Diameter dependence of the Raman D -band in isolated single-wall carbon nanotube

PHYSICAL REVIEW B, VOLUME 64, 041401(R)

Diameter dependence of the Raman *D*-band in isolated single-wall carbon nanotubes

M. A. Pimenta,[1] A. Jorio,[2] S. D. M. Brown,[2] A. G. Souza Filho,[2,3] G. Dresselhaus,[4] J. H. Hafner,[5] C. M. Lieber,[5] R. Saito,[6] and M. S. Dresselhaus[2,7]

[1]*Departmento de Física, Universidade Federal de Minas Gerais, CP 702, 30123-970 Belo Horizonte, Brazil*
[2]*Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307*
[3]*Departamento de Física, Universidade Federal do Ceará, Fortaleza-CE, 60455-760 Brazil*
[4]*Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307*
[5]*Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138*
[6]*Department of Electronic Engineering, University of Electro-Communications, Tokyo 182-8585, Japan*
[7]*Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307*

(Received 23 February 2001; published 21 June 2001)

Raman *D*-band spectra are reported for several different SWNTs using two different laser energies ($E_{\text{laser}} = 1.58$ and 2.41 eV). At a fixed E_{laser}, individual isolated SWNTs exhibit different diameter-dependent *D*-band frequencies ω_D around an average value. For both semiconducting and metallic tubes, ω_D decreases with decreasing nanotube diameter, though ω_D for isolated metallic SWNTs is higher than for isolated semiconducting SWNTs. The average *D*-band frequency depends linearly on E_{laser}, as previously observed for SWNT bundles, suggesting that the *D*-band in SWNTs is activated by defects or by the finite size of the SWNTs.

DOI: 10.1103/PhysRevB.64.041401 PACS number(s): 78.67.Ch, 78.30.−j

The disorder-induced Raman band (*D* band) is a feature common to all sp^2 hybridized disordered carbon materials. This *D* band is associated with phonons close to the *K* point of the graphite Brillouin zone (BZ), and the *D* band becomes Raman active for disordered carbon materials due to the loss of translational symmetry.[1] The *D*-band frequency ω_D, appearing between 1250 and 1450 cm^{-1}, shows a strong linear dependence on the excitation laser energy (E_{laser}). This E_{laser} dependence of the *D*-band phonon frequency in sp^2 carbons has been attributed to an electronic transition between bands with a linear dispersion relation, which is in resonance with the incident photon.[2–5] In the case of single-wall carbon nanotubes (SWNTs), phonons within the interior of the graphite Brillouin-zone become Raman-active due to the folding of the 2D graphite Brillouin zone, thus giving rise to phonons at the center of the 1D carbon nanotube Brillouin zone.[6,7] Therefore, several features are expected to appear in the Raman spectra of SWNTs around 1300 cm^{-1}, the frequencies and Raman cross-sections being strongly dependent on the nanotube diameter d_t and chiral angle θ.

In laser energy (E_{laser}) dependent studies of the *D* band and of its overtone, the G' band, it was shown[8–10] that the *D*-band frequency of bundles of SWNTs $\overline{\omega_D}$ exhibits a basic linear E_{laser} dependence, somewhat similar to other carbon sp^2 materials, but also with some marked differences. First, $\overline{\omega_D}$ for SWNT bundles for a given E_{laser} is always smaller by about 20 cm^{-1}, as compared to other sp^2 carbon materials. Moreover, a plateau or oscillation was observed in the E_{laser} dependence of $\overline{\omega_D}$, in the E_{laser} range where the optical interband transition for *metallic* SWNTs occurs.[8,9] The intensity of the *D*-band feature was also found to be especially large in this ''plateau'' range of E_{laser}. Two major questions remain concerning the nature of the *D*-band in SWNTs: Is this band active in a perfect SWNT or is it activated by the presence of defects and/or by the finite size of the nanotubes? Does the *D*-band frequency depend on the SWNT diameter?

In order to address these questions, we have here performed a Raman study of the *D*-band feature for over 35 different *isolated* SWNTs, using two different E_{laser} values (1.58 and 2.41 eV). The observation of Raman spectra (including the *D* band) of *isolated* SWNTs is possible due to resonance with the one-dimensional van Hove singularities in the density of electronic states.[11,12] We here show that for a given E_{laser}, the different isolated SWNTs actually exhibit different ω_D values. However, the mean value of the *D*-band frequency ω_D for isolated SWNTs depends on E_{laser}, similar to the general case of sp^2 carbon materials, and this mean value of ω_D is consistent with the same dependence $\overline{\omega_D}(E_{\text{laser}})$ that is observed for SWNT bundles. The observed E_{laser} dependence of ω_D and I_D for isolated tubes suggests that the associated phonons are not at the center of the 1D Brillouin zone of SWNTs, and that these phonons are activated by the presence of defects or by the finite size of the nanotubes. By comparing the Raman spectra of the *D* band with that of the tangential *G* band for different SWNTs probed with a given E_{laser}, it is shown that ω_D decreases with decreasing d_t for both semiconducting and metallic tubes. Moreover, we observed that ω_D for metallic SWNTs is higher than ω_D for semiconducting SWNTs at the same E_{laser}.

Isolated SWNTs were prepared by a chemical vapor deposition method on a Si/SiO_2 substrate containing nanometer size iron catalyst particles.[12] The samples exhibit a concentration of 6 ± 3 SWNTs per μm^2, and a broad diameter distribution ($1 \leqslant d_t \leqslant 3$ nm).[12] Resonant Raman spectra from 100 cm^{-1} to 3000 cm^{-1} were obtained from individual isolated SWNTs on this substrate, using a Kaiser Optical Systems, Hololab 5000R: Modular Research Micro-Raman Spectrograph (1 μm laser spot) with 25 mW power. Spectra

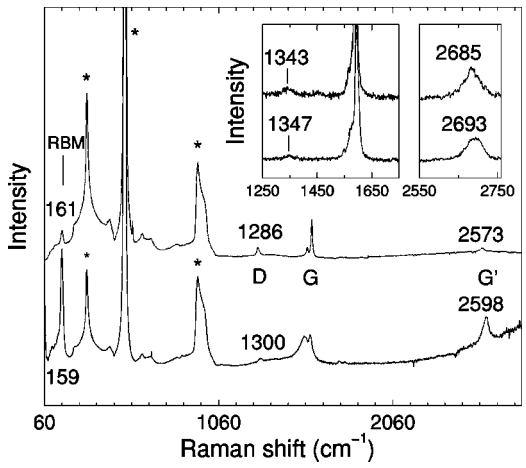

FIG. 1. Raman spectra taken on two different spots excited by $E_{\text{laser}}=1.58$ eV. The features marked with asterisks are attributed to the Si substrate. The insets show the *D*-band, *G*-band and G'-band resonant Raman spectra for two isolated SWNTs excited by $E_{\text{laser}}=2.41$ eV.

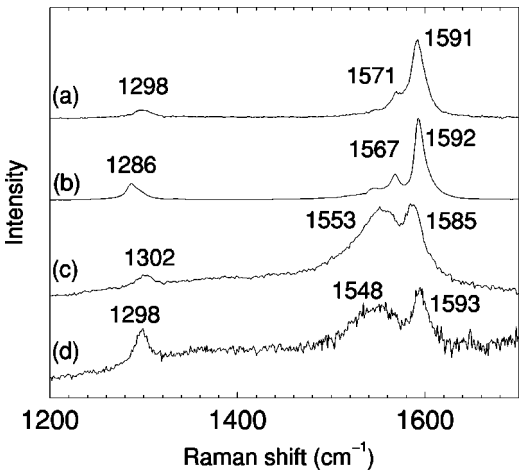

FIG. 2. Raman spectra of four different *isolated* SWNTs ($E_{\text{laser}}=1.58$ eV). The frequencies for the *D* band and for the two most intense *G*-band peaks are displayed in cm^{-1}.

were taken out on more than 30 different isolated SWNTs in several samples using 785 nm (1.58 eV) and 514.5 nm (2.41 eV) laser excitation lines.

Figure 1 shows Raman spectra coming from two different light spots, in the spectral range 100–2800 cm^{-1}, obtained with $E_{\text{laser}}=1.58$ eV. The most intense Raman features associated with the SWNTs are the radial breathing mode (RBM) band at $\sim$160 cm^{-1}, the *D* band at $\sim$1300 cm^{-1}, its overtone (the G' band) at $\sim$2600 cm^{-1}, and the tangential *G* band between 1500 and 1600 cm^{-1}, with the upper (lower) spectrum of Fig. 1 typical of a semiconducting (metallic) nanotube.[13] Although the same E_{laser} was used, the *D*-band frequencies for these two isolated SWNTs are different (1286 and 1300 cm^{-1}), as are the G'-band frequencies (2573 and 2598 cm^{-1}), corresponding to their respective $2\omega_D$ values. The insets to Fig. 1 show Raman spectra of two different isolated SWNTs obtained with $E_{\text{laser}}=2.41$ eV, where now ω_D and $\omega_{G'}$ are at 1343/1347 and 2685/2693 cm^{-1}, respectively.

For SWNT bundles, it was found[8] that $\overline{\omega}_D$ (in cm^{-1}) depends on E_{laser} (in eV) as $\overline{\omega}_D=1210+53\,E_{\text{laser}}$, according to which, $\overline{\omega}_D$ for SWNT bundles, investigated with $E_{\text{laser}}=1.58$ and 2.41 eV, is expected to be 1294 and 1338 cm^{-1}, respectively. The predicted $\overline{\omega}_D$ value at $E_{\text{laser}}=2.41$ eV is close to (but somewhat smaller) than ω_D measured for the isolated SWNTs shown in the insets to Fig. 1. We have measured Raman spectra at $E_{\text{laser}}=2.41$ eV for 12 other isolated SWNTs and we obtained values for ω_D, ranging between 1337 and 1354 cm^{-1}. For $E_{\text{laser}}=1.58$ eV, we find that the predicted $\overline{\omega}_D=1294$ cm^{-1} for bundles lies between the measured range of ω_D, from 1286 to 1304 cm^{-1}, for isolated nanotubes, suggesting that for a given E_{laser}, $\overline{\omega}_D$ for SWNT bundles corresponds to an average value of ω_D for isolated SWNTs. Therefore, we find that an ensemble of isolated SWNTs also exhibits a $\overline{\omega}_D$ frequency dependence on E_{laser} similar to the dispersion observed for SWNT bundles.

As we discuss below, the different ω_D values obtained with one unique energy E_{laser} are related to a ω_D dependence on d_t.

It is well known that the SWNT diameter d_t can be estimated by the RBM frequency ω_{RBM} (Ref. 6) and, according to a recent Raman study of isolated nanotubes,[12] ω_{RBM} is related to d_t by $\omega_{\text{RBM}}=248$ cm^{-1} nm/d_t. However, in the present case, ω_{RBM} cannot be used to assign the diameter of the nanotube associated with the *D*-band, since different SWNTs may be associated with the RBM and *D*-band features in a given Raman spectrum coming from a light spot containing about 6 SWNTs. This is due to the fact that the resonant Raman windows associated with the RBM and the *D* bands have different widths, since the energy difference between the scattered photons for the RBM and the *D* band is about 0.16 eV. Such a case occurs in Fig. 1, where both spectra show RBM peaks centered around 160 cm^{-1} and, therefore, the associated SWNTs both have diameters of about 1.55 nm. The SWNTs associated with these ω_{RBM} are necessarily metallic, since only metallic nanotubes with diameters around 1.55 nm can be in resonance in a Raman experiment for $E_{\text{laser}}=1.58$ eV (see inset to Fig. 3). However, the *G* band shown in the upper spectrum is typical of a semiconducting nanotube, whereas the broad tangential band in the lower spectrum is associated with a metallic SWNT.[13] On the other hand, the energy difference of the scattered photons associated with the *D* band and the tangential *G* band is only 0.036 eV. Therefore, the same SWNT is likely to be associated with both the *D* band and the tangential *G* band in the Raman spectrum of isolated SWNTs.

It is well known that, relative to the graphite E_{2g_2} mode at 1582 cm^{-1}, the *G* band of SWNTs is split into six different components, the smaller the d_t, the larger the splitting of the *G*-band components. Therefore, the SWNT diameter related to an observed *D* band can be estimated by the *G*-band profile in the same spectrum.[7]

Figure 2 shows four spectra coming from different isolated SWNTs on the Si/SiO_2 substrate. From the splittings between the two main features in the *G* bands shown in Fig.

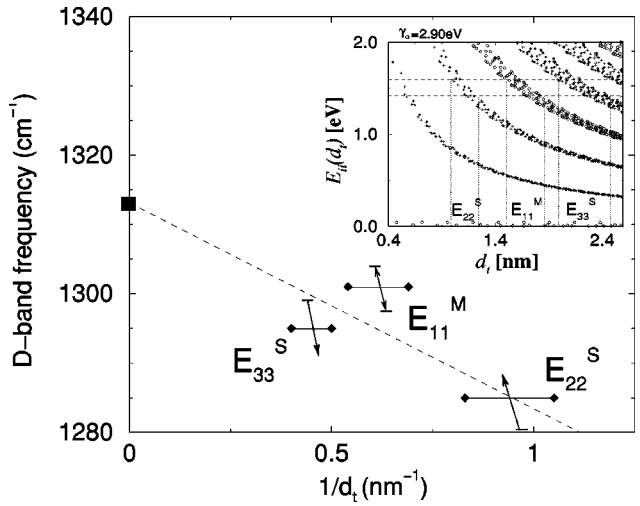

FIG. 3. ω_D for *isolated* SWNTs as a function of inverse diameter ($1/d_t$). The horizontal lines between the diamond symbols define the range in diameter where isolated SWNTs can be resonant with $E_{\text{laser}}=1.58$ eV. The dispersion in ω_D observed for the different SWNTs is indicated by the arrows. The dashed line defines a linear extrapolation of ω_D going to the *D*-band frequency for sp^2 carbon (square mark, from Ref. 3) for $d_t \rightarrow \infty$. The inset shows the d_t dependence of the optical E_{ii} transitions for SWNTs from $0.4 < d_t < 2.5$ nm. The horizontal dashed lines show the resonant limit for the Stokes process between $E_{\text{laser}}=1.58$ eV and $E_{\text{laser}}-E_{\text{ph}}$. The vertical lines in the inset mark the SWNT diameter ranges that can be resonant with E_{laser}.

2, we can identify spectrum (a) as coming from a semiconducting SWNT with a larger diameter than the semiconducting SWNT in (b), and spectrum (c) as coming from a metallic SWNT with a larger diameter than the metallic SWNT in (d). Comparing the ω_D values in Fig. 2 for spectra (a) and (b), and spectra (c) and (d), we see that, for both semiconducting and metallic SWNTs, ω_D depends on d_t, i.e., the smaller the d_t, the smaller the ω_D.

The observation of the *D* band in the Raman spectra of an *isolated* SWNT is limited by the resonance conditions on SWNTs. In our resonant Raman Stokes experiment with $E_{\text{laser}}=1.58$ eV, resonance occurs with optical transitions E_{ii} falling close to the energies 1.58 eV and 1.42 eV, since the energy of the *D*-band phonons is about 0.16 eV. Considering the diameter distribution of our sample, resonance will occur with optical transitions E_{22}^S, E_{11}^M, and E_{33}^S (see inset to Fig. 3), corresponding to SWNTs with d_t in the interval $0.95 < d_t < 1.20$ nm for E_{22}^S, $1.45 < d_t < 1.85$ nm for E_{11}^M, and $2.00 < d_t < 2.50$ nm for E_{33}^S. The ω_D values we observed for 14 different semiconducting SWNTs range from 1280 to 1299 cm^{-1}, but the distribution is not random, and exhibits a tendency to be dispersed in two blocks of ω_D values centered at 1285 and 1295 cm^{-1}. In Fig. 3 we tentatively plot ω_D vs $1/d_t$. The vertical lines in the inset to Fig. 3 define the diameter ranges where isolated SWNTs can be resonant with $E_{\text{laser}}=1.58$ eV, and the observed dispersion in ω_D for the different SWNTs is indicated in the main figure by the arrows. We can define an average linear extrapolation of ω_D going to ~ 1313 cm^{-1} for $d_t \rightarrow \infty$, corresponding to the ω_D value for disordered sp^2 carbons at $E_{\text{laser}}=1.58$ eV.[3] However, from Fig. 3 we see that at $E_{\text{laser}}=1.58$ eV, metallic SWNTs with the same d_t values as semiconducting SWNTs have ω_D values higher by (10 ± 3) cm^{-1}, suggesting a different slope for the ω_D vs d_t dependence between metallic and semiconducting SWNTs. The mechanism for the upshift of ω_D for metallic nanotubes relative to semiconducting tubes is not yet clear.

Comparing the behavior of the *D* band for isolated semiconducting and metallic SWNTs, we find, as described above, that ω_D depends on d_t in both cases. This d_t dependence, superimposed on the general $\overline{\omega_D}=\omega_0+53E_{\text{laser}}$ linear dependence, might explain the plateau reported for the E_{laser} dependence of $\overline{\omega_D}$ of SWNT bundles[8,9] in the range of E_{laser} spanning the E_{11}^M band (see inset to Fig. 3). Figure 3 indicates that an increase in E_{laser} would bring SWNTs with a decreasing diameter in resonance with a given electronic transition E_{ii}. Thus, as E_{laser} passes through each band of electronic transitions (such as E_{11}^M), there is an *increase* in ω_D due to the general ω_D dispersive behavior (also found in sp^2 carbons[5]) and also a superimposed *decrease* in ω_D, since smaller SWNTs become resonant within each of the E_{ii} bands as E_{laser} increases. Thus, the average $\overline{\omega_D}$ over all SWNTs within the diameter distribution that are resonant within the E_{11}^M band shows a much smaller dispersion than for sp^2 carbons over the E_{11}^M energy width (see inset to Fig. 3). Note that the expected $\overline{\omega_D}$ range for bundles when E_{laser} passes through the E_{11}^M resonance conditions[8] is ~ 10 cm^{-1}, which is about the same magnitude as the changes we observed due to the diameter dependence of ω_D at constant E_{laser} and to the ω_D difference between metallic vs semiconducting SWNTs of the same d_t (see Fig. 3). Therefore, this kind of the linear oscillatory behavior observed in the $\overline{\omega_D}(E_{\text{laser}})$ dependence for SWNT bundles is expected to occur for all resonances with interband transitions E_{ii}, as observed recently by Grueneis *et al.*[10] Notice that a similar type of oscillatory behavior has been previously reported by Milnera *et al.*[14] also for the radial breathing mode resonance Raman phenomena.

It was also previously reported that, for SWNT bundles, the *D*-band intensity is larger for metallic SWNTs than for semiconducting SWNTs.[8,9] We have measured the *D*-band feature on more than 30 different isolated SWNTs, and for these tubes, the *D*-band intensity appears to be random from one nanotube to another. We also measured isolated SWNT spectra for which the intensities I_{RBM}, I_G, and $I_{G'}$ were quite strong, but where I_D was extremely weak or absent. Therefore, our measurements on isolated SWNTs do not account for the high *D*-band intensity observed for metallic SWNTs in bundles.[8,9] Our results suggest that the *D*-band intensity depends on random characteristics, such as defects in the nanotube lattice or the finite size of the nanotubes, and that the large intensity observed for bundles is due to a better resonance condition for metallic SWNTs, considering the laser energies that were used and the SWNT diameter distribution of the samples.[8,9] However, for isolated SWNTs, I_D

obtained with $E_{laser}=2.41$ eV is generally weaker than that at $E_{laser}=1.58$ eV, as is also observed for SWNT bundles.[9]

In summary, the observation of the *D*-band feature for *isolated* single-wall carbon nanotubes implies resonance with the one-dimensional van Hove singularities in the density of electronic states. We show here that, using the same E_{laser}, different isolated SWNTs exhibit different ω_D values, around the average $\overline{\omega_D}$ for SWNT bundles. This result is interpreted in terms of a d_t dependence of ω_D in isolated SWNTs. As d_t increases, ω_D for SWNTs increases and extrapolates to ω_D for sp^2 carbons in the limit of $d_t \rightarrow \infty$. At constant d_t, ω_D is higher for metallic than for semiconducting SWNTs. The E_{laser} dependence of ω_D for isolated SWNTs follows the same general trend as is observed for all sp^2 carbon materials, that is, the average value of ω_D increases with increasing E_{laser}. This $\omega_D(E_{laser})$ dependence for isolated SWNTs suggests that the associated phonons are not at the center of the 1D Brillouin zone of SWNTs, and each different E_{laser} probes phonons with different wave vectors within the interior of the 1D BZ of SWNTs, similarly to sp^2 carbons.[3–5] These phonons become Raman active due to the finite size of the SWNTs or to the presence of defects, which break the translational symmetry along the nanotube axis, explaining the fact that the *D*-band intensity I_D appears to be random from one nanotube to another. Finally, we argue that the anomalous $\overline{\omega_D}(E_{laser})$ plateau behavior observed for SWNT bundles might be explained by considering the diameter dependence of ω_D for isolated SWNTs and the resonant nature of the Raman process.

We acknowledge the NSF/CNPq joint collaboration program that makes possible exchange trips between MIT and UFMG researchers (Grant No. NSF INT 00-00408 and CNPq Grant No. 910120/99-4). This research utilized MRSEC Shared Facilities supported by the National Science Foundation under Grant No. DMR-9400334 and NSF Laser Facility grant 9708265-CHE. Also A.J. and A.G.S.F., respectively, acknowledge financial support from CNPq-Brazil, and CAPES-Brazil, while R.S. acknowledges a Grant-in-Aid (No. 11165216) from the Ministry of Education, Japan. MIT authors acknowledge Grant No. NSF DMR 98-04734 and Grant No. INT 98-15744.

[1] F. Tuinstra and J.L. Koenig, J. Chem. Phys. **53**, 1126 (1970).

[2] A.V. Baranov, A.N. Bekhterev, Y.S. Bobovich, and V.I. Petrov, Opt. Spectrosc. **62**, 612 (1987).

[3] M.J. Matthews, M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, and M. Endo, Phys. Rev. B **59**, R6585 (1999).

[4] I. Pocsik, M. Hundhausen, M. Koos, and L. Ley, J. Non-Cryst. Solids **227-230B**, 1083 (1998).

[5] C. Thomsen and S. Reich, Phys. Rev. Lett. **85**, 5214 (2000).

[6] R. Saito, G. Dresselhaus, and M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).

[7] A. Kasuya, Y. Sasaki, Y. Saito, K. Tohji, and Y. Nishina, Phys. Rev. Lett. **78**, 4434 (1997).

[8] M.A. Pimenta, E.B. Hanlon, A. Marucci, P. Corio, S.D.M. Brown, S.A. Empedocles, M.G. Bawendi, G. Dresselhaus, and M.S. Dresselhaus, Braz. J. Phys. **30**, 423 (2000).

[9] S.D.M. Brown, A. Jorio, G. Dresselhaus, and M.S. Dresselhaus (unpublished).

[10] A. Grueneis, M. Hulman, Ch. Kramberger, T. Pichler, H. Peterlik, H. Kuzmany, H. Kataura, and Y. Achiba, in the *Proceedings of the International Winter School on Electronic Properties of Novel Materials—2001*, edited by H. Kuzmany, M. Mehring, and J. Fink (American Institute of Physics, Melville, New York, in press).

[11] A. Jorio, A.G. Souza Filho, G. Dresselhaus, M.S. Dresselhaus, R. Saito, J. Hafner, C.M. Lieber, F.M. Matinaga, M.S.S. Dantas, and M.A. Pimenta, Phys. Rev. B (to be published, 2001).

[12] A. Jorio, R. Saito, J.H. Hafner, C.M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, and M.S. Dresselhaus, Phys. Rev. Lett. **86**, 1118 (2001).

[13] M.A. Pimenta, A. Marucci, S. Empedocles, M. Bawendi, E.B. Hanlon, A.M. Rao, P.C. Eklund, R.E. Smalley, G. Dresselhaus, and M.S. Dresselhaus, Phys. Rev. B **58**, R16 016 (1998).

[14] M. Milnera, J. Kurti, M. Hulman, and H. Kuzmany, Phys. Rev. Lett. **84**, 1324 (2000).