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Jesús Marquina, Emmanuel Flahaut, Jesus Gonzalez. High-pressure optical absorption studies of double-walled carbon nanotubes.. physica status solidi (RRL) - Rapid Research Letters, 2012, 6 (9-10), pp.382-384. 10.1002/pssr.201206280 . hal-03468712

HAL Id: hal-03468712 https://hal.science/hal-03468712

Submitted on 7 Dec 2021

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> **To link to this article**: DOI:10.1002/pssr.201206280 Official URL: <u>http://dx.doi.org/10.1002/pssr.201206280</u>

To cite this version:

Marquina, Jesús and Flahaut, Enmanuel and Gonzalez, Jesus *High-pressure optical absorption studies of double-walled carbon nanotubes*. (2012) Physica status solidi (RRL) - Rapid Research Letters, vol. 6 (n° 9-10). pp. 382-384. ISSN 1862-6254

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High-pressure optical absorption studies of double-walled carbon nanotubes

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Received 27 June 2012, revised 15 August 2012, accepted 17 August 2012 Published online 22 August 2012

Keywords double-walled carbon nanotubes, optical absorption, high-pressure effects, Van Hove singularities

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In this Letter the electronic properties of double-walled carbon nanotubes (DWCNTs) were studied by transmission measurements as a function of hydrostatic pressure up to 10 GPa. The energies of the optical transitions between the Van Hove singularities decrease with increasing pressure, which can be attributed to pressure-induced hybridization and symmetry-breaking effects. We observed a linear behaviour in the pressure-induced shift of the optical transitions. This is in good agreement with previous studies on single-walled carbon nanotubes (SWCNTs).



High-resolution TEM image of a bundle of DWCNTs (A), histogram of the number of walls (B), and diameter distribution for CNT samples plotted from 100 HRTEM images (C).

1 Introduction Carbon nanotubes are attracting increasing scientific interest due to their unique structure and properties (which strongly depend on the geometrical parameters of a nanotube) and to the prospect for numerous applications [1–3]. The double-walled carbon nanotube (DWCNT) is the most important member of the multi-walled carbon nanotube family that can be produced in significant quantities [4]. These tubes consist of two concentric cylindrical graphene layers. Typical values of their inner and outer diameters range from approx. 0.40 to 2.5 nm and from approx. 1.0 to 3.2 nm, respectively [5, 6].

Their physical properties strongly depend on the geometrical parameters of the nanotubes, such as diameter and chirality [7]. An understanding of the structural, electronic and vibrational properties of DWCNTs is of great importance, and one efficient approach is to study the changes associated with the variation of thermodynamic parameters, such as external pressure and temperature [8, 9]. The pressure-induced structural phase transition of carbon nanotubes has been probed by Raman spectroscopy [10-12], X-ray scattering [13, 14], neutron diffraction [15], and transmission measurements [16, 17]. Changes in the gap of semiconducting single-walled CNTs (SWCNTs) under hydrostatic pressure have also been considered theoretically, showing that the pressure coefficients for the band gap can be positive or negative with strong chirality dependence [18]. Recent experiments showed that the observed collapse pressure for DWCNTs does not depend on pressuretransmitting media and that it occurs at a pressure higher than that for pristine and filled SWCNTs. This renders DWCNTs ideal fillers for composite nanomaterials for high-load mechanical support [19].

2 Experiment DWCNTs were synthesized by catalytic chemical vapor deposition as described in Ref. [6] in more detail. To enable absorption measurements, a dedicated cell holder and a particular set of optical fiber probes adapted to the specific high-pressure cell were designed, machined and assembled. This setup allowed us to feed white light to the sample with eight 100 µm diameter silica fibers embedded in a ceramic needle through the bottom diamond holder hole, and to collect the light transmitted through the pressure chamber with another bundle of eight identical fibers. A two-step hole with a 150 µm bottom diameter was drilled in the gasket based on Inconel 718 to create the pressure chamber and ensure that all the transmitted light collected had travelled through the sample. Details on the high-pressure cell and the optical experiments can be found elsewhere [20, 21]. A nanotube suspension was prepared in a 4:1 methanol-ethanol mixture. For pressure-dependent optical experiments, a drop of nanotube suspension was sealed in a gasketed diamond anvil cell for the application of hydrostatic pressure. The pressure generated in the pressure cell was determined by the spectral shift of the R_1 fluorescence line of the ruby. The intensity, $I_{\text{sample}}(\omega)$, of the radiation transmitted through the sample placed in the cell and the intensity, $I_{\rm ref}(\omega)$, of the radiation transmitted through the pressuretransmitting medium in the pressure chamber were measured. From $I_{\text{sample}}(\omega)$ and $I_{\text{ref}}(\omega)$, the optical density spectra were calculated according to $D(\omega) = -\log_{10}(I_{\text{sample}}(\omega)/$ $I_{ref}(\omega)$).

3 Results and discussion Figure 1 displays the pressure-dependent optical density spectra for the DWCNTs. The optical transitions between pairs of Van Hove singularities resulting in well-defined absorption bands are arbitrarily labeled E_1 and E_2 .

In Fig. 2, the optical absorption spectra of DWCNTs and SWCNTs [22] (left) and the Kataura plot (right) are shown simultaneously. As is apparent from Fig. 2, a greater number of peaks are observed in DWCNTs than in SWCNTs. This is because much more allowed transitions



Figure 1 Pressure-dependent optical density spectra of unoriented DWCNTs in bundles. The optical transition energies are labeled E_1 and E_2 .



Figure 2 (online colour at: www.pss-rapid.com) Left: Optical absorption spectra of DWCNTs (solid line) and pristine SWCNTs (dashed line) [22] at room temperature and pressure. Right: Calculated gap energies between mirror-image spikes in the density of states for $\gamma = 2.9$ eV. Solid circles indicate metallic SWCNTs and open circles the semiconducting ones (taken from Ref. [22]). Arrow shows diameter distribution for the DWCNTs. The horizontal lines serve as a guide for the eyes.

are involved. As a first approximation to explain the absorption spectrum of DWCNTs, it is possible to use the theoretical predictions of the Kataura plot. In this plot, it is clear that the first and second lowest energy gaps between spikes come from the semiconducting tubes, the third one comes from the metallic tubes, the fourth and fifth one come from the semiconducting, an so on. We know that each absorption peak consists of a set of narrow absorption bands of the DWCNT constituents. For the diameter distribution observed, it seems that each absorption peak is due to both semiconducting nanotubes and metallic nanotubes. Thus it is difficult to quantify the semiconducting and metallic character for each absorption peak. However, previous studies have shown that the conductivity type dominant in these DWCNTs samples is semiconducting [8, 9]. Therefore, the above and the Kataura plot suggest a predominantly semiconducting character for the two peaks E_1 and E₂.

The E_1 and E_2 bands in the optical absorption spectra are shifted to lower energy with increasing hydrostatic pressure. According to theoretical investigations, a redshift of the optical absorption bands under pressure can be attributed to pressure-induced deformation of the nanotubes, causing hybridization effects and symmetry breaking [23]. In order to obtain quantitative information on the energies of the optical transitions, the background was subtracted from the measured spectra using a baseline. We thus only obtain the absorption resulting from optical transitions. The spectra were then fitted with a Lorentzian and a Gaussian profile for the E_2 and E_1 bands, respectively. The obtained optical transition energies of the Lorentzian and Gaussian terms describing the absorption features of the DWCNTs are shown in Fig. 3 as a function of pressure. The optical transitions show a small red-shift with increas-



Figure 3 Pressure dependence of the optical transition energies obtained from the fits of the absorption spectra. The solid lines are linear fits to the experimental data.

ing pressure in agreement with previous research [16, 24, 25]. The obtained values for the linear pressure coefficient were -1.74 and -1.78 meV/kbar for the E₁ and E₂ bands, respectively. Both pressure coefficients are of the same order of magnitude as the E₁₁ values reported in Refs. [24, 25] for SWCNTs. In the (7,5) nanotube, it has been reported that the E₁₁ transition has a pressure coefficient equal to -1.8 meV/kbar [25]. This chirality has also been observed in our samples of DWCNTs (see Ref. [9]).

On the other hand, previous research has shown that a structural phase transition at about 2 GPa was observed in SWCNTs [16, 26]. However, in our samples the pressure had increased up to 10 GPa and no phase transition was observed. One possible explanation for this behavior is given in Refs. [18, 26, 27], according to which the transition pressure is proportional to the inverse cube of the tube diameter. Since the DWCNTs studied have very small internal diameters ranging from 0.40 to 2.5 nm, the transition occurs at a higher pressure. Another possible reason for this behavior would be that the outer tubes provide an unperturbed environment to their interior so that the transition takes place at a higher pressure. Our results are in good agreement with those obtained in a recent study that showed that the collapse pressure was observed at 21 GPa (for tubes with a diameter of 1.56 nm), and that the outer tube provides chemical screening to the inner tube [19].

4 Summary We investigated the optical properties of DWCNTs at high pressures. From the experimental results it is found that the E_1 and E_2 values decrease with increasing hydrostatic pressure, which is in good agreement with previous research. We did not observe any difference in the pressure coefficients between the E_1 and E_2 bands. It was not possible to give an unambiguous assignment of Van Hove singularities to each optical absorption band. Thus, it is necessary to explore a broader range of the spectrum and perhaps perform experimental measurements at the level of individual DWNTs.

Acknowledgements This research was supported in part by the Franco Venezuelan Postgraduate Cooperation Program (PCP) "Nanotubos de Carbono" and by the CDCHTA (C-1720-11-05-B) of the Universidad de los Andes, Mérida, Venezuela. J.G. acknowledges the support of MALTA-Consolider Ingenio 2010 (CSD2007-00045). We would like to thank the reviewers for their insightful comments and suggestions, and Françoise Salager Meyer for editing this manuscript.

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