walled tubes of diameter 0.95 nm and semiconducting tubes of diameter 1.2 nm .²² All the tube diameters have been determined by using the inverse relationship between diameter and RB energy.¹²

Figure 1 shows spectra on two locations on the sample in the energy range of the RB modes. The spectrum at the bottom shows a RB mode at 204 cm^{-1} which corresponds to a diameter of 1.096 nm and can be assigned to single walled tubes. Tubes with several different chiralities fall within the interval of the peak width and an assignment to one chirality

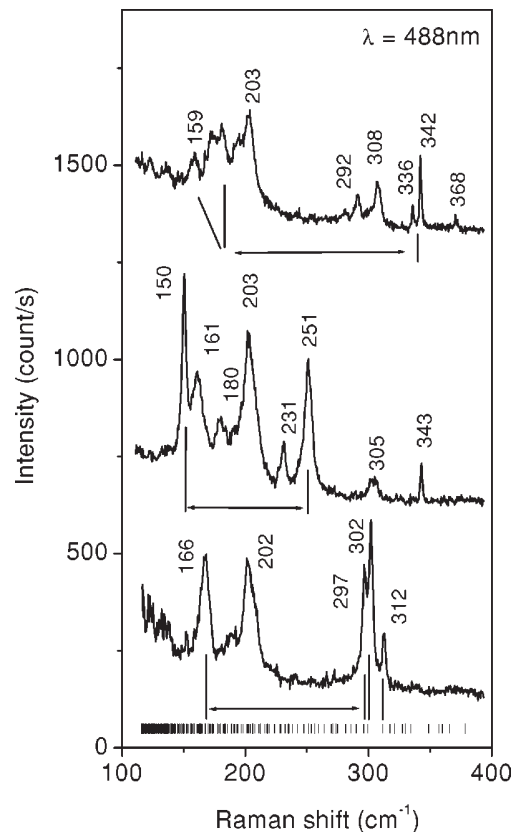


FIG. 2. Room-temperature Raman spectra of RB modes along a tube bundle containing double walled carbon nanotubes with different internal and external diameters.

cannot be made. The nonhomogeneous line shape is an indication that several diameters contribute to the observed peak. The spectrum at the top with two peaks at 167 and 302 cm^{-1} is consistent with DWCNT's with external and internal diameters of 1.340 and 0.741 nm . The diameter of the internal tube is close to the diameter (0.747 nm) which corresponds to the chirality $(9,1)$ and $(6,5)$. The two chiralities have by accident the same diameter and are both predicted to be semiconducting.¹ There are tubes with chirality $(7,4)$ and $(8,2)$ with a similar diameter and they may also contribute to the observed band at 302 cm^{-1} . From the internal and the external diameter we find that the deduced interlayer distance (0.30 nm) is smaller than in graphite (0.336 nm).

We recorded several series of spectra along single bundles and we show here three spectra (Fig. 2) out of 50 along one tube bundle which have RB modes in the $280\text{--}350\text{-cm}^{-1}$ range corresponding to tubes with particularly small diameter. We have indicated the calculated RB energies for all possible chiralities near the horizontal axis. The number of RB mode energies gets considerably smaller above 250 cm^{-1} . The spectrum at the bottom shows three main bands at 166 , 202 , and 300 cm^{-1} with corresponding diameters of 1.35 , 1.1 , and 0.741 nm . The three peaks at 300 cm^{-1} are narrower than in Fig. 1 and can be assigned to tubes of chirality $(7,4)$, $(9,1)$, $(6,5)$, and $(8,2)$. The tubes with chirality $(7,4)$ and $(8,2)$ both predicted to be metallic¹ fall within 1 cm^{-1} of the predicted values (Table I). It is inter-

TABLE I. Experimental and predicted RB energies.

Experiment	Theory	Difference	Diameter	Chirality
cm^{-1}	cm^{-1}	cm^{-1}	nm	(n,m)
297.0	296.2	0.8	0.756	(7,4) metallic
302.0	299.4	2.6	0.747	(9,1), (6,5) semiconducting
312.0	311.6	0.4	0.718	(8,2) metallic
336.0	334.3	1.7	0.669	(8,1) semiconducting
342.0	348.9	-6.9	0.641	(7,2) semiconducting
368.0	365.7	2.3	0.612	(5,4) semiconducting

esting to note that the peak at 302 cm^{-1} which corresponds to two different chiralities both predicted to be semiconducting, has a larger intensity and is shifted to larger energies. We can pair the RB modes at 300 cm^{-1} with RB mode at 166 cm^{-1} and we deduce an interlayer spacing of $0.297\text{--}0.316 \text{ nm}$. In the spectrum in the middle of Fig. 2 we observe several RB modes between 150 and 343 cm^{-1} . We can assign the modes at 251 and 150 cm^{-1} to double walled tubes corresponding to tube diameters of 0.89 and 1.49 nm and resulting interlayer spacing 0.3 nm . The spectrum at the top of Fig. 2 shows several RB modes at higher Raman shifts (336 , 342 , and 368 cm^{-1}). The RB modes in this range correspond to tubes of diameter 0.666 , 0.653 , and 0.610 nm which are particularly small and can be assigned to chiralities $(8,1)$, $(7,2)$, and $(5,4)$. They can be associated to double walled tubes with RB modes of the external tube at 180 cm^{-1} and the deduced interlayer spacing varies between 0.31 and 0.34 nm for RB modes between 170 and 185 cm^{-1} .

While the peaks at 336 and 368 cm^{-1} fall within 3 cm^{-1} of the predicted values for tubes with chirality $(8,1)$ and $(5,4)$, the peak at 343 cm^{-1} falls between the values for tubes with chirality $(8,1)$ and $(7,2)$ (Table I) and could be associated with either of the two. In fact, an increased bond length due to the higher curvature would shift the RB modes to lower energy but this should also be observed for the other tubes in the same diameter range. A reduced interlayer spacing would lead to a compression of the internal tube in a DWCNT and could explain the upshift of the RB mode.

Recently, doubled walled CNT's have been synthesized through high-temperature annealing ($1200 \text{ }^\circ\text{C}$) of single walled tubes filled with C_{60} .²³ The Raman spectra using the 514.5-nm excitation of these tubes showed additional bands at 260 , 315 , and 377 cm^{-1} with line widths of $>8 \text{ cm}^{-1}$. The diameter difference of inner and outer diameter (0.71 nm) or interlayer distance (0.36 nm) was found to be systematically larger than in graphite (0.335 nm) in contrast to our findings here on catalytic CVD grown DWCNT's.

A systematic upshift of the RB modes of single walled CNT's has been associated to intertubular interaction and distortion in bundles²⁴ and theoretical calculations indicate an upshift of up to 10% for tubes in bundles.²⁵ Furthermore, a theoretical study has recently shown that gas absorption within the interstitial channels of a bundle of CNT's can increase the RB mode energy²⁶⁻²⁸ by 2.7% . This can cer-

tainly influence the position of the RB modes of the external tubes but less likely the RB modes of the internal tubes. Taking into account the influence of the neighboring tubes on the RB mode of the external tube we find that the deduced interlayer spacing is larger (0.32 nm) and brings the interlayer spacing closer to graphite.

Table I shows that the differences between the experimental and theoretical values of the RB modes are different for semiconducting and metallic tubes. This difference can be explained by resonance effects, sensitive to changes in the electronic structure of the tube. Inelastic light spectra of single shell carbon nanotubes²⁹ and of our DWCNT taken with an excitation source at 488.0 nm have been found to be downshifted compared to spectra taken at 514.5 nm and this can explain the differences observed for two types of DWCNT's. But the deduced different interlayer distance in the two types of double walled tubes could also indicate differences in the growth mechanism of catalytic CVD grown and annealed doubled walled tubes. Annealing causes a growth of an internal tube whereas in the CVD method presumably the external tube grows on the inner tube. This is consistent with the tendency that the layer grown later in the process forms before an interlayer distance corresponding to the value observed in graphite is reached.

Among the observed chiralities of the internal tubes we have found neither a zigzag $(n,0)$ nor an armchair (n,n) tube and in the diameter range of the internal tubes we find among the chiralities which have not been observed, three semiconducting and three metallic tubes. This fact indicates that the growth of the tubes with chiralities other than zigzag or armchair may be favored due to their lower symmetry. Finally we note the particularly narrow line shape of some of the RB modes of the internal tubes which in fact made it possible to assign the chirality of the tubes. The dispersion of the tubes on the bilayer substrate and selection of a single tube bundle using a microscope has the effect to reduce the broadening due to size dispersion. The narrow line shape shows the high coherence length and harmonicity for RB modes of internal tubes. The RB modes are localized on a very narrow tube and we expect that DWCNT's are as a result exceptionally good thermal conductors.

We have observed RB modes of DWCNT's by inelastic light scattering. The narrow diameter of the internal tubes grown by the catalytic CVD method, the higher sensitivity of the RB mode for smaller diameter and the reduced number of chiral vectors in this diameter range as well as the narrow

linewidths made it possible to assign the chirality of the internal tubes. We observe two metallic as well as several semiconducting tubes and no zigzag ($n,0$) or armchair ($0,m$) tubes. Differences between experimental and theoretical energies of the RB modes are found to be larger for semi-

conducting tubes and attributed to mostly electronic resonance effects.

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