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Rapid Research Note

The Pressure Dependence of the High-Energy Raman Modes in Empty and Filled Multiwalled Carbon Nanotubes

C. THOMSEN and S. REICH

Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin, Germany

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The pressure dependence of the Raman-active modes in carbon nanotubes has become of interest because it revealed a number of unforeseen experimental results. Among the surprises were a large logarithmic pressure dependence of the low-energy radial breathing mode and a lack of different pressure slopes in the high-energy region for the various modes of semiconducting nanotubes [1, 2]. The former implied a significant influence of neighboring tubes in a bundle which was described by a van-der-Waals interaction. The latter effect turned out to be a consequence of the missing mirror planes in a general chiral nanotube. Its eigenvectors cannot simply be classified as axial and circumferential; instead, chiral tubes have more complicated eigenvectors, which have been calculated with ab initio methods recently [3]. The observed shifts in the Raman spectra show a uniform, average pressure slope. In metallic nanotubes split pressure slopes were found experimentally [4].

These results on single walled tubes (SWNT) were complemented by measurements on multiwalled tubes (MWNT) by Thomsen et al. [5] and, recently again by Venkateswaran et al. [6]. Both groups found the MWNT to have smaller pressure slopes (2.7 and 2.4 TPa^{-1}, respectively, for the normalized pressure derivatives) than the single walled tubes (3.7 TPa^{-1}) [2]. For a nice compilation of the Raman pressure work on nanotubes see Ref. [6].

The purpose of this note is to extend our analysis of the elastic properties of single and multiwalled nanotubes which is based on elasticity theory, to the recent results of Venkateswaran et al. [6] on multiwalled nanotubes and explain their experimental findings. They reported two types of measurements on MWNT with two different pressure media, first the usual 4:1 mixture of methanol/ethanol and secondly He, and they find that the pressure slopes are nearly the same, the one for He as pressure medium being slightly smaller (2.4 and 2.3 TPa^{-1}). For He as a pressure medium one would believe that it easily fills the inner core of the nanotube while the larger methanol/ethanol molecules remain mostly outside or at least are not effective in transmitting the applied hydrostatic pressure to the interior of the nanotube. We make now the approximation that He as pressure medium makes the nanotube look like a hollow cylinder with a finite wall thickness and open ends, and the methanol/ethanol mixture makes it appear as the same cylinder with closed ends. Within elasticity theory the ratio of axial strains for a given hydrostatic pressure is given by [5]

$$\frac{u_{zz}^{\mathrm{open}}}{u_{zz}^{\mathrm{closed}}} = 1 - \left(\frac{R_1}{R_2}\right)^2, \tag{1}$$

where R_1 and R_2 are the inner and outer radius of the MWNT at ambient pressure. As is shown in [5] this result does not change for a circumferential mode, and is thus valid for chiral tubes as well. Equation (1) is independent of any elastic constant of the nanotube since only the pressure medium changed for otherwise identical tubes. For the values cited by Ref. [6] for the radii of their tubes ($R_1 = 25$–35 Å, $R_2 = 100$–125 Å)[1]), Eq. (1) predicts a reduction to 93% of the pressure slope when filling the pressure cell with He rather than with the methanol/ethanol mixture. The

[1]) Coincidentally, their average R_1, R_2 amount to precisely the same geometrical factor A in our model as reported in [5].

latter is reported to have $2.4 \pm 0.1\,\mathrm{TPa}^{-1}$ which implies a predicted $2.2 \pm 0.2\,\mathrm{TPa}^{-1}$ for the He-filled nanotube. (The larger error results from the uncertainties in the radii given.) Our result shows that within elasticity theory the effect of filled and empty multiwalled nanotubes is well described, and it agrees with the experimental indication of a slightly smaller pressure slope in tubes measured with He as pressure medium.

Alternatively, if one believes that multiwalled tubes are always filled (regardless of pressure medium) due to the relatively large inner-core diameters then, from Eq. (4) in Ref. [5], we predict the ratio of pressure dependences of SWNT and MWNT through their respective strains.

$$\frac{u_{zz}^{\mathrm{SW}}}{u_{zz}^{\mathrm{MW}}} \approx 1.5 \tag{2}$$

is the ratio of strain in axial direction of an empty SWNT to the one of a filled MWNT (or to empty MWNTs, which is nearly the same). Starting with $3.7\,\mathrm{TPa}^{-1}$ for SWNT this predicts $2.5\,\mathrm{TPa}^{-1}$, very close to the value observed by Ref. [6].

In conclusion, we have shown that the experimental results of pressure studies with different pressure media are well explained by our elasticity model of carbon nanotubes. This means that the effects of the molecular structure on the elastic properties of multiwalled nanotubes is small. For single walled nanotubes ($R_1 = 5.3$ Å, $R_2 = 8.7$ Å) our model predicts a difference in pressure slopes of 63% for filled and empty tubes.

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