Unusual High Degree of Unperturbed Environment in the Interior of Single-Wall Carbon Nanotubes

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Double wall carbon nanotubes were prepared by vacuum annealing of single wall carbon nanotubes filled with C_{60}. Strong evidence is provided for a highly defect free and unperturbed environment in the interior of the tubes. This is concluded from unusual narrow Raman lines for the radial breathing mode of the inner tubes. Lorentzian linewidths scale down to 0.35 cm^{-1} which is almost 10 times smaller than linewidths reported so far for this mode. A splitting is observed for the majority of the Raman lines. It is considered to originate from tube-tube interaction between one inner tube and several different outer tubes. The highest RBM frequency detected is 484 cm^{-1} corresponding to a tube diameter of only 0.50 nm. Labeling of the Raman lines with the folding vector is provided for all inner tubes. This labeling is supported by density functional calculations.

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Because of their unusual properties, new phases of carbon such as fullerenes or carbon nanotubes have been attracting considerable interest for basic science and technological applications ever since their discovery in 1985 [1] and 1991 [2], respectively. This interest was dramatically raised with the discovery of single-wall carbon nanotubes (SWCNTs) in 1993 [3] and their large scale production in 1996 [4]. Among others, nanoelectronics, nanomechanics, and nanosensors are promising new fields for high tech applications. In addition, the interior of single-wall tubes has been repeatedly announced as an unusual nanoreactor for the growth of novel materials [5,6]. Growth under completely shielded conditions can be expected to produce unique materials.

Raman scattering has been proven to be a key technique for the analysis of SWCNTs, among others, due to their photoselective resonance response for the radial breathing modes (RBM) [7]. This response has been used repeatedly to determine the diameter distribution function of laser ablation or arc discharge grown material [8]. The resonance enhanced scattering is a consequence of optical transitions between Van Hove singularities which dominate the density of states (DOS) in the conduction band and in the valence band. Transition energies scale with the inverse diameter d of the tubes as $E_{ii} \approx 2ina_{CC}\gamma_0/d$, where γ_0 is the π-overlap integral with an accepted value of 2.9 eV, a_{CC} is the carbon-carbon distance for the tubes, and n equals 1 for semiconducting and 2.5 for metallic tubes. From a refined inspection the transition energies depend also on the helicity of the tubes [9]. Resonance experiments are therefore capable of providing general information on the electronic structure of the tubes. Experiments on single tubes demonstrated very sharp resonances of widths down to several 10 meV [10]. RBM frequencies scale also with the inverse diameter as $\nu_{RBM} = C_1/d + C_2$, where C_1 is a constant with approximate value of 234 cm^{-1} nm as evaluated from *ab initio* calculations [11]. C_2 is a constant of the order of 10 cm^{-1}, which corrects the frequencies for intertube interaction in SWCNT bundles [8,12]. Again, a dependence on helicity was suggested from the *ab initio* calculations but has not been demonstrated thus far experimentally. Very recently, luminescence and absorption have shown a fine structure which originates from individual tubes suspended in a micellar arrangement [13,14].

We demonstrate here that the interior of the tubes is indeed a curved nanospace with an unexpected high degree of perfectness. This information is retained from a Raman line shape analysis of double-wall tubes grown from nanotubes filled with C_{60} molecules. Raman lines for the response from the radial breathing mode of the inner shell tubes exhibit an unusual narrow width with Lorentzian components down to 0.35 cm^{-1} or 30 μeV. This is almost 10 times smaller than linewidths of nanotubes reported thus far [15]. In addition, scattering intensities for lines from the inner shells can be more than 10 times higher than intensities for lines from the outer shells, which provides further evidence for the unperturbed interior of the tubes. The highest RBM frequency detected was 484 cm^{-1}, which corresponds to a tube diameter of only 0.495 nm. The number of observed Raman lines from the inner tubes is about a factor of 3 larger than the geometrically allowed tubes. This is a strong hint for a possible combination of different types of outer tubes with one type of inner tube.

The nanotubes used in this work were grown as bundled species and subsequently filled with C_{60} fullerenes as described previously [16]. The diameter

distribution of the outer tubes was Gaussian with a mean diameter of 1.39 ± 0.02 nm and a width (variance) of 0.1 nm, as determined from the first and second spectral moments of the Raman response recorded for the RBM. Concentration of the filling was close to 100% as determined from a Raman and electron energy loss spectroscopy analysis. Heating of the filled tubes up to 1300 °C in a dynamic vacuum for about 12 h transformed the fullerenes to a set of inner tubes as was reported previously in [17]. The double-wall character of the transformed product was checked by high resolution (hr) TEM. In many areas of the tube material, nice double-wall species were observed. Raman spectra were generally recorded by an intensity calibrated triple spectrometer at 90 K using up to 20 different laser lines. For the high resolution experiments the spectrometer was switched to the additive mode and recording was at 20 K. The spectral resolution was determined by fitting the laser line to a Gaussian profile. Then this profile was taken as the Gaussian part of Voigtian lines used for the fit of the Raman lines. Depending on the wavelength of the laser the Gaussian width was between 0.4 and 0.7 cm^{-1}. The widths of the Lorentzian components in the Voigtian lines are considered as the widths (lifetime) of the phonons. *Ab initio* density functional calculations were carried out on the basis of the Vienna Ab Initio Simulation Package (VASP) [18] in order to obtain a better understanding of the electronic structure and of the phonon frequencies of the inner shell tubes.

Figure 1 depicts selected Raman spectra of the RBM. The top spectrum, recorded with a 514 nm laser at 90 K, is almost identical to the spectrum reported by Bandow *et al.* [17,19]. The broad group of lines around 180 cm^{-1} and the lines between 250 and 400 cm^{-1} represent the response of the RBM of the outer and inner tubes, respectively. Shifting to lower temperatures (20 K) and high resolution (spectrum 515hr) did not alter the pattern essentially. However, the response from the inner tubes became dramatically enhanced and dominated by very narrow lines for excitation with the yellow and red lasers. This is demonstrated by the spectra 568hr, 633hr, and 676hr in Fig. 1. The Lorentzian components of the lines observed for the inner tubes are unusually narrow, of the order of 0.5 cm^{-1} but even reduce down to 0.35 cm^{-1} in several cases. Connected with the narrowing of the Raman lines the resonance excitation for several lines becomes extremely strong. Peak intensities are more than 10 times higher than for the response from the outer tubes. This implies very sharp transitions between the Van Hove singularities and/or enhanced electron-phonon coupling. In addition, an unexpected large number of lines is observed. A detailed inspection (676hr, 568hr) reveals that it originates from a splitting in basically two or even three components separated by 0.5 to 2 cm^{-1}. This splitting may be a consequence of the much coarser diameter distribution for the inner tubes as compared to the outer tubes. Therefore, several outer tubes match to

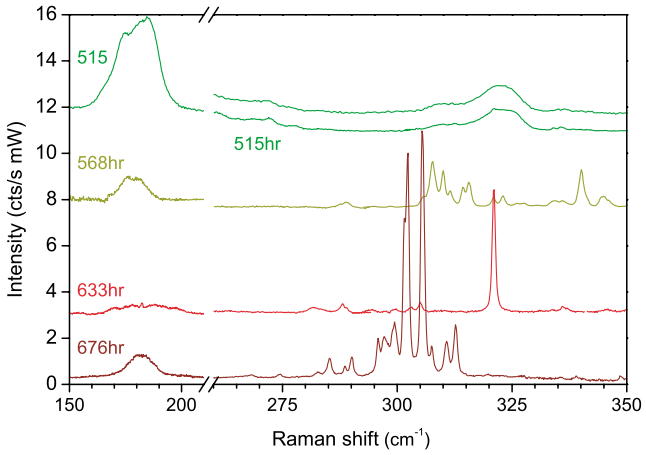

FIG. 1 (color online). Raman response of the radial breathing mode of double-wall carbon nanotubes, excited by different lasers as indicated (hr stands for high resolution). The top spectrum was recorded for 90 K, all other spectra for 20 K. The response is intensity calibrated.

one inner tube until the diameter of the former is large enough to allow for the next larger inner tube. Intertube distances observed experimentally by TEM range between 0.34 and 0.38 nm. For an average distance between shells of 0.36 nm, up to three outer tubes fit to the same inner tube. Since the tube-tube interaction depends strongly on the difference between tube diameters and also on the mutual orientation of the tubes, the RBM lines appear split.

In order to obtain a full assignment of the folding vector (n, m) to the observed Raman peaks, we have recorded spectra for excitation with 15 different laser lines in the high resolution mode at 20 K. More than 450 Raman lines were analyzed. The observed lines are depicted in Fig. 2 on a frequency scale. For the correlation between tube diameters labeled by (n, m) and RBM frequencies, the linear relation between ν_{RBM} and $1/d$ was used with $C_1 = 235$ cm^{-1} nm and $C_2 = 9$ cm^{-1}. The main body of the lines is recorded between 250 and 390 cm^{-1}, which corresponds to diameters for the inner tubes of 0.98 and 0.62 nm and hence to outer tube diameters of 1.70 and 1.34 nm, respectively. From the high frequency side we learn that tubes up to 1.34 nm diameter can be easily filled. Eventually, Raman shifts up to 484 cm^{-1} could be observed but intensities became very low. A shift of 484 cm^{-1} corresponds to an inner and outer tube diameter of 0.495 and 1.22 nm, respectively. We conclude that this is the absolute limit up to which tubes can be filled in very good agreement with calculations [20]. A systematic analysis which takes into account the frequencies of the lines and the resonance conditions for their observation allowed for the first time to provide a full (n, m) assignment of the observed peaks. Thus far, assignments were only suggested from single tube experiments [15] and very recently for a set of semiconducting tubes [14]. In our case all peaks down to intensities of the

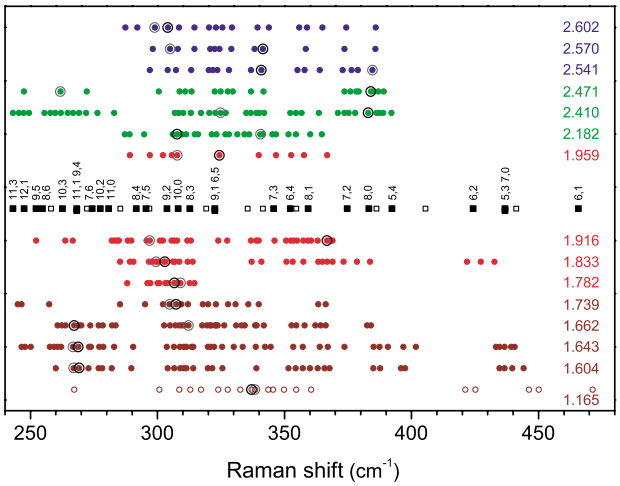

FIG. 2 (color online). List plot of observed Raman lines for the radial breathing mode (RBM) of the inner tubes. Lasers used for excitation are noted on the right-hand side in eV. Heavy and light circles indicate the strongest and the second strongest peaks in the spectrum. Full and open squares represent the geometrically allowed semiconducting and metallic tubes, respectively. The numbers are the components of the folding vector.

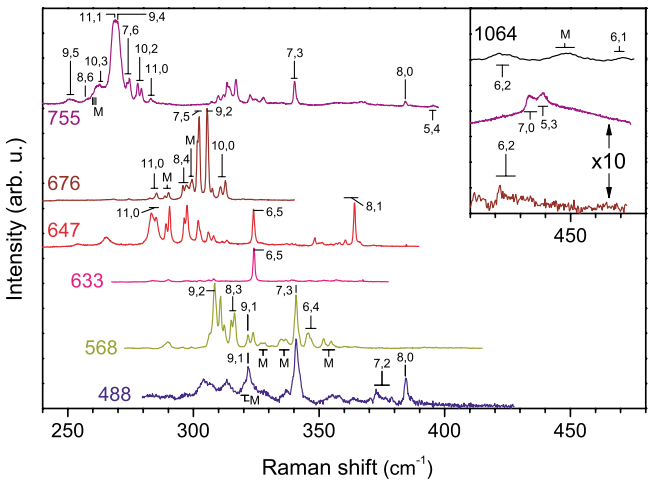

FIG. 3 (color online). Assignment of the observed Raman lines to the folding vectors (n, m). M indicates metallic tubes. The horizontal bars describe the width of the splitting due to intertube interaction. Seven lasers were selected for the presentation as indicated. Intensities for the different lasers are not drawn to scale in this figure. The resolution of the spectrum recorded with 1064 nm (Fourier-transform–Raman) was only 2 cm^{-1} and recording was at 110 K.

order of 0.01% of the maximum observed intensity could be assigned, and almost all geometrically allowed tubes between 0.50 and 0.98 nm diameter were observed in the experiment. Except for the very small tubes where chirality effects start to become important, excellent agreement between observed and assigned frequencies is obtained. Our final assignment was obtained from a minimization of the root mean square error between experimental and calculated frequencies by fitting C_1 and C_2. It differs by about 5% (in frequency for equal (n, m)) from the assignment provided in Ref. [14]. In Fig. 3 seven lasers were selected to provide the best review of the response from the tubes and the final assignment. The obvious trend for the shift of the line bunches from the upper left to the lower right indicates that in all cases the same transition, namely E^s_{22}, is responsible for the resonance excitation. Only for frequencies higher than 450 cm^{-1} (see the inset of Fig. 3) E^s_{11} transitions become important. The inset of Fig. 3 represents the response from the very narrow tubes excited with three different lasers. The double peak structure around 436 cm^{-1} deserves particular attention. It is assigned to the (7, 0) and (5, 3) tubes which exhibit equal diameters and hence equal frequencies within the tight binding picture. From VASP calculations we know that zigzag tubes exhibit lower RBM frequencies than armchair tubes for the same tube diameter [11]. Hence, the lower peak at 433 cm^{-1} in the doublet is safely assigned to (7, 0), whereas the peak at 439 cm^{-1} originates from (5, 3). The frequencies calculated explicitly from VASP for the particular case are 420 cm^{-1} for the RBM frequency of (7, 0) and 429 cm^{-1} for the (5, 3) tube, where in both cases the shift of 9 cm^{-1} from the intertube interaction was added. The line shape analysis reveals again a splitting for both components of the doublet.

The extremely narrow Raman lines indicate a long lifetime for the phonons and hence very clean and highly defect free conditions inside the tubes. Any line broadening from surrounding inhomogeneities is highly shielded. The observed temperature dependence indicates that linewidths may even become more narrow for still lower temperatures. We may well talk about a "nano clean room" for this environment. The small linewidths are not unusual *per se*. For high quality single crystals of C_{60}, low temperature linewidths for IR active modes were reported as small as 0.1 cm^{-1} [21]. The clean room conditions inside may be of particular importance during the growth process of the inner tubes as they are grown without catalyst. The conditions guarantee that dangling bonds are not saturated, but rather allow or even promote tube growth.

The interpretation of the line splitting suggests to use Lennard-Jones (LJ) potentials to describe the tube-tube interaction. Such potentials have been parametrized for the carbon-carbon interaction [22] in graphite. Since the difference in diameter for two outer tubes which correspond to the same inner tube is rather small, of the order of 0.015 nm, the difference in the interaction energy turns out to be less than 0.1 cm^{-1} and can thus *per se* not explain the splitting. To understand the latter, additional effects are important. First, any relative change of the mutual position of the hexagons in the two shells may contribute to the distance of the carbon atoms. Using the LJ potential it is easy to show that maximum shifts of the

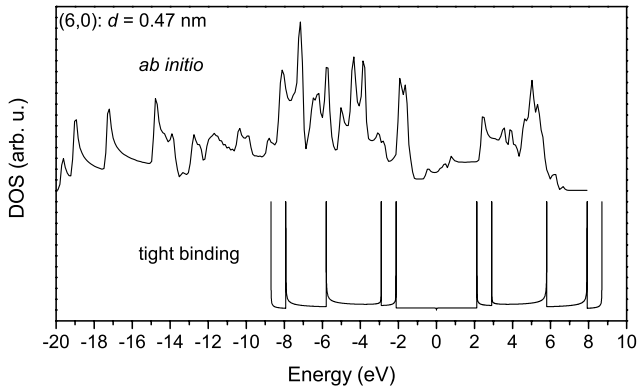

FIG. 4. Density of states for a narrow metallic tube as calculated by *ab initio* and by tight binding. In the former case the structure between the two first Van Hove singularities can provide visibility to the Raman lines, even for laser energies below the E_{11}^{m} gap.

order of 5 cm^{-1} can be expected from this. Second, the tubes are grown at high temperatures where optimum arrangements between the two shells will be established. However, at room temperature the two coupled tubes will end up somewhere off the minimum of the LJ potential. Similarly, the balance between curvature energy and van der Waals energy can shift the equilibrium position away from the original van der Waals minimum and thus leads to a much stronger splitting for the same value of δr.

The observation of the metallic tubes, particularly for those with very small diameter, provides experimental evidence for the shortcomings of the tight binding model. *Ab initio* calculations show that for such tubes (except for the armchair configuration) considerable structure is established in the DOS even for energies lower than E_{11}^{m}, which can provide moderate resonance for the Raman lines of such tubes. An example is given in Fig. 4.

Finally, the narrowest tubes observed here exhibit a diameter of only about 0.50 nm. Such tubes are already close to the very narrow tubes grown in zeolite cavities [23]. Such tubes exhibit diameters of 0.42 nm with helicities (3, 3), (5, 0), or (4, 2). Thus the tubes we studied here approach the very narrow zeolite grown nanotubes. As compared to the latter, the inner shell tubes in the double-wall carbon nanotubes exhibit a very high degree of perfectness. As the very narrow tubes grown in the zeolites exhibit superconductivity [24], we may expect superconductivity in the narrow species of the inner tubes as well.

Summarizing, double-wall carbon nanotubes prepared from C_{60} molecules inside laser ablation grown tubes exhibit a highly unexpected behavior. The unusual narrow linewidths in Raman experiments indicate a very low phonon scattering rate which probably is almost reduced to thermally induced phonon-phonon interaction. The low scattering rate is evidence for highly shielded and defect free growth conditions inside the tubes and assigns the inside as a perfect reaction space with nanodimension. The narrow lines and their unexpected large number require a detailed analysis of line splitting. An assignment of all observed peaks to the folding vectors of the tubes is possible, including the metallic species. The smallest observed inner tubes extend to a range where the standard rules for the metallicity of the tubes are not valid any more. All these aspects provide a challenging field for experimental and theoretical studies of the highly perfect SWCNTs of the inner shell. The demonstrated clean and highly defect free interior of the tubes can be expected to attract particular attention in the field of new materials preparation.

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[1] H. Kroto *et al.*, Nature (London) **318**, 162 (1985).
[2] S. Iijima, Nature (London) **354**, 56 (1991).
[3] S. Iijima *et al.*, Nature (London) **363**, 603 (1993).
[4] A. Thess *et al.*, Science **273**, 483 (1996).
[5] K. Hirahara *et al.*, Phys. Rev. Lett. **85**, 5384 (2000).
[6] T. Pichler *et al.*, Phys. Rev. Lett. **87**, 267401 (2001).
[7] A. Rao *et al.*, Science **275**, 187 (1997).
[8] H. Kuzmany *et al.*, Eur. Phys. J. B **22**, 307 (2001).
[9] H. Kataura *et al.*, Synth. Met. **103**, 2555 (1999).
[10] A. Jorio *et al.*, Phys. Rev. B **63**, 245416 (2001).
[11] J. Kürti *et al.*, Phys. Rev. B **58**, R8869 (1998).
[12] L. Henrard *et al.*, Phys. Rev. B **60**, R8521 (1999).
[13] M. J. O'Connell *et al.*, Science **297**, 593 (2002).
[14] S. M. Bachillo *et al.*, Science **298**, 2361 (2002).
[15] A. Jorio *et al.*, Phys. Rev. Lett. **86**, 1118 (2001).
[16] H. Kataura *et al.*, Synth. Met. **121**, 1195 (2001).
[17] S. Bandow *et al.*, Chem. Phys. Lett. **337**, 48 (2001).
[18] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[19] S. Bandow *et al.*, Phys. Rev. B **66**, 075416 (2002).
[20] F. Zerbetto (private communication).
[21] C. C. Homes *et al.*, Phys. Rev. B **52**, 16 892 (1995).
[22] J. P. Lu and W. Yang, Phys. Rev. B **49**, 11 421 (1994).
[23] Z. K. Tang *et al.*, Appl. Phys. Lett. **73**, 2287 (1998).
[24] Z. K. Tang *et al.*, Science **292**, 2462 (2001).