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The energy dispersion of the D* (G′) band shows a strong diameter dependence according to Raman measurements on double walled carbon nanotubes. The Raman shift of the small diameter inner tubes shows an average softening. There is an oscillation around an average linear behavior with slopes of 108 cm^{-1}/eV and 61 cm^{-1}/eV for the outer and inner tubes, respectively. We show that the experimental observation can be reproduced by simple model calculations if the curvature effects are taken into account. The phonon softening with increasing curvature was proven by first principles calculations.

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1 Introduction

The D* (also called G′) band of sp^2 carbon materials is a two-phonon band, the overtone of the disorder induced D band [1]. The position of these bands shifts more less linearly to higher frequencies with increasing laser excitation energy [2–6]. This dispersion can be explained by double resonance theory [7]. The slope of the linear dispersion in graphene is about twice as large for the D* as for the D band. In the case of single walled carbon nanotubes (SWCNTs) the effect is strongly influenced by the presence of Van Hove singularities (VHSs) in the electronic joint density of states. The extra enhancement due to matching the VHSs was discussed as a triple resonance effect for the D band in Ref. [8]. The chirality dependence of the triple resonance condition results in an oscillation of the dispersion around an average linear behavior. The dispersion of the D band of SWCNTs was succesfully described in [8, 9] within the triple resonance approximation, by using a simple model 2D phonon dispersion for graphene. The 1D phonon dispersions for SWCNTs were obtained by cutting out from the 2D model dispersion, according to their chiralities, in the spirit of zone folding approximation.

A strong diameter dependence of the position and dispersion of the D* band was observed in the Raman spectrum of double walled carbon nanotubes (DWCNTs) [5]. The contribution of the inner and outer tubes can be separated unambigously by ^{13}C isotope enrichment [10, 11]. In the natural carbon samples, the position of the D* band of the inner tubes is downshifted as compared to the D* band of the outer tubes, except for the 1.16 eV excitation, where the ordering of the two bands is reversed. The

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slope of the average linear dispersion is much less for the inner tubes as compared to the outer tubes (61 cm^{-1}/eV vs. 108 cm^{-1}/eV). The experimental observations suggest a clear phonon softening for the small diameter inner tubes. This softening was proven by first principles calculations for many inner tube – outer tube pairs. Taking into account this phonon softening, otherwise using the same procedure as in Refs. [8, 9], the different dispersion of the of D* band for inner and outer tubes can be explained.

2 Experimental and theoretical methods

DWCNTs, started from peapods with natural carbon content and with ^{13}C enriched inner tubes, were prepared as published earlier [10]. Raman spectra were taken in the $E_{\text{laser}} = 1.16 – 2.71$ eV range.

Calculations were carried out for isolated SWCNTs, that is the interaction between the walls in DWCNTs was neglected in this study. We used the VASP density functional theory (DFT) code [12] at the LDA level and PAW method to calculate the optimized geometry and the phonon dispersion for many different SWCNTs. Long range force constants were taken into account to ensure high accuracy of the frequencies: supercells of at least 3 conventional unit cells were used to calculate the Hessian matrices. The helical symmetry of SWCNTs [13] was exploited in these calculations. As a result of this, the necessary steps in the calculation of the force constants decreased significantly. Exploiting the helical symmetry allowed us to carry out the DFT calculations for as large as ≈ 700 carbon atoms in the supercell.

In the triple resonance approximation the electron bands were handled within the usual zone folding method. However, downscaling of the energies for small diameter tubes, according to our previous DFT results [14], was needed, as we will see in the next paragraph. The wave vector of the corresponding phonon is determined by the positions of the VHSs near by the K and K′ points in the 2D k-space of graphene. For the phonon frequencies, the same 2D model dispersion was used as in Ref. [8] for the D band of SWCNTs:

$$\omega(k_r, k_\phi) = \omega_K + \omega_1 \cdot k_r \cdot [1 - \delta \cdot k_r \cdot \cos(3k_\phi)], \tag{1}$$

k_r and k_ϕ are the polar coordinates of $k - k_K$; ω_K, ω_1 and δ are fitting parameters. The 1D dispersion was simply cut out from Eq. (1) with the appropriate parallel lines.

3 Results and discussions

Using the method presented above, we have calculated the DFT phonon dispersion for 8 chiral nanotubes. In order to avoid complications due to the individuality (family behavior) of the tubes, inner and outer tubes were chosen in pairs, where the chiral indices for the outer tubes were obtained simply by doubling the indices for the inner tubes: (7,1), (6,4), (8,2) and (7,4) from the 0.58 nm – 0.76 nm diameter range, and (14,2), (12,8), (16,4) and (14,8) from the twice as large diameter range.

Figure 1a shows (the positive part of) the helical Brillouin zones (BZs) for these tubes, mapped onto the 2D k-space of graphene. The number of parallel lines for a given tube is equal to the greatest common divisor (gcd) of the (n_1, n_2) chiral indices. (The lines for the $m = 0$ helical quantum number always span a range between a Γ point and an M point.) The number of phonon bands within the helical BZ is $6 \cdot gcd$. That is the reason we ommitted the achiral tubes here, because gcd is large for them.

Figure 1b shows the DFT calculated phonon dispersion of the (7,4) and (14,8) tubes, in the frequency range which is relevant for D and D* bands, in the region around 2/3 of the helical BZ. A clear softening can be seen for the smaller diameter tube.

Figure 2 shows both the measured and the calculated D* dispersions. The linear fit to the experimental points has a slope of 108 cm^{-1}/eV and 61 cm^{-1}/eV for the outer and inner tubes, respectively. The theoretical points are the results of the triple resonance approximation. The $\omega_{\text{D*}} = 2 \cdot \omega_{\text{D}}$ frequencies are plotted as a function of E_{ii}. E_{ii} is the (symmetric) transition energy between i-th VHSs, as obtained from simple tight binding model [13]. ω_{D} is the frequency calculated from Eq. (1). Note, that each tube can contribute to this “scatterplot” by more than one point, depending on how many VHSs fall within the given excitation energy range. Without allowing diameter dependence for the ω_1 parameter the points for inner

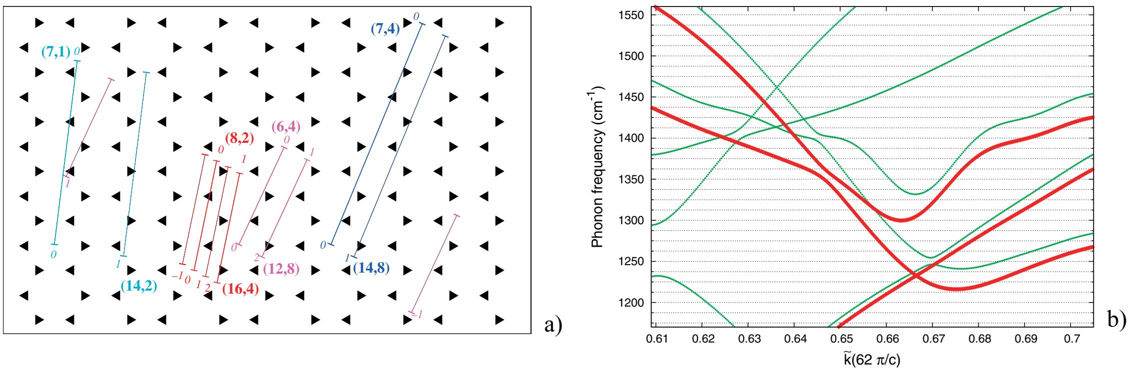

Fig. 1 (online colour at: www.pss-b.com) a) 1D helical Brillouin zones for 8 tubes on the 2D graphene map (triangles are the K and K′ points). Note the differences in *m* helical quantum numbers for the inner and outer tubes in corresponding pairs. b) Phonon softening due to curvature effects in the vicinity of 2/3 of the helical Brillouin zone. The phonon dispersions were obtained by DFT calculations. Thick (red) and thin (green) lines correspond to (7,4) and (14,8) nanotubes, respectively. *c* is the length of the traditional unit cell, $N = 62$ is the expansion factor for the helical BZ (they are the same for both tubes).

and outer tubes would follow the same curve. However, introducing diameter dependence results in a splitting for the two groups of tubes. An $\omega_1(d) = 133 - 26.1/d^2$ cm^{-1} diameter dependence was obtained from the fit to the experimental dispersion. Similar softening was suggested already empirically [15].

Due to the fact, that not only the slope but the absolute value as well decreases with decreasing diameter, it is impossible to obtain crossing between the curves for the outer and for the inner tubes, in contrast to the experiment. One possible explanation is the following. We know from earlier DFT calculations [14] that the Van Hove energies follow the more less 1/d behavior only to $d \approx 0.8$ nm, below that a gradual decrease of the energies occurs due to curvature effects. For $d = 0.7$ nm this redshift is already in the order of 0.5 eV. Exactly this was taken into account for the "scatterplot" in Fig. 2: the whole theoretical plot was shifted to smaller energy values by 0.5 eV. After this redshift the experimental and theoretical average lines for the dispersion of inner as well as for the outer tubes coincide almost perfectly.

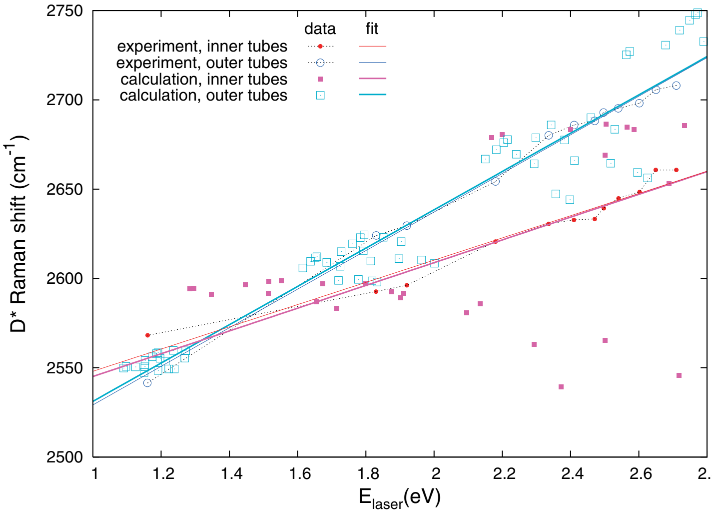

Fig. 2 (online colour at: www.pss-b.com) Raman D* dispersion: comparison between theory and experiment.

4 Conclusions

The position of the D* bands in the Raman spectrum of DWCNTs shows an average linear shift (with a small oscillation around it) in the measured 1.16–2.71 eV laser excitation energy range. The dispersion of the D* band has (an anomalous behavior and) a strong diameter dependence. The measured slope of the average linear shift is 61 cm^{-1}/eV and 108 cm^{-1}/eV for the inner and outer tubes, respectively. The frequency of the inner tubes is smaller, except for the 1.16 eV excitation, where the ordering of the two bands is reversed. The experimental observations can be reproduced by simple model calculations if the curvature effects are taken into account. The difference in the slope and the absolute position for the inner and outer tubes is a consequence of curvature effects. The phonon softening with decreasing diameter was proven by first principles calculations, exploiting the helical symmetry of the tubes. The crossing of the two dispersion curves can be explained by the redshift in the electron excitation energies with decreasing diameter.

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