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Anharmonic effects in single-walled carbon nanotubes

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Abstract

We have investigated the temperature and excitation energy dependence of Raman spectra of single-wall carbon nanotubes (SWCNTs). The measured Raman shifts for D and G bands of SWCNTs show a softening behavior upon increasing temperature (83–733 K). A theoretical model is developed to study the frequency shifts for these two Raman modes as a function of temperature; the calculated results agree well with the experimental data. The calculation indicates that the virtual optical-phonon couplings dominate contributions to the temperature variance of frequency shifts for D and G bands of SWCNTs while the pure-volume effect is very weak. Measurements of peak positions and linewidths of D and G bands are also carried out at three different excitation wavelengths (325, 514.5 and 785 nm). It is found that not only does the peak position of the D band exhibit a linear increase, but also the linewidth of the G band does upon increasing excitation energy. In addition, we also measure the relative intensity ratios of the D band to the G band (I_D/I_G) with temperature and excitation energy in this work.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are known to exhibit many interesting mechanical and electrical properties due to their unique one-dimensional structures [1], and are regarded as one of the most promising candidates for the construction of nanoscale electronic devices [2]. It is known that a usual SWCNT is wrapped from a two-dimensional graphene sheet, whose properties can be reasonably well described now [3, 4]. The diameter of each freestanding SWCNT ranges from 0.6 to 6 nm, with a length of about 1 μm [5]. Since 1998, ultra-small carbon nanotubes with diameters in a range of 0.3–0.5 nm have attracted much

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attention [6–10]. In particular, the discovery of superconductivity in 4 Å diameter nanotubes in zeolite matrix [11] and in nanotube ropes [12] has initiated both experimental and theoretical investigation of this kind of SWCNTs [13–16].

In this work, we investigate the temperature effect on Raman bands of SWCNTs. Study of the temperature effect on the Raman spectra can provide us with important insights into the relationship between the spectra, vibrational properties and geometric structure of SWCNTs. As previously reported, three main Raman modes of SWCNTs, i.e. the RBM (the radial breathing mode in the range of 100–600 cm⁻¹), the D band (disorder-induced mode in the range of 1300–1400 cm⁻¹) and the G band (tangential mode at about 1600 cm⁻¹), are all found to be sensitive to temperature. Both the peak position and linewidth would change with temperature [17–20]. Numerous theoretical investigations of Raman features of the RBM based on the first-principles calculation have been performed [21, 22]. It is also known that the D and G bands are present due to a combination of the in-plane movement of C–C stretching and bending. However, the detailed mechanism of temperature effects on Raman shifts has not been well illustrated. The origin of downshift of these two bands upon increasing temperature is only speculated to be due to the C–C stretching and pure-temperature effect [22–24]. Therefore, in this work we mainly discuss temperature effects on Raman shifts of these two modes, based on a model that has been used to analyze temperature-dependent Raman shifts of semiconductor and nanostructured materials, such as Ge, GaN and ZnO nanocrystals and Si nanowires [25–30]. According to the calculation result, we first confirm that anharmonic optical-phonon couplings make the main contribution to the temperature dependence of frequency shifts for Raman D and G bands of 4 Å diameter SWCNTs.

In addition, the excitation energy effect on Raman bands of SWCNTs has also been investigated. The frequency shift of the Raman D band upon increasing excitation energy exhibits a hardening behavior in carbon-related materials, such as graphite, glassy carbon, highly oriented pyrolytic graphite (HOPG), SWCNTs and carbon nanofibres (CNFs) [30–34]. Following the experimental observation, the double resonance theory has been proposed, which is based on the idea that local defects within the tubes allow for optical transitions throughout the whole *k*-space and therefore enhancement of different phonon modes [35–38]. Interestingly, we find that not only does the peak position of the D band exhibit a linear increase but also the linewidth of the G band does upon increasing excitation energy. The phenomenon does not exist solely in the Raman G band of SWCNTs and it can also be found in a variety of carbon-related materials, though it has not been paid much attention in previous works [31, 32]. By comparing previous experimental values with ours, we further confirm the validity of this observation. The results may provide a valuable reference to better understand vibrational properties of SWCNTs lattice.

2. Experimental procedures

A powder sample of SWCNTs with high purity was purchased from Chengdu. Before being observed by a high-resolution transmission electron microscope (HRTEM) (JEOL JEM-2010), the sample was treated with ultrasonic dispersion in a water–ethanol solution. The HRTEM images were taken to measure the average diameter of the sample at an accelerating voltage of 200 kV. Raman spectra were acquired by using a Labram-HR micro-Raman system equipped with a microscope attachment and a liquid-nitrogen-cooled charge-coupled detector. A Linkham temperature stage with a quartz window was used to vary the sample temperature from 83 to 733 K in flowing nitrogen atmosphere. In this measurement, the powder sample was placed on the microscope slide in the stage and covered by an ultrathin cover slip to avoid being disturbed by gas flow. No polarizer was used and a backscattering geometry was employed to

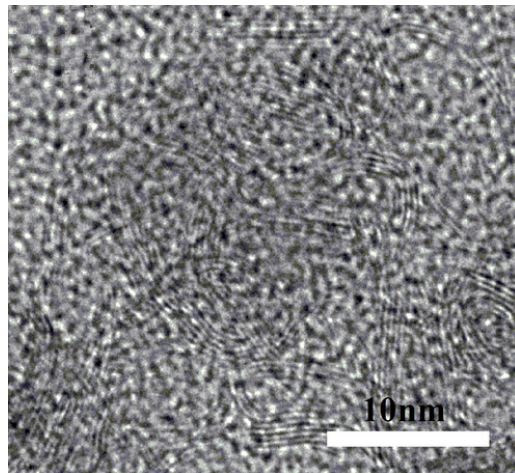


Figure 1. An HRTEM image of the sample of SWCNTs.

collect the Raman signal. The 514.5 nm line of a Ar-ion laser was used to excite the sample upon increasing temperature. After completing this process, the temperature is cooled down to room temperature. Then the sample was excited under three different laser energies of 325, 514.5, and 785 nm (3.82, 2.41, and 1.58 eV, respectively). In all cases, the laser power supplied through the objective lens was ~ 3 mW and a light spot with a diameter of ~ 2 μm was focused on the sample. The Raman spectral resolution of this system was estimated to be ~ 2 cm^{-1} .

3. Results

Figure 1 is an HRTEM image of the sample. We can see many parallel doubled dark lines, which are typical images of SWCNT bundles. The diameter of SWCNTs is estimated to be 4 \AA according to a log-normal fitting [39]. There are three possible structures for this kind of SWCNTs: the zigzag (5, 0), the armchair (3, 3), and the chiral (4, 2) tubules whose diameters are, respectively, 0.392, 0.407, and 0.414 nm. Calculations based on the local-density-functional approach indicate that while the (5, 0) and the (3, 3) nanotubes are metallic, the (4, 2) nanotubes are semiconducting with a small indirect band gap [40–42].

Figure 2 shows Raman spectra of the sample at different temperatures ranging from 83 to 733 K. Raman peaks of D and G bands explicitly shift to lower frequency upon increasing temperature. We also find the Raman intensity of these two modes becomes very weak when the temperature increases to 580 K. In figure 2, Raman signals above 580 K have been amplified. The result is very similar to that reported by Tang *et al* [43]. This may be related to the change in the structure of SWCNTs with temperature. In the following section, we will further discuss the detailed mechanism of temperature effects on Raman shifts of D and G bands.

Figure 3 shows Raman spectra of the sample in the region of D and G bands under three different laser energies. It is obvious that the peak position of the D band shifts to higher frequency upon increasing laser energy. This phenomenon has been well explained by the double resonance theory [35–38]. However, the most common process involved in Raman scattering is single resonance, which is based on the assumption that only Γ -point modes ($q \sim 0$) contribute to the scattering, and therefore frequency shifts of the modes should not depend on excitation energy, as for the Raman G band.

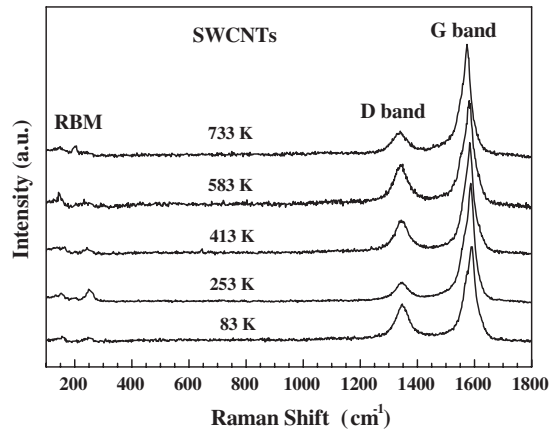


Figure 2. Raman spectra of the sample of SWCNTs taken in the temperature range from 83 to 733 K.

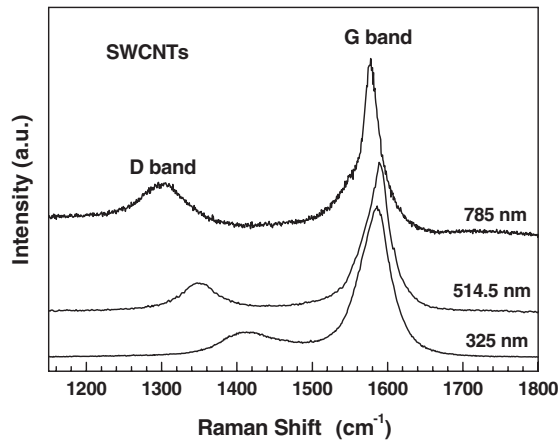


Figure 3. Raman spectra in the region of D and G bands of SWCNTs excited under three different laser energies.

4. Discussion

4.1. Temperature effects on anharmonic self-energy shifts of Raman D and G bands

In order to understand the origin of different frequency shifts of Raman modes upon increasing temperature, one may resort to the lattice dynamical theory of anharmonic crystals. Although detailed treatments of anharmonic lattice dynamics are very complex, involving the techniques of many-body theory, we can employ an approximate model for our present purpose. It is widely accepted that temperature-dependent Raman shift can be attributed to two effects, one being the thermal expansion or volume change and the other the optical-phonon anharmonic couplings to lower frequencies of acoustic phonons [25–27]. The Raman shift with temperature may thus be written in the following form:

$$\Delta(T) = \Delta^E(T) + \Delta^A(T). \quad (1)$$

The first term $\Delta^E(T)$ in the above equation represents the renormalized frequencies of independent harmonic oscillators in the dilated lattice as a result of the volume change from thermal expansion; the term is called a quasi-harmonic or pure-volume contribution as well. For SWCNTs, this term can be expressed as [26, 27]

$$\Delta^E(T) = \Omega_0 \exp\left\{-\gamma \int_0^T [2\alpha_r(T') + \alpha_a(T')] dT'\right\}, \quad (2)$$

where Ω_0 is the harmonic frequency of the optical mode; γ is the Grüneisen parameter of the LO phonon, which is an important thermodynamic parameter to study effects of pressure and temperature on the material physical and chemical characteristics. The temperature dependence of γ is unknown for SWCNTs. Therefore, we assume here that the parameter is independent of temperature and has a value of 1.24 for both D and G bands as given by [44]. Uncertainty introduced by this assumption will not significantly affect the discussion and conclusion [22, 45].

In equation (2), α_r and α_a are the coefficients of thermal expansion (CTEs) in the radial and axial directions of SWCNTs, respectively. Due to the limitation of the measurement condition in the nanoscale, there exist no experimental data for CTEs of individual SWCNTs. In present work, we take the theoretical value of CTEs of a (3, 3)-SWCNT [46]:

$$\alpha_r = -6.969 \times 10^{-8} + 1.180 \times 10^{-9}T - 3.409 \times 10^{-13}T^2 \quad (3)$$

$$\alpha_a = -1.169 \times 10^{-8} + 2.700 \times 10^{-9}T - 8.900 \times 10^{-13}T^2, \quad (4)$$

where the temperature T is in K and ranges between 0 and 2000 K.

The second term $\Delta^A(T)$ on the right-hand side of equation (1) is the pure-temperature contribution to the anharmonic self-energy shift, which arises from high-order anharmonicities in the crystal potential. It can be expressed as [26, 27]

$$\Delta^A(T) = M_1 \left[1 + \frac{2}{e^x - 1}\right] + M_2 \left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2}\right], \quad (5)$$

where M_1 and M_2 are fitting parameters, and $x = \hbar\omega_0/2k_B T$, $y = \hbar\omega_0/3k_B T$. The first term corresponds to coupling the optical phonon to two identical lower-energy phonons (three-phonon process), while the second term corresponds to coupling the optical phonon to three identical lower-energy phonons (four-phonon process). It should be pointed out that the transitions of optical-phonon couplings contributing to anharmonic self-energy shifts in equation (5) are not real transitions but virtual transitions. Ω_0 was fixed by $\omega_0 = \Omega_0 + M_1 + M_2$, where ω_0 is given by extrapolating the least-squares fitting result of the experimental data to 0 K.

In addition, the inter-tube interactions that arise in the lattice are usually assumed to be weak and are approximated by van der Waals interaction [9]; its influence on the temperature-dependent Raman shift is not considered in this work.

A good fitting to the experimental data has been obtained by using equations (1)–(5), as shown by the solid line in figure 4. It is noteworthy that in our work Raman shifts of these two modes do not show a linear decrease upon increasing temperature, which is different from previous reports [18, 20]. There is a total change of about 14 and 17 cm^{-1} within the whole temperature range for Raman shifts of D and G bands, respectively.

Figure 5 shows separately calculated contributions to frequency shifts of these two Raman modes with temperature by pure-volume and pure-temperature effects. Referenced values and fitting parameters are all listed in table 1. From this figure, one can easily find that the pure-temperature effect is much stronger than the pure-volume effect. At 800 K, the calculated results indicate that anharmonic optical-phonon couplings are very strong, and this effect surely makes a main contribution to temperature-dependent Raman shifts of D and G bands. However,

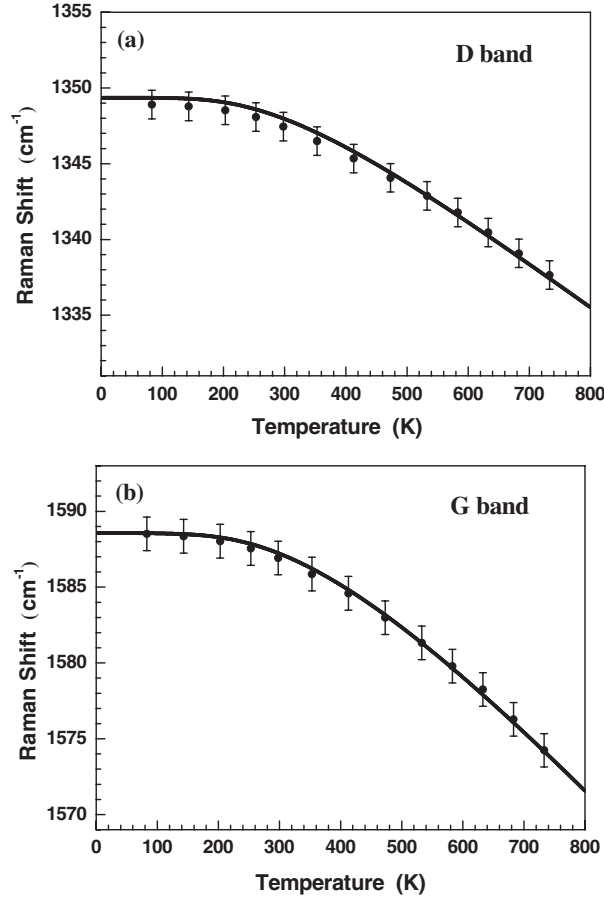


Figure 4. Raman shifts of (a) the D band and (b) the G band as a function of temperature. The circles represent the data measured from the experimental spectra in figure 2, and the solid line is a fitting result by using equations (1)–(5).

Table 1. List of parameters used in the calculation. The Grüneisen constant γ was taken from [44]. ω_0 was given by extrapolating the least-squares fitting result of the experimental data to 0 K. M_1 and M_2 were obtained by fitting frequency shifts of Raman D and G bands upon increasing temperature by using equations (1)–(5).

Raman mode	γ	ω_0 (cm ⁻¹)	M_1 (cm ⁻¹)	M_2 (cm ⁻¹)
D band	1.24	1349.4	-18.0 ± 0.8	0.8 ± 0.1
G band	1.24	1588.6	-25.0 ± 1.0	0.4 ± 0.1

the pure-volume effect is very weak within the temperature range; even at 800 K only ~ 2 cm⁻¹ of downshift is caused by this effect in both modes. This fact shows that the effect of volume change from thermal expansion is not remarkable for SWCNTs. Anharmonic terms of optical-phonon couplings always enter to higher order when expanding in the amplitude of the lattice vibrations. This result is first confirmed via an explicit calculation in our work.

One can also find that temperature effects on Raman D and G bands are almost negligible below 300 K, and this can be attributed to weak vibrations of carbon atoms and non-activated

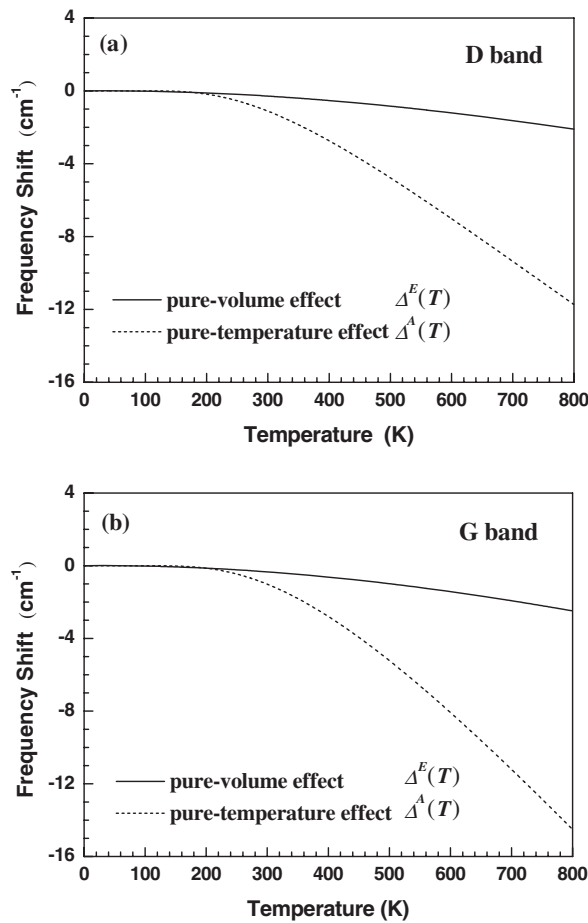


Figure 5. Calculated pure-volume $\Delta^E(T)$ and pure-temperature $\Delta^A(T)$ contributions to Raman shifts of (a) the D band and (b) the G band with temperature, respectively.

optical-phonon couplings at lower temperatures from the above discussions. In figure 4, if assuming the variation of Raman shift with temperature is approximately linear above 300 K, we can obtain that temperature coefficients of Raman shifts of D and G bands are about -0.025 and -0.029 $\text{cm}^{-1} \text{K}^{-1}$, respectively. The value of the D band is comparable to that of 4 Å diameter SWCNTs reported by Ye *et al* [47] and larger than those of large-sized tubes [17, 20]. Raman features of the G band are not significantly affected by the tube diameter due to the tangential vibration of carbon atoms. The value of G band is also comparable to previous reports, no matter what the tube diameter is [17, 20, 47].

4.2. Excitation energy effects on phonon linewidth of Raman G band and I_D/I_G ratio

Figure 6(a) shows the measured values of frequency shifts of the D band in this work and previously reported values for different carbon-related materials [31, 32]. The ratios at which the D band shifts are, however, comparable to each other, where 47.2 $\text{cm}^{-1} \text{eV}^{-1}$ is for SWCNTs, 46.4 $\text{cm}^{-1} \text{eV}^{-1}$ for glassy carbon and 51.3 $\text{cm}^{-1} \text{eV}^{-1}$ for polyparaphenylene. The carefully measured linewidth of G band is found to exhibit a linear broadening with a slope of

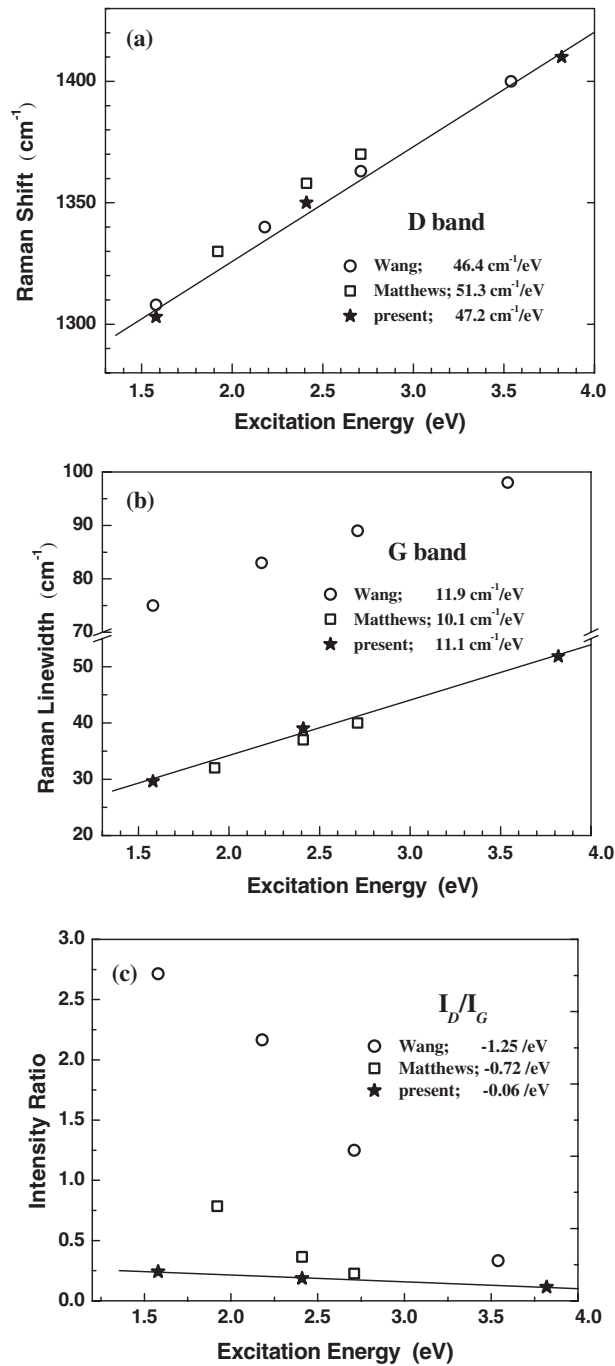


Figure 6. (a) Measured Raman shifts of the D band, (b) phonon linewidths of the G band, and (c) I_D/I_G ratios as a function of the excitation energy. Open circles and squares denote results measured from the experimental spectra of Wang *et al* [31] for glassy carbon and Matthews *et al* [32] for polyparaphenylene, respectively. The solid line is a linear fit to the experimental values. The numbers give the corresponding slopes for the data.

$11.1 \text{ cm}^{-1} \text{ eV}^{-1}$. This finding is quite interesting, and is also compared with previous works in figure 6(b), which shows the linear broadening of the G band has a quite close slope for the carbon-related materials.

The double-resonance theory cannot yet explain a hardening behavior of the linewidth of the G band upon increasing excitation energy. Nevertheless, it is known that the Kohn anomaly plays a key role in the behavior of phonon linewidths [15, 48, 49]. In this theory, electron–phonon coupling (EPC) is the major source of broadening for the Raman G band in graphite and carbon nanotubes. According to previous calculation results, there exists a simple inverse relationship between the linewidth of the Raman G band and the lifetime of electrons in SWCNTs [49]. So we suppose that the lifetime of electrons may decrease upon increasing the excitation energy. Consequently, this will lead to the broadening of the Raman G band.

In addition, we also measure the relative intensity ratios of the D band to the G band (I_D/I_G) as a function of temperature and excitation energy. There is no remarkable variation of the I_D/I_G ratio upon increasing temperature, so we do not present the result here. However, it is unexpected for us to find the I_D/I_G ratio exhibits a linear decrease upon increasing excitation energy. In order to confirm the validity of our observation, we further measure and analyze I_D/I_G ratios in other works [31, 32]. We present these interesting results in figure 6(c). Since it is known that the intensity ratio is taken as a measure of defect concentration in carbon nanotubes [36, 50, 51], we can conclude that the excitation energy has remarkable effects on the density of defects both in carbon nanotubes and in many carbon-related materials from our work.

In order to better characterize these phenomena, a further investigation based on the first-principle calculation of phonon density of states and electron–phonon interactions is a requisite.

5. Conclusions

In this work, the temperature and excitation energy dependences of Raman spectra of SWCNTs have been measured. Based on a theoretical model, we calculate the frequency shifts of D and G bands as a function of temperature. A good agreement between experimental observation and theoretical calculation confirms that the pure-temperature effect dominates the contribution to the temperature-dependent Raman shifts of D and G bands and the pure-volume effect is quite small within the experimental temperature range. Anharmonic optical-phonon couplings are much stronger at high temperatures. However, at low temperatures both effects are not remarkable. In addition, a linear broadening of the G band and a linear decrease of I_D/I_G ratio upon increasing excitation energy are also found in a variety of carbon-related materials. These results are discussed and compared with other research works.

Acknowledgments

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