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Jesus Gonzalez, Chrystian Power, Edgar Belandria, Jean-Marc Broto, Pascal Puech, et al.. Pressure dependence of Raman modes in DWCNT filled with PbI₂ semiconductor. *physica status solidi (b)*, 2006, 244 (1), pp.136-141. 10.1002/pssb.200672583 . hal-03595821

HAL Id: hal-03595821

<https://hal.science/hal-03595821>

Submitted on 3 Mar 2022

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To link to this article :

URL : <http://dx.doi.org/10.1002/pssb.200672583>

To cite this version : Gonzalez, Jesus and Power, Ch. and Belandria, Edgar and Broto, J.-M and Puech, Pascal and Sloan, Jeremy and Flahaut, Emmanuel (2006) [*Pressure dependence of Raman modes in DWCNT filled with PbI₂ semiconductor.*](#) *physica status solidi b*, vol. 244 (n° 1). pp. 136-141. ISSN 0370-1972

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Pressure dependence of Raman modes in DWCNT filled with PbI₂ semiconductor

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PACS 61.46.Fg, 62.50.+p, 63.22.+m, 78.30.Na, 81.07.De

Unpolarized Raman spectra of tangential modes on DWNTs filled with 1D nanocrystalline PbI₂ semiconductor excited with 647 nm were studied at room temperature and elevated pressure up to 30 GPa. The tangential optical phonon modes of the carbon nanotubes are sensitive to the in plane stress and split into a contribution associated with the external and internal tube. Up to 11 GPa we find a pressure coefficient for the internal tube of 3.7 cm⁻¹ GPa⁻¹ and for the external tube of 6.3 cm⁻¹ GPa⁻¹. In addition, the tangential band of the external tubes broadens and decreases in amplitude. The corresponding Raman features of the internal tubes appear to be considerably less sensitive to pressure. In the range 11 to 15 GPa we observed a discontinuity in the slope (red shift) of the pressure dependence of the frequency of the tangential modes. This phase transition is associated to a possible structural distortion of the nanotube cross-section. When increasing the pressure furthermore up to 30 GPa the pressure coefficients for the tangential modes associated to the internal and external tubes are the same (10.6 cm⁻¹ GPa⁻¹). All findings lead to the conclusion that the outer tubes act as a protection shield fore the inner tubes (at least up to 11 GPa).

1 Introduction

Carbon nanotubes have attracted intense scientific interest due to their fascinating essentially one-dimensional electronic and vibrational band structure, their unique mechanical properties as well as the prospect for numerous applications. Raman spectroscopy has become a widespread tool for the analysis and characterization of carbon nanotubes and numerous high-pressure Raman scattering studies, on single-wall carbon nanotubes (SWNTs) and multi-wall carbon nanotubes, have made important contributions towards the understanding of the physical properties of these materials [1–3]. A discontinuous reduction in the intensity of the low frequency radial breathing modes (RBMs) near 2 GPa has been observed in SWNTs, accompanied, in some cases, by changes in the pressure coefficients of the tangential modes to lower values. These experimental findings have been attributed to a pressure induced hexagonal [1] or oval [2] distortion of the cylindrically shaped cross section of the bundled nanotubes. In

addition, high-pressure X-ray diffraction (XRD) measurements together with theoretical calculations suggest a structural distortion at around 1.5 GPa, which is also associated with a pressure-induced nanotube polygonization [4]. Raman spectroscopy at ambient pressure has been also successfully employed in the study of the more recently observed [5] and synthesized in bulk quantities [6] double-wall carbon nanotubes (DWNTs), suggesting that the outer tubes provide an unperturbed environment to their interior [7] and that the interaction in a DWNT bundle is stronger than the inner-outer tube interaction [8]. Metal halides can be introduced into carbon nanotubes (CNTs) by capillarity. These experiments made possible the study of low-dimensional crystal growth when the incorporated material is constrained to a few atomic layers in thickness by the encapsulating van der Waals surface of the carbon nanotubes. The preparation of highly anisotropic one-dimensional (1D) structures confined into CNTs in general is a key objective in carbon nanotube research [5, 6]. In this work, we study the effect of high-pressure on DWNTs filled with PbI_2 by means of Raman spectroscopy in order to investigate their structural stability and compare it with that of SWNTs, elucidating the differences induced by the inner-outer tube interaction.

2 Experimental

Raman spectra of the DWNTs were recorded in the back-scattering geometry using a micro-Raman, triple grating system (DILOR XY800) equipped with a cryogenic CCD detector. The spectral resolution of the system was about 1 cm^{-1} . High pressure Raman measurements were carried out using a membrane cylindrical type diamond anvil cell (MDAC). The 4:1 methanol-ethanol mixture was used as pressure transmitting medium and the ruby fluorescence technique was used for pressure calibration. For excitation, the 647 nm line of an Ar^+ laser was focused on the sample by means of a $20\times$ objective, while the laser power was kept below 5 mW, measured directly before the cell, in order to eliminate laser-heating effects on the probed material and the concomitant softening of the observed Raman peaks [12, 13]. The phonon frequencies were obtained by fitting Lorentzian functions to the experimental peaks.

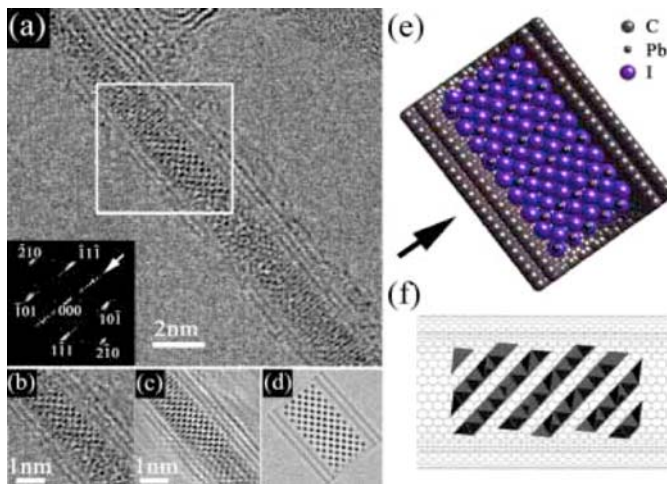


Fig. 1 (online colour at: www.pss-b.com) HRTEM image of a DWNT continuously filled with PbI_2 . The inset FFT indicates that this crystal is being viewed in a $[121]$ projection. (b) Detail from the boxed region in (a). (c) shows an image produced by applying an adaptive filter followed by an inverse Fourier transform to an FFT produced from (b). (d) 'Best fit' image simulation obtained from the structural model in (e) with the incorporated PbI_2 crystallite arranged in a $[121]$ orientation with respect to the beam direction. (f) If we now look at the DWNT/ PbI_2 composite in a 'side on' projection (i.e. in the direction of the large arrow in (e)), we see that the PbI_2 layers are arranged at ca. 45° to the tubule axis.

3 Results and discussion

Double-wall carbon nanotubes were prepared by the technique developed by Flahaut and co-workers [6]. A systematic analysis of TEM images reveals that samples produced by this method contain approximately 77% of DWNTs, the high proportion of DWNTs was also confirmed by electron diffraction [14] with a small admixture of about 18% single-wall carbon nanotubes (SWNTs), and roughly 5% triple-wall carbon nanotubes [6]. The DWNTs filling is made by “capillary technique”. It consists in introducing in a quartz glass the product of interest and DWNTs. The temperature is raised up to few degrees above the fusion point of PbI_2 and the sample is then cooled down slowly ($<1^\circ\text{C}$ per minute). In this way, we obtain a confinement of PbI_2 inside the DWNT. The excess PbI_2 surrounding the CNTs was removed by sonicating the filled nanotubes in a concentrated NaOH solution (6N) for a short time, immediately followed by filtration on a polycarbonate membrane [6]. As a consequence, PbI_2 crystalline structure is modified perpendicularly to the tube axe (see Fig. 1). The obtained crystals could be described in terms of 1D fragments derived principally from 2H form of PbI_2 , although some evidence for the formation of fragments derived from 4H PbI_2 in some nanotubes was observed [6]. Additionally, PbI_2 apparently does not crystallize in rigid narrow DWCNT with internal diameter of less than 2 nm [6].

At normal pressure, from the analysis of Raman spectra and tube diameters inferred from the TEM images [6], the tangential mode frequency of the external (G_3) semiconducting tubes (about 1.3–1.6 nm diameter) represents the unresolved A_1 and E_1 tangential modes, and the internal (G_2) semiconducting tubes in DWNTs (about 0.6–0.9 nm diameter) is associated to the A_1 tangential mode and can be separated, respectively, into 1593 cm^{-1} and 1580 cm^{-1} . In addition, a broad component around 1558 cm^{-1} is

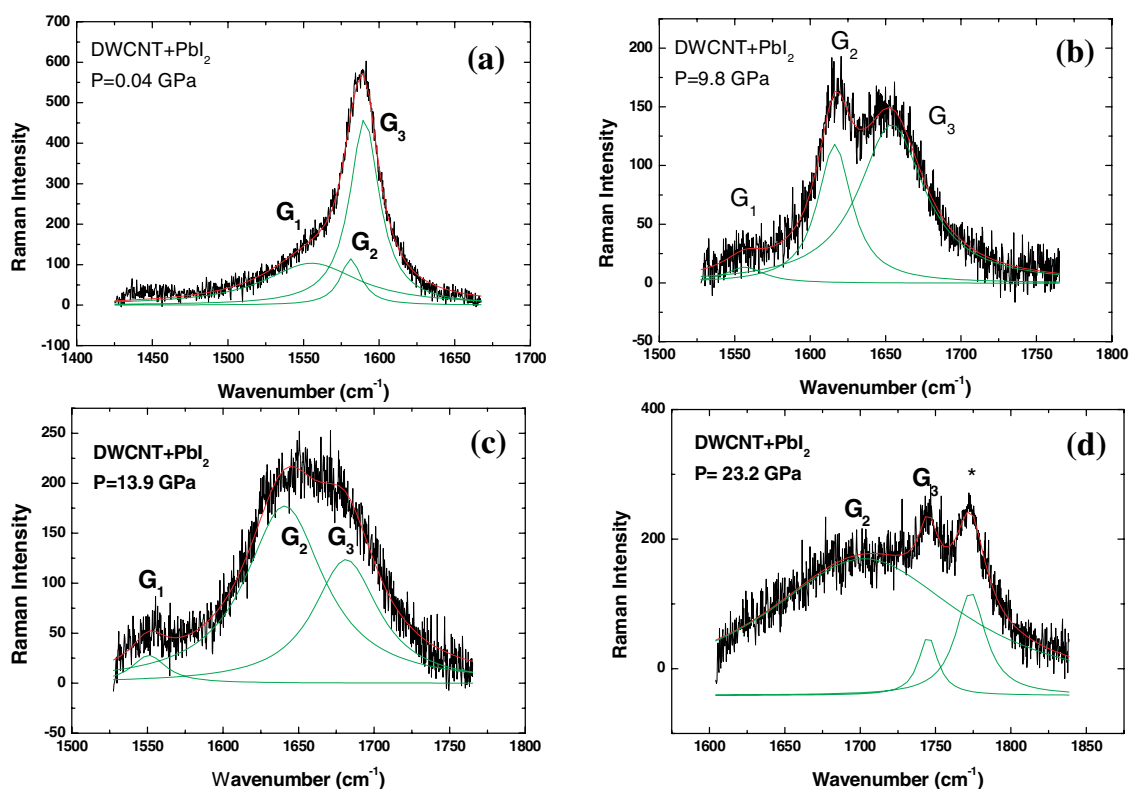


Fig. 2 (online colour at: www.pss-b.com) Raman spectra at different pressures in the upstroke: a) 0.04 GPa; b) 9.8 GPa; c) 13.9 GPa; d) 23.2 GPa.

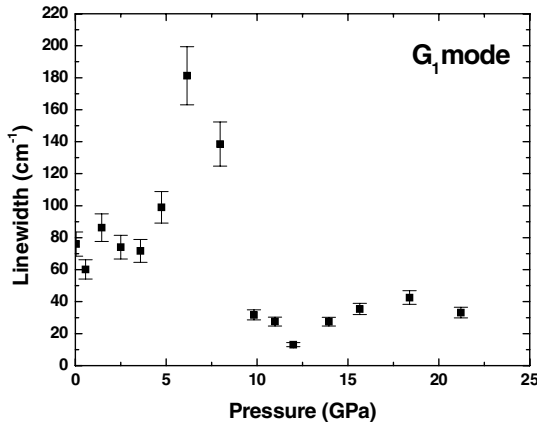


Fig. 3 Pressure dependence of the linewidth for the tangential G_1 mode.

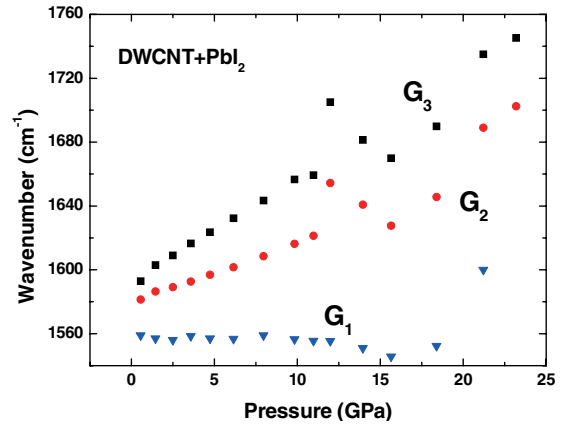


Fig. 4 (online colour at: www.pss-b.com) Pressure dependence of the frequency for the tangential modes G_1 , G_2 and G_3 of DWCNT with PbI_2 .

also observed which corresponds to the external (G_1) metallic tubes with $d \sim 1.3\text{--}1.6$ nm. This phonon gave asymmetric Breit Wigner Fano (BWF) type Raman scattering lines with 647.1 nm excitation. The renormalized phonon frequencies of these BWF lines are at 1558 cm^{-1} , which are considerably smaller than the phonon frequencies of semiconducting tubes ($\sim 1593\text{ cm}^{-1}$). This downshift has been explained by the effect of screening the C–C interaction due to the conduction electrons of metallic tube [15]. In the diamond anvil cell the low frequency radial breathing modes (RBMs) and the raman active phonons of 2H and 4H PbI_2 polytypes was not observed (spectral range $50\text{--}120\text{ cm}^{-1}$) [16]. Figure 2 shows the Raman spectra as a function of applied pressure in the high frequency range obtained using the methanol-ethanol pressure medium. We observe a splitting of the G-band, the in-plane optical zone centre phonon mode of graphite. The splitting can be attributed to the internal and external tubes as will be shown below [17].

As observed with increasing pressure, the semiconducting tangential modes (G_2 and G_3) shift towards higher wavenumbers and the metallic G_1 mode has a very small pressure coefficient. In addition, the tangential band of the external and internal tubes broadens and decreases in amplitude. As an example in Fig. 3 we show the pressure dependence of the linewidth for the tangential G_1 mode, where the phase transition is clearly observed.

The fitted band positions are shown as a function of applied pressure in Fig. 4. The experimental points are fitted with a linear law up to 11 GPa and the coefficients are presented in Eqs. (1)–(3), where the frequency is expressed in cm^{-1} and the pressure in GPa:

$$\omega(G_3) = 1593 + 6.33P(\text{GPa}), \quad (1)$$

$$\omega(G_2) = 1580 + 3.71P(\text{GPa}), \quad (2)$$

$$\omega(G_1) = 1558 - 0.17P(\text{GPa}). \quad (3)$$

Up to 11 GPa we find a pressure coefficient for the internal (G_2) tube of $3.7\text{ cm}^{-1}\text{ GPa}^{-1}$ and for the external (G_3) tube of $6.3\text{ cm}^{-1}\text{ GPa}^{-1}$. The corresponding Raman features of the internal tubes appear to be considerably less sensitive to pressure [15]. The pressure dependence of the phonon, corresponding to the external (G_1) metallic tubes, is negative and very small. The same behaviour was first reported in Ref. [18], where an abrupt decrease of the pressure dependence of this tangential mode was observed.

In the range 11 to 15 GPa we observed a discontinuity in the slope (red shift) of the pressure dependence of the frequency of the tangential modes. This phase transition is associated to a possible structural distortion of the nanotube cross-section. When increasing the pressure furthermore up to 30 GPa the

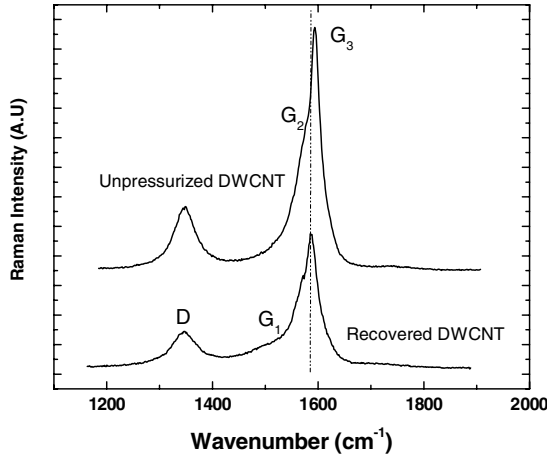


Fig. 5 Changes in tangential bands induced by the pressure cycle.

pressure coefficients for the tangential modes associated to the internal and external semiconducting tubes are the same ($10.6 \text{ cm}^{-1} \text{ GPa}^{-1}$). In this range the linear pressure dependence of the frequency is showed in Eqs. (4) and (5):

$$\omega(G_3) = 1500 + 10.73P(\text{GPa}), \quad (4)$$

$$\omega(G_2) = 1459 + 10.58P(\text{GPa}). \quad (5)$$

At 23.2 GPa a new high frequency phonon at about 1773 cm^{-1} is observed (see Fig. 1d). This result corresponds to a new and unidentified phase transition. After the pressure cycle is completed, we observe significant changes of the tangential and radial bands in the form of a peak down-shift and some irreversible broadening, as we observed in the Fig. 5.

4 Conclusions

DWNTs give the opportunity to distinguish pressure induced spectral changes from internal and external walls in multi wall carbon nanotubes. The splitting of the G-band can be explained by considering a tangential discontinuity of the stress component as one goes from the external wall to the internal tube. The ratio of the pressure coefficient of internal and external walls remains the same independent of the medium. All findings lead to the conclusion that the outer tubes act as a protection shield fore the inner tubes (at least up to 11 GPa). In the diamond pressure cell no experimental evidence of the phonons corresponding to the PbI_2 nanowires were observed.

Acknowledgement This research was supported in part by the CDCHT (Universidad de los Andes, Mérida, Venezuela) and the FONACIT (Venezuela) project number F-2005000214. J.G. acknowledges partial support of this research by the PCP-Nanotubes (France–FONACIT–Venezuela) and Fundación Polar (Venezuela). E.B. acknowledges support by the ACFIMAN (Venezuela).

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