Single- and double-resonance Raman \( G \)-band processes in carbon nanotubes


1Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, MG, 30123-970 Brazil
2Department of Physics, Tohoku University and CREST JST, Sendai 980-8578, Japan
3Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel
4Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307, USA
5Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307, USA
6Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307, USA

(Received 2 February 2004; revised manuscript received 3 May 2004; published 23 June 2004)

This work reports Raman spectroscopy measurements from single wall carbon nanotubes (SWNTs) addressing the nature of the \( G \)-band resonance Raman spectra. Experimental results on different samples are presented, i.e., aligned and misaligned SWNT samples, as well as isolated and bundled SWNTs. It is shown that the Raman spectra from nondefective SWNTs, both isolated and bundled, are composed of strong first-order single resonance Raman features. Defective materials, however, are found to exhibit lower intensity spectra with contributions from both single resonance and defect-induced double resonance features.

DOI: 10.1103/PhysRevB.69.241403 PACS number(s): 78.30.Na, 78.20.Bh, 78.66.Tr, 63.22.+m

Raman spectroscopy is one of the most powerful techniques for studying carbon nanotubes.\(^1\)\textsuperscript{-3} The so-called \( G \)-band, appearing in the frequency range from 1520 to 1630 cm\(^{-1}\) (roughly centered at the 1582 cm\(^{-1}\) graphite frequency), contains multiple components and gives a clear spectroscopic signature of carbon nanotubes. The frequencies of the various \( G \)-band peaks exhibit a clear and well-established dependence on diameter \((d_i)\), as well as a dependence on whether the nanotube is metallic or semiconducting.\(^1\)\textsuperscript{-4} Even though the \( G \)-band Raman modes have been widely used for many years for the study and characterization of carbon nanotube samples, the nature of the scattering process for the \( G \)-band in nanotubes is still under debate.

The debate concerns whether the Raman signal from the \( G \)-band in SWNTs originates from a single-resonance first-order Raman process (light absorption, \( q=0 \) phonon emission/absorption, light emission)\(^1\)\textsuperscript{-3,5,6}\) or from a defect-induced double resonance Raman process (light absorption, \( q \neq 0 \) phonon emission/absorption, scattering by a defect, light emission).\(^6\)\textsuperscript{-8} This simple and fundamental issue is of major importance for the physics of carbon nanotubes. There are several SWNT Raman features that are well established as defect-induced double resonance features, e.g., the \( D \) band,\(^1\)\textsuperscript{-3} the acoustic modes and the \( D^* \) band (\( \sim 1620 \) cm\(^{-1}\)),\(^9\) and these features can only be observed in the presence of defects. The question then arises, whether or not they are strong \( G \)-band Raman spectrum from a nondefective carbon nanotube? Would the radial breathing mode (RBM) feature, largely used for SWNT diameter characterization,\(^1\)\textsuperscript{-3} then also be connected to defect-induced double resonance processes?\(^10\) Answering these questions is important, since their answers have a strong influence on how Raman spectroscopy can be used to characterize SWNTs. Answering these questions is the goal of this paper that provides a consistent picture to explain present and previous experimental results concerning this debate.

Micro-Raman spectra were recorded in a backscattering configuration using both single and triple monochromators, equipped with cooled charge coupled devices (CCDs), by using different excitation laser lines. The spectra were recorded from different samples: (i) a fiber of an aligned SWNT bundle,\(^11\) with an overall diameter of \( \sim 1 \) mm size and the nanotubes in the sample \((d_i=1.3\pm0.2 \) nm\) exhibiting exceptionally good alignment along the fiber axis (better than \( \pm 5^\circ \));\(^12\) (ii) isolated nanotubes on a Si/SiO\(_2\) substrate with a random orientation,\(^13\) low tube density, and a diameter range \( 1<d_i<2 \) nm; (iii) isolated nanotubes on a sapphire substrate prepared so that the SWNTs are all aligned, and with a diameter range \( 0.7<d_i<1.7 \) nm.\(^14\) The Raman spectra are fit using a sum of Lorentzian peaks. For isolated SWNT measurements, atomic force microscopy (AFM) imaging of some samples was carried out to locate isolated SWNTs that could be further measured with resonance Raman spectroscopy. The AFM measurements were made with a Nanoscope IV MultiMode SPM from Veeco Instruments operating in the intermittent contact (Tapping) mode, using standard Si probes.

Figure 1 shows the \( G \)-band Raman spectra obtained from a SWNT fiber at two different locations, as shown in the inset to the upper panel. The upper spectrum comes from location 1, at the center of the fiber, and it has been acquired with both incident and scattered light polarized along the fiber axis, i.e., the (ZZ) configuration. At this location, the cross-polarized (XX) spectra are \( \sim 120 \) times less intense than the (ZZ) spectra, due to the antenna effect,\(^1\)\textsuperscript{-3} indicating an excellent degree of alignment for the SWNT bundles. The (ZZ) spectra can be fit using two sharp Lorentzians (11 cm\(^{-1}\) FWHM) located at \( \omega_G=1564 \) cm\(^{-1}\) and \( \omega_G=1593 \) cm\(^{-1}\), while the (XX) spectra, although less intense, clearly exhibit
FIG. 1. (Color online) G-band resonance Raman spectrum from a fiber of aligned SWNT bundles ($E_{\text{laser}} = 2.71$ eV). The inset to the upper panel shows an optical image of the sample. The spectrum in the upper panel was taken from location 1 (see upper inset) with the (ZZ) polarization scattering geometry, and the spectrum in the lower panel was acquired from location 2. The inset to the lower panel shows the $E_{\text{laser}}$ dependence of the two peaks indicated by arrows. The solid curves in this inset are predictions for the $E_{\text{laser}}$ dependence of the G-band double resonance features (Refs. 6 and 7).

Contributions from the $E_2$ symmetry features, as previously discussed,1–3,15 the well-known disorder-induced D-band is almost absent, the integrated D-band area being ∼35 times smaller than the integrated area of the G-band Lorentzian peaks.

The lower panel of Fig. 1 shows the G-band spectrum from location 2, which is at the edge of the same fiber, where misalignment and defects (structural and impurities) are expected. The G-band intensity is much lower in location 2, about 35 times less intense than in location 1. Many peaks are observed in the spectrum at location 2, clearly different from the spectrum at location 1. Eight Lorentzian peaks are used for fitting the spectra at location 2. Four lower frequency $G^-$ peaks can be clearly distinguished in the spectrum. Four upper frequencies $G^+$ peaks were used, since it is expected that the same number of $G^+$ and $G^-$ peaks will be related independently to the LO and to the TO branches of 2D graphite, respectively, on the basis of the model (either single or double resonance) used to explain the multipeak feature.1–3,7 The integrated area for the D-band in location 2 is only 3 times smaller than in location 1, the D-band in location 2 being relatively much more intense than in location 1 when compared with the G-band intensity. The Lorentzian peaks used to fit the D and G bands in location 2 exhibit similar integrated areas.

Figure 2 shows similar spectra to those shown in Fig. 1, but taken with different $E_{\text{laser}}$ lines. The left panels come from location 1 and exhibit no significant dependence on $E_{\text{laser}}$. The right panels come from location 2, and interestingly, some of the peaks are dispersive, while some are not.

FIG. 2. The left panels show the G-band Raman spectra in the (ZZ) polarization geometry at location 1 [see inset in Fig. 1(a)], using four different laser energies, as displayed in the figure. The right panels show the spectra measured with the same laser energies in location 2 of the sample. The peak frequencies are displayed in cm$^{-1}$.

For example, the dark gray peak does not change frequency when $E_{\text{laser}}$ is changed, while the light gray peak down-shifts with increasing $E_{\text{laser}}$. The $E_{\text{laser}}$ dependence for these two gray colored peaks is shown in the lower inset to Fig. 1 (points) together with predictions from the double resonance model (lines).6,7

Based on the experimental results in Figs. 1 and 2, the assignment of the scattering nature for the G-band peaks can be discussed. The (ZZ) spectrum obtained in location 1, the region of aligned defect-free SWNTs in the SWNT fiber (see Fig. 1), exhibits two sharp peaks. This result is in agreement with group theory predictions for first-order Raman scattering using this scattering configuration, where only two A symmetry modes are expected to be Raman active.1–3,15 Considering the average tube diameter of $d_t = 1.3$ nm, the G-band Lorentzian frequencies (1565 and 1593 cm$^{-1}$) are also in agreement with the expected results for the A modes in carbon nanotubes.1–3,5 Furthermore, these features are not $E_{\text{laser}}$ dispersive (see left panels of Fig. 2). Therefore, they are assigned as first-order single resonance Raman features.

The spectra obtained in location 2, where defects and misalignment are expected, clearly show results that cannot be explained by only considering first-order Raman modes, even considering that the G-band is composed of 6 peaks and contribution from different SWNTs within the bundles. Eight peaks are observed, some of the peaks are dispersive, while some of the peaks are not dispersive, as shown in the lower inset to Fig. 1 and in Fig. 2. These spectra can be explained as composed of both first-order single resonance Raman peaks and defect-induced double resonance features.

Considering electronic transitions occurring at $E_{\text{laser}}$
2.34 eV up to 2.71 eV. The frequency behavior of the light
resonance features. However, the dispersion of these data cannot
be described by that predicted by the double resonance
model, because the dispersion of the TO phonon branch. The
dispersion of the TO phonon branch in 2D graphite is small when compared with
the dispersion of the LO phonon branch. The G+ feature was
fit using four Lorentzians for consistency with G+. These
data show a tendency to upshift as \( E_{\text{laser}} \) is increased, consist-
tent with a contribution to the G+ feature from double reso-
ance features. However, the dispersion of these data cannot
be described by that predicted by the double resonance
model, because the G+ feature has unresolved contributions
from both single and double resonance processes.

From the arguments developed here, the analysis of the
\( E_{\text{laser}} \) dependence of the G-band feature from defective mate-
rials requires both single and double resonance contribu-
tions to achieve a consistent fit. This result explains why
previously published work did not show the correct disper-
sion for the double resonance feature.7 By considering the
G-band spectra from defective SWNTs to originate only
from double resonance processes, no detailed analysis could
be carried out.

It is important also to discuss results on isolated SWNT
samples. Figure 3 shows data for \( \omega_G \) (a), \( \omega_{G'\pm} \) and \( \omega_{G''\pm} \) (b) as a function of \( E_{\text{laser}} \) for 11 different spot positions, i.e., 11
different isolated SWNTs, six isolated SWNTs on top of a
sapphire substrate (open symbols), and 5 SWNTs on top of a
Si/SiO2 substrate (filled symbols), plus one set of data (stars)
from Ref. 8. Each set of points connected by lines comes from
one individual different SWNT.

The solid line in Fig. 3(a) represents the prediction from
the double resonance model for the D-band \( \omega_D \). The solid line was downshifted to fit the
experimental results according to Ref. 18.

In conclusion, a consistent picture that explains present
and previously reported results for the scattering nature of

\( \approx 2.41 \) eV, the difference between the single and double reso-
nance frequencies are estimated to be about 8 cm\(^{-1}\) for \( E_1 \)
symmetry phonons, and 4 cm\(^{-1}\) for \( E_2 \) symmetry phonons.\(^6\)\(^7\)

Therefore, the G− peaks observed in the spectra from loca-
tion 2, and shown in Figs. 1 and 2, are assigned as follows:
the peak at 1569 cm\(^{-1}\) is assigned to a \( E_1 \) single resonance
process; the peak at \( \approx 1562 \) cm\(^{-1}\) to a double resonance pro-
cess; these peaks are separated by 7 cm\(^{-1}\) for \( E_{\text{laser}} \)
=2.41 eV, in agreement with the estimated 8 cm\(^{-1}\). The peak
at \( \approx 1546 \) cm\(^{-1}\) is assigned to unresolved double and single
resonance \( E_2 \) symmetry modes. Finally, using the zone fold-
ing picture, the \( \approx 20 \) cm\(^{-1}\) splitting between the 1548 cm\(^{-1}\)
and the 1525 cm\(^{-1}\) features agrees with the frequency splitting
expected for the \( E_2 \) and \( E_3 \) symmetry modes. In this
case, the 1525 cm\(^{-1}\) feature can be assigned to an \( E_3 \) sym-
metry disorder-induced peak.\(^6\)\(^7\)

With increasing laser energy, the splitting between the
single and double resonance features is expected to increase.\(^6\)
This behavior is clearly observed for the two G− features
shown in Fig. 2 by gray colored Lorentzians. The upper fre-
cency first-order single resonance feature always appears at
1569 cm\(^{-1}\), in agreement with previous experimental\(^5\)
and theoretical\(^1\) results for the \( E_3 \) symmetry mode. The light
grey peak (assigned as a double resonance feature) down-
shifts from 1565 to 1558 cm\(^{-1}\) when \( E_{\text{laser}} \) is increased from
2.34 eV up to 2.71 eV. The frequency behavior of the light
grey peak exhibits the dispersive behavior expected for a
double resonance feature, considering the results to be an
average over contributions from many different nanotubes
within the bundle.\(^6\)\(^7\)

A small dispersive behavior has also been observed for the
\( E_2 \) and \( E_3 \) peaks. These small dispersive behaviors could
be consistently fit by using one nondispersive peak, and one
dispersive peak obeying the double resonance prediction.
However, as discussed above, the two features are too close
in frequency and they cannot be clearly distinguished in the
experimental spectra.

A fitting analysis for the high frequency upper G+ feature
is hard to make, since the peaks all overlap with each other.
This overlap of several features can be understood for both
single and double resonance features based on a zone folding
picture, since close to the I point the dispersion of the LO
phonon branch in 2D graphite is small when compared with
the dispersion of the TO phonon branch. The G+ feature was
fit using four Lorentzians for consistency with G+. These
data show a tendency to upshift as \( E_{\text{laser}} \) is increased, consist-
tent with a contribution to the G+ feature from double reso-
ance features. However, the dispersion of these data cannot
be described by that predicted by the double resonance
model, because the G+ feature has unresolved contributions
from both single and double resonance processes.

From the arguments developed here, the analysis of the
\( E_{\text{laser}} \) dependence of the G-band feature from defective mate-
rials requires both single and double resonance contribu-
tions to achieve a consistent fit. This result explains why
previously published work did not show the correct disper-
sion for the double resonance feature.\(^7\) By considering the
G-band spectra from defective SWNTs to originate only
from double resonance processes, no detailed analysis could
be carried out.
the G-band of SWNTs is presented. Basically, the G-band in defect-free aligned SWNTs originates from single resonance processes, thus implying that the knowledge developed from the first-order single resonance G-band Raman spectra can be used for the characterization of high quality samples. The G-band in defective SWNT samples, however, can exhibit different peaks, originating from both single and double resonance processes, and they have been assigned here for SWNT bundles. Both single resonance and double resonance features are found to exhibit contributions of similar intensity to the spectra of defective materials, the extra resonance in the double resonance process allowing observation of an effect one order higher in perturbation theory. Therefore, a complete analysis involving both single and double resonance features must be developed to understand their G-band spectra. Interestingly, it turns out that the averaged results from SWNT bundles deliver illuminating messages leading to a clearer answer for the importance of the single and double resonance nature of the G-band scattering processes in SWNTs, while in the case of isolated SWNTs, much care must be taken in the analysis, since different single resonance conditions select different symmetry modes and different defects could lead to a different double resonance spectrum.

Finally, it is important to comment that for the RBM feature, no significant $E_{\text{laser}}$ dependence or differences between RBM spectra from locations 1 and 2 at the SWNT fiber have been observed. Up to now there is no evidence for a double resonance behavior for the RBM feature in the literature, neither from bundles nor from isolated SWNTs. The questions raised at the beginning of this text can be answered: A perfect carbon nanotube should exhibit strong first-order single resonance G-band and RBM features.

The authors acknowledge Professors J. H. Hafner and C. M. Lieber for the SWNTs on Si/SiO$_2$ samples, and Professor K. I. Winie and R. Haggenmueller for SWNT/poly(methylmethacrylate) composite fibers. The authors also acknowledge Professor A. G. Rinzler for kindly providing his SWNT samples. Work supported by the CNPq/NSF program (NSF INT 00-00408 and CNPq 910120/99-4) and Instituto de Nanociências, Brazil. A.J. has financial support from PRPq-UFMG. The MIT authors acknowledge support under NSF DMR 01-16042. R.S. acknowledges a Grant-in-Aid (No. 33440091) from the Ministry of Education, Japan. M. Lieber for the SWNT samples. Work supported by the CNPq/NSF program (NSF INT 00-00408 and CNPq 910120/99-4) and Instituto de Nanociências, Brazil. A.J. has financial support from PRPq-UFMG. The MIT authors acknowledge support under NSF DMR 01-16042. R.S. acknowledges a Grant-in-Aid (No. 33440091) from the Ministry of Education, Japan. E.J., A.I., and G.D. acknowledge support from the U.S.-Israel Binational Science Foundation (Grant No. 2000218).

16 It is important to stress that the symmetry identifications become less clear for higher order defect-induced scattering processes. However, the use of cutting lines and cutting line indices [see, Ge. G. Samsonidze, R. Saito, A. Jorio, M. A. Pimenta, A. G. Souza Filho, F. A. Grüneis, G. Dresselhaus, and M. S. Dresselhaus, J. Nanosci. Nanotechnol. 3, 431 (2003)] simplifies the symmetry identification in the different scattering processes.