

**Resonant Raman spectroscopy of single-wall carbon nanotubes under pressure**

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We performed high pressure resonant Raman experiments on well characterized purified single-wall carbon nanotubes up to 40 GPa using argon as pressure transmitting medium. We used two different exciting wavelengths, at 632.8 nm and 514.5 nm. In contrast with other studies no clear sign of phase transformation is observed up to the highest studied pressure of 40 GPa. Our results suggest that the progressive disappearance of the radial breathing modes observed while increasing pressure should not be interpreted as the sign of a structural phase transition. Moreover, a progressive change of profile of the tangential modes is observed. For pressures higher than 20 GPa the profile of those modes is the same for both laser excitations. We conclude that a progressive loss of resonance of single-wall carbon nanotubes under pressure might occur. In addition, after high pressure cycle we observed a decrease of intensity of the radial breathing and tangential modes and a strong increase of the *D* band.

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**I. INTRODUCTION**

Among all the elements carbon is certainly one of the most fascinating as it can exhibit different structures such as diamond, graphite, fullerenes or nanotubes. Diamond is an electrical insulator and is up to now the hardest material known. Its specific properties are due to the  $sp^3$  character of carbon bonds. Graphite corresponds to a  $sp^2$  hybridization state and is a semimetal. Carbon fullerenes and nanotubes have extremely interesting properties in view of technological applications and are considered as serious candidates for the future development of nanotechnology.

The electronic properties of single wall carbon nanotubes (SWNT) strongly depend on their geometrical features. They are governed by their chirality  $(n, m)$  which describe the rolling direction of the graphene plane with respect to the graphite lattice. Different chiralities can correspond to tubes having almost the same diameter but different electronic properties, one part being semiconductor and the other one metallic. It has been theoretically demonstrated that when  $(n-m)/3$  equals an integer, the considered tube is metallic.<sup>1</sup> Otherwise, for any other choice of chirality, it is a semiconductor. As a consequence, in a standard preparation of SWNT, both semiconductor and metallic tubes are present. Due to the one dimensional character of SWNT, their electronic density of states exhibit several peaks corresponding to *van Hove singularities* that play an extremely important role in optical scattered spectroscopy. In particular, in Raman spectroscopy, the matching between the exciting (scattered)

energy and allowed transitions between two van Hove singularities gives rise to a strong resonant effect. For a diameter centered around 1.3 nm the semiconducting tubes are resonant for a laser excitation at 514.5 nm, and the metallic tubes are resonant at 632.8 nm.<sup>2</sup> The resonant character of the Raman scattering makes of this technique a privileged tool for the study of SWNT,<sup>3</sup> in particular under high pressure conditions.

SWNT are expected to stand up, through pressure application, strong geometrical changes that preserve their nanostructured character. This has motivated an important number of experimental<sup>4-15</sup> and theoretical works.<sup>16-23</sup> Based on changes observed in the Raman spectrum under pressure some authors have concluded to a phase transition at low pressure, around 2 GPa.<sup>4,7,24</sup> Nevertheless this transition was not confirmed by other studies, especially by x-ray diffraction.<sup>12,14,15</sup> Another phase transition was also observed around 10 GPa.<sup>6,12</sup>

In order to light these questions we have measured the behavior under hydrostatic pressure (from ambient to 40 GPa) of the Raman responses of semiconducting and metallic SWNT. The changes under pressure of the lineshape of the radial breathing modes (RBM) and tangential modes (TM) are analyzed in details. A progressive disappearance of the RBM under pressure is found. For pressures higher than 20 GPa the line shapes of the TM of the semiconducting and metallic SWNT are similar. These results are discussed in the framework of different assumptions.

II. EXPERIMENTS

Highly bundled purified SWNT sample was provided by MER corporation (Arizona). Sample characterizations by TEM, x-ray and neutron diffraction reveal a high degree of purity and homogeneity, and a size of bundles around 50 tubes.<sup>25</sup> The diameter distribution is centered around 1.3 nm, with a full width of 0.2 nm. A fit of the bare SWNT diffraction peaks yields a distance between two adjacent nanotubes in a bundle of  $17 \pm 1$  Å. Due to the purification process those tubes have many defects and are opened. It has been recently shown on this same sample that argon atoms enter the interstitial sites inside the bundles and also the inner cavity of the tubes.<sup>26</sup>

The samples were loaded in a gasketed diamond anvil cell (anvils of 350 μm culet diameter) using argon as pressure transmitting medium. This pressure transmitting medium ensures quasihydrostatic conditions on the sample. The R1-line emission of a tiny ruby chip was used for pressure calibration. Raman scattering experiments were carried out at 300 K using a Jobin-Yvon HR-800 Labram spectrometer with double-notch filtering and air cooled CCD detector. Less than 5 mW of the 514.5 nm (2.41 eV) radiation from an argon-ion laser, and of the 632.8 nm (1.96 eV) radiation from an helium-neon laser, was focused to a spot size of approximately 2 μm on the sample inside the high-pressure cell.

Raman spectra excited at 514.5 nm or 632.8 nm were recorded in a first series of experiments named *experiment A*. In these experiments, pressure was increased in steps of 1 or 2 GPa from ambient pressure to 40 GPa. In a second series of experiments named *experiment B*, the Raman response was alternatively recorded using the 514.5 nm and 632.8 nm excitations at each pressure step. This procedure ensures that Raman spectra were recorded for both excitations wavelengths in the same pressure conditions. In addition, special care was taken to maintain the same position of the laser spot on the sample. Pressure was increased in steps of 5 GPa and the maximum reached pressure was 31 GPa.

III. RESULTS

The Raman spectra at ambient pressure of this sample is shown in Fig. 1. With regards to the resonance conditions, and for the tubes under consideration (diameter around 1.3 nm±0.2 nm), the Raman response measured at 514.5 nm is typical of semiconducting tubes whereas the 632.8 nm response features metallic tubes, with the observation of a Breit Wigner Fano (BWF) component in the TM range which proves that the metallic tubes are organized in bundles.<sup>27</sup>

In Fig. 2 is reported the evolution under pressure of the most intense RBM peak recorded during the experiment A. At ambient pressure this peak is at 195 cm<sup>-1</sup> for the metallic tubes and at 185 cm<sup>-1</sup> for the semiconducting tubes. As the frequency of RBM is directly proportional to the inverse of tube diameter for bundled nanotubes,<sup>28</sup> we can estimate that the diameter difference between the associated semiconducting and metallic nanotubes is less than 0.1 nm.

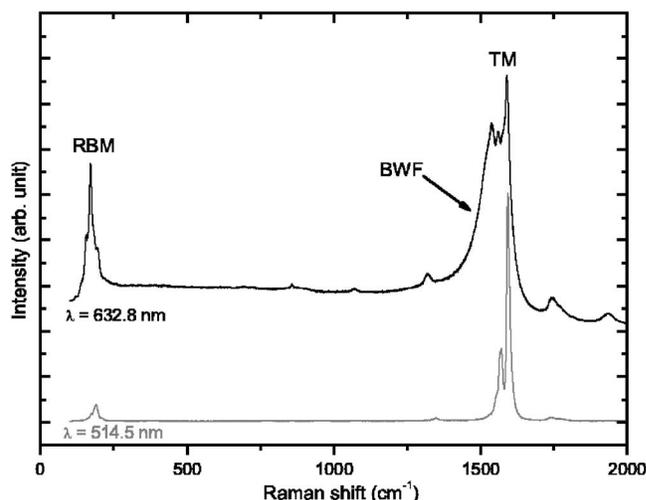


FIG. 1. Raman spectra of SWNT at ambient pressure recorded using two different laser excitation (632.8 nm top and 514.5 nm bottom). The Breit Wigner Fano component (BWF) is pointed out. No pressure transmitting medium was used to record those spectra.

Under pressure we observe (i) the shift towards higher frequency, (ii) the broadening of the peaks, and (iii) the dramatic decrease of the RBM intensity. The more striking result is that the RBM signal vanishes around 5 GPa with the green laser excitation while it disappears around 10 GPa with the red one. This result suggests a different pressure sensitivity between the semiconducting and the metallic tubes, that, as will be discussed later, must be of electronic origin. To ensure that this behavior does not result from differences in the experimental pressure conditions, we have performed another experiment for which at each step of pressure the Raman spectra are measured using both excitation

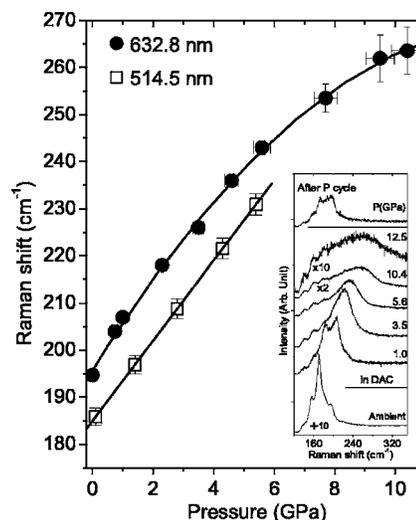


FIG. 2. Pressure dependence of the most intense component of the radial breathing modes (RBM) of SWNT for a laser excitation of 514.5 nm (squares) and 632.8 nm (circles) up to the signal disappearance (experiment A). The right inset shows the spectra of the RBM at different pressures for a laser excitation of 632.8 nm. The two ambient pressure spectra were taken outside the diamond anvil cell.

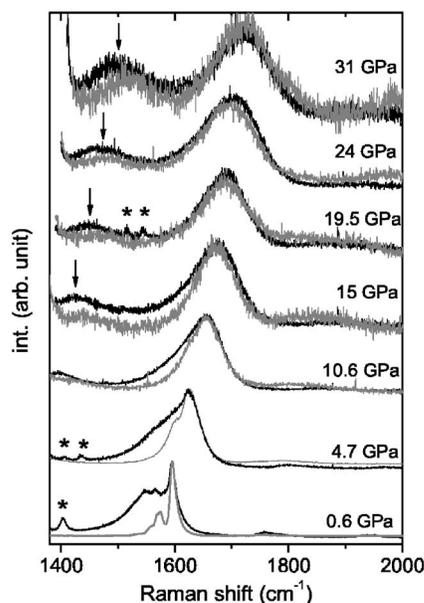


FIG. 3. Tangential modes Raman spectra as a function of pressure for both laser excitations: 514.5 nm in gray and 632.8 nm in black (experiment A). All the spectra are normalized. The stars indicate the presence of the ruby fluorescence. The peak visible at  $1400\text{ cm}^{-1}$  at the higher pressures comes from the stressed diamond of the diamond anvil cell. The new band for pressures higher than 15 GPa is pointed out.

wavelengths (experiment B). The larger pressure step in the experiment B with respect to the experiment A does not allow to display the precise dependence of the RBM frequency with pressure. Nevertheless, the result of the experiment A, namely the vanishing of the RBM at a lower pressure (around 5 GPa) in the Raman experiment using the 514.5 nm incident wavelength than in the one using the 632.8 nm incident wavelength (around 10 GPa) is confirmed.

In the experiment B we focus on the pressure dependence of the TM that we discuss first. The observed behavior under pressure of the TM part of the Raman spectrum is displayed in Fig. 3. When the pressure increases from the ambient pressure to 31 GPa, we observe a progressive shift towards higher frequency of the TM likely related to the hardening of carbon-carbon interactions. A progressive loss of intensity and a broadening of the modes are also observed. Below 10 GPa the profiles of TM measured using green and red excitations respectively are different. Around 10 GPa the BWF component is still clearly present but its relative intensity has considerably decreased. Above 20 GPa the BWF component vanishes, and the profile of TM are similar for both laser excitations. It must be pointed out that TM are still present at 31 GPa for both excitations even if their intensities are significantly weaker than at ambient pressure. In the high pressure range, the profile of the TM is more or less symmetric and it can be fitted by a single Lorentzian component.

For pressures higher than 15 GPa a broad component, that we assign to the D band, appears in the experimental window. The shift of this band under pressure is  $5.5 \pm 0.5\text{ cm}^{-1}/\text{GPa}$  leading to an extrapolated position at ambient pressure of  $1330 \pm 10\text{ cm}^{-1}$  ( $1350 \pm 10\text{ cm}^{-1}$ ) for the

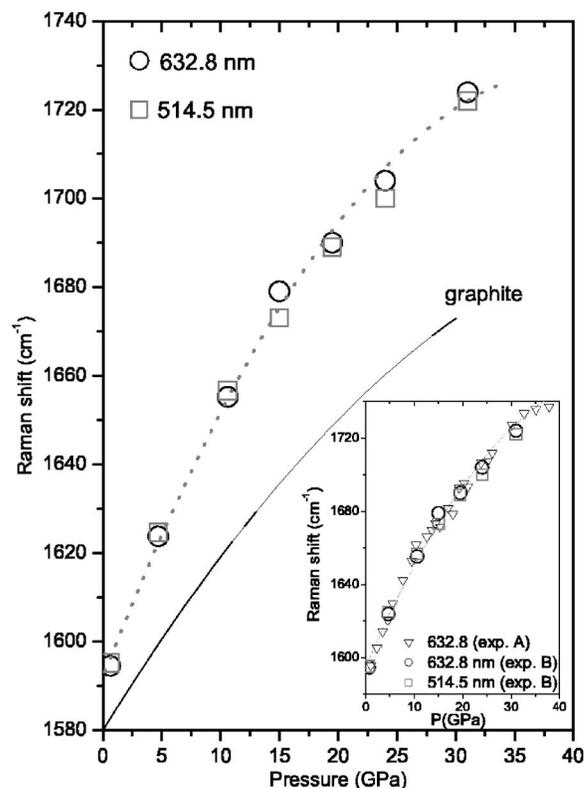


FIG. 4. Pressure dependence of the most intense tangential mode (TM) of SWNT for laser excitations of 632.8 nm and 514.5 nm (experiment A). The continuous line is the Raman data from graphite from Ref. 30. The inset corresponds to the experiments A and B.

red (green) laser excitation in agreement with the ambient pressure frequency of the D band in SWNT (Fig. 1). The progressive increase of the D band intensity is likely the signature of an increase of disorder in the structure of SWNT under pressure. It must be noticed that at the maximum pressure reached (31 GPa) the position of this band appears to differ between both laser excitations, as observed for the D band at ambient pressure in carbon nanotubes (Fig. 1) or graphite.<sup>29</sup> This feature is explained by a double resonant process. Our results could suggest that this second order resonant mechanism of the D band is preserved under pressure.

In Fig. 4 is reported the position of the most intense peak of the TM band as a function of pressure and for both laser excitations measured in the experiment B. As the profile of the modes strongly depends on pressure, it is extremely difficult to properly determine the exact number of peaks necessary to fit each Raman response. We have tried to perform a precise decomposition of the TM band at the different pressures using several Lorentzian components, plus one BWF contribution in the spectrum excited at 632.8 nm. Our conclusion is that this approach gives rise to inconsistent results that strongly depend on the number of components when we try to follow the behavior of the different modes with pressure. This appears to be a consequence both of the extreme broadening of the peaks and evolution of their relative intensities under pressure. Consequently the unique feature that

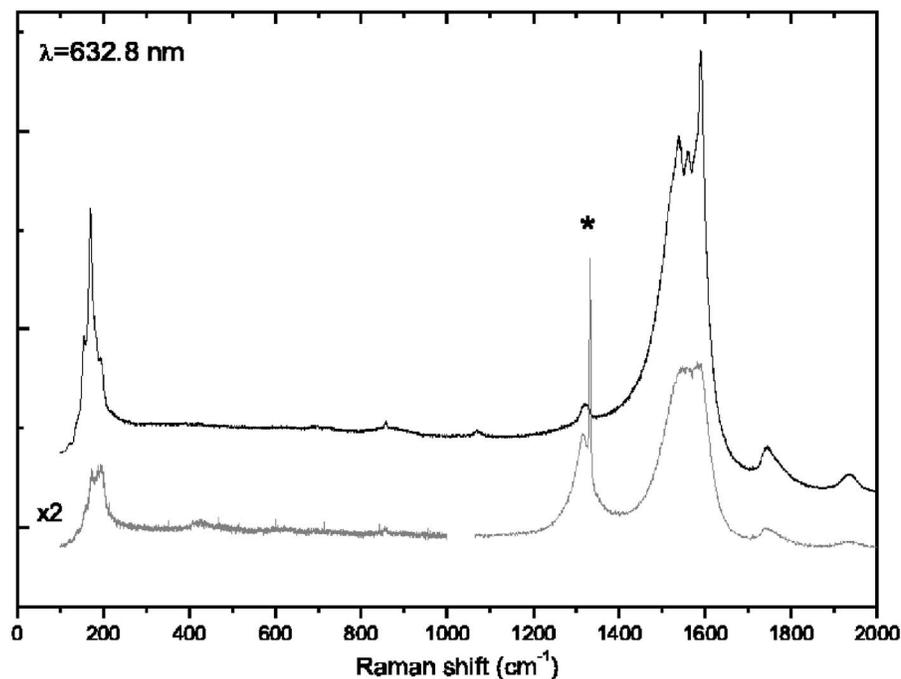


FIG. 5. Comparison of Raman spectra before (above) and after (under) high pressure cycle up to 40 GPa (experiment B). The exciting wavelength is 632.8 nm. The pointed sharp peak is due to the response of the diamond anvil.

can be plotted with a good accuracy is the position of the most intense peak of the TM band. From Figs. 3 and 4 it is clear that the shift with pressure of the TM is the same for both laser excitations. For pressures lower than 10 GPa the behavior is almost linear with a shift of  $6.5 \text{ cm}^{-1}/\text{GPa}$  which is very close to what has been observed in previous studies.<sup>24</sup> For pressures higher than 10 GPa a slight quadratic effect is observed. Such quadratic effect on Raman shift under pressure has already been observed for graphite.<sup>30</sup>

Let us now consider the pressure dependance of the TM in *experiment A*, that as was explained before was only measured with 632.8 nm excitation. The TM were visible up to the highest attained pressure of 40 GPa and the same quadratic behavior is observed (inset of Fig. 4).

In Fig. 5 is displayed the Raman spectrum measured at ambient pressure after the application of a 40 GPa pressure. Both TM and RBM are still present showing the strong resilience of SWNT under the application of high pressure. However we observe a decrease of the intensity of TM and RBM modes and a strong enhancement of the *D* band. The profile of TM and RBM are also different because of a broadening of the modes. In view of these observations, the application of such high pressure has not caused the total deterioration of SWNT, but there is evidence of damage in their structure. The transformation of a part of the tubes into graphite or amorphous carbon cannot be discarded.

#### IV. DISCUSSION

The behavior of the Raman spectrum under pressure that we have observed are discussed in the framework of previous results and theoretical studies.

As mentioned in the Introduction several Raman studies have already been performed on SWNT under pressure.<sup>4-10,24</sup> The vanishing of the RBM around 2 GPa was

associated in some cases to a slope change in the TM pressure evolution. On the basis of theoretical works<sup>20,23</sup> these results were tentatively interpreted as the signature of a phase transition occurring around 2 GPa. In our experiments the vanishing of the RBM does not occur at the same pressure in the spectra excited at 514.5 nm (2.41 eV) and 632.8 nm (1.96 eV). Below 2 GPa, the TM line shapes are different at both excitations wavelengths, meaning that at low pressure the metallic (semiconducting) tubes are still in resonance with the 1.96 eV (2.41 eV) laser excitation. Consequently, the behavior of the RBM can be understood by considering that the structural transition does not occur at the same pressure for metallic and semiconducting SWNT. However theoretical calculations have shown that if a phase transition occurs under pressure it should mainly depend on the diameter of the considered tubes and not on the chirality.<sup>22</sup> Taking into account these latter predictions, the diameter difference corresponding to the studied RBM peaks (0.1 nm) is not enough to explain the difference in the RBM pressure attenuation (5 GPa) in terms of phase transformation.

The intensity attenuation of the RBM, and more generally the complete behavior of the Raman spectrum under pressure can be assigned to a loss of resonance of Raman modes. The study of the profile of TM under pressure could be considered as a clue to confirm this assumption. In the experimental part we have seen that under pressure the TM profiles become progressively closer for both laser excitations and absolutely identical for pressures higher than 20 GPa. Similar TM profiles independently of the excitation wavelengths were also observed in alkali-doped SWNT.<sup>31</sup> This behavior was assigned to the signature of the loss of the resonance. In that case, doping of SWNT causes the progressive filling of the unoccupied electronic states and the transitions between the van Hove singularities are no longer possible.<sup>31</sup> As a consequence, the Raman response becomes nonresonant and independent of the wavelength of the laser excitation. The

observation of the same experimental feature under pressure let us reasonably conclude on the progressive loss of resonance of SWNT. This loss of resonance observed in our high pressure experiments should be associated to significant changes in the electronic structure and optical properties of SWNT under pressure.

Application of hydrostatic high pressure can strongly modify the electronic structure of materials. In our case it could cause a progressive increase of intertube interactions due the shorter distance between rolled graphene planes leading to a loss of the one dimensional character. These stronger interactions could cause the formation of intertube bonds as predicted by some theoretical calculations.<sup>18</sup> It must be noticed that a recent study of graphite under pressure has shown that for pressures higher than 17 GPa graphite undergoes a phase transition with bonding changes and bridging carbon atoms between graphite layers.<sup>36</sup> In our experiments, the Raman spectra before and after high pressure cycles are extremely similar, excepted a general decrease of intensity and an enhancement of the *D* band. Consequently, there is no experimental proof that irreversible interlinking has occurred and this hypothesis can be considered as hardly probable.

Added to hydrostatic compression we can also consider uniaxial strain components applied to the tubes. For pressure higher than 15 GPa argon is known to be a less hydrostatic pressure transmitting media and might cause uniaxial stress on tubes. Some experiments have already been performed to study the electronic properties of SWNT under uniaxial strain.<sup>32</sup> In such conditions a band gap can be opened in the electronic structure of metallic SWNT and the one of the semi conducting tubes can also be modified. Those changes in electronic properties could also explain the observed loss of resonance.

Recently, on the same kind of sample that the one used in the present experiment, Rols *et al.*<sup>26</sup> have shown that argon enters the tubes. The presence of argon inside the tubes can be responsible of additional strain components that could cause the loss of resonance. There is up to now no theoretical calculations considering this hypothesis. To confirm this assumption it might be valuable to perform resonant Raman experiments using different pressure transmitting media than argon. This study is under way and will be published elsewhere.<sup>33</sup>

Another hypothesis that could be advanced to explain the observed loss of resonance is a progressive evolution of the tubes cross section. Several theoretical studies have been performed to study the change of the shape of SWNT under hydrostatic pressure.<sup>16–23</sup> Depending on chirality and diameter of the tubes those studies have shown that the cross section of the tubes could be modified under pressure. Starting from an almost perfect circular cross section, the shape of the tube becomes oval, polygonized or peanut-shaped. Sluiter *et al.*<sup>22</sup> have predicted a complete phase diagram for the shape of SWNT under pressure depending mainly on the tube diameter. Even if there is a huge dispersion of results concerning the pressure transition values there is a large agreement between calculations on their existence. Those morphological changes of SWNT must inevitably induce modifications of their electronic properties. For instance a theoretical study has shown that SWNT with polygonized

cross section could have electronic properties dramatically affected by hybridization effects.<sup>34</sup> These changes are governed by the degree of the polygon representing the cross section of the tube and the sharpness of the edge angles. In another theoretical study some authors have shown metal-insulator and insulator-metal transitions in collapsed SWNT.<sup>35</sup> Thus electronic properties of SWNT depend on the shape of their cross section. If the theoretically predicted changes really occur under pressure, they might be responsible of the progressive loss of resonance. In a recent x-ray diffraction study Kawasaki *et al.* have observed progressive changes in the diffraction pattern of SWNT for pressures up to 11.2 GPa.<sup>14,15</sup> Their conclusion is that structural changes might occur but are highly difficult to detect and are extremely sensitive to the quality of the hydrostaticity conditions. In a neutron powder diffraction study performed at pressures up to 5 GPa in nonhydrostatic conditions, Rols *et al.*<sup>13</sup> have interpreted the strong variation of the (10) Bragg peak as a progressive deformation of the tube section from circular to hexagonal. Even if pressure induced structural changes are highly probable, the experimental determination of their exact nature has proven to be elusive up to now. In any case they could be considered as responsible of the observed loss of resonance in SWNT under pressure in our experiments.

Concerning pressure stability two facts should be considered. (a) Our study does not show evidence of any critical behavior. In fact we do not observe sudden changes in the Raman spectra or in the pressure derivatives characterizing the peak positions. Both Raman profiles and peak position evolve progressively with pressure. This is in contrast with other published experimental studies where phase transformations based on these criteria were observed around 2 or 10 GPa. (b) As already explained, it has been demonstrated that for our particular type of tubes, argon is intercalated inside the tubes<sup>26</sup> whereas in other non purified and not opened tubes such intercalation is less evidenced. We are then tempted to attribute the observed evolution of the Raman spectra to the argon filling of the tubes, which could introduce a steric barrier responsible of the observed pressure stability.

## V. SUMMARY AND CONCLUSION

We have performed high pressure Raman experiments on purified SWNT bundles (average diameter of SWNT = 1.3 nm) using two different exciting wavelengths: 514.5 nm and 632.8 nm. It was thus possible to follow the behavior of the metallic and semiconducting SWNT for pressure up to 40 GPa. We used argon as pressure transmitting medium which is known to enter the tubes. Even if no clear sign of phase transformation is observed up to the highest studied pressure (40 GPa), it is possible that an extremely progressive evolution of the tube cross section occurs under pressure. Such structural evolution might be extremely difficult to detect by Raman spectroscopy. We have observed that the vanishing of the RBM does not occur in the same pressure range in the Raman spectrum measured using 514.5 nm

(5 GPa) and 632.8 nm (10 GPa), respectively. Then, the vanishing of the RBM cannot be considered as a sign of a first order structural phase transition. We have found that the profile of the TM becomes progressively similar for both laser excitations with increasing pressure. For pressures higher than 20 GPa the TM signals are similar in shape and position for both excitation wavelengths. This feature is the consequence of the evolution of the electronic structure of SWNT that could be due to (i) hydrostatic and complex strains applied to the tubes associated to a possible loss of the one dimensional character and/or (ii) to progressive evolution of the shape of the tubes. We have thus shown that the use of

several laser excitations to study the Raman response of SWNT under pressure is extremely valuable.

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