Intrinsic and Extrinsic Effects in the Temperature-Dependent Photoluminescence of Semiconducting Carbon Nanotubes

D. Karaiskaj,* C. Engtrakul, T. McDonald, M. J. Heben, and A. Mascarenhas

Center for Basic Science, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401, USA
(Received 1 November 2005; published 16 March 2006)

The temperature dependence of the band gap of semiconducting carbon nanotubes was measured for ten different nanotube species. The unprecedented effectiveness in avoiding the effect of external strain, or any other effects originating from the surrounding environment, lead to an accurate measurement of the band gap temperature dependence, giving fundamental insight into the nanotube electron-phonon interaction. Small but reproducible energy shifts of the emission lines with temperature were observed, showing a moderate chirality dependence, well in agreement with recent theoretical calculations. In addition to the energy shift, a substantial narrowing of the emission lines was also observed. The removal of the temperature shift of the band gap allows the precise measurement of the effect of external strain on carbon nanotubes in different environments.

Although, the first experiments on the photoluminescence (PL) of single-walled carbon nanotubes (SWNTs) were interpreted in the context of the noninteracting electron model, it has now become increasingly clear that many-body interactions play an important role in determining the optical transition energies [1]. The effect of temperature on the PL electronic band gap E_g of carbon nanotubes has enormous importance in determining the role of the electron-phonon interactions [2]. The difficulty in experimentally determining the temperature behavior of the optical transitions of nanotubes lies in the surrounding environment. It is the encapsulation by the surfactant that avoids bundling and makes the PL of the nanotubes possible. While cooling the suspension can lead to strain effects, heating it can remove the surfactant molecules and lead to energy shifts due to rebundling. The first attempts of temperature studies on carbon nanotubes grown on silicon pillars have provided important insight into their temperature behavior [3] and how the environment, such as different inert gases, can affect their emission [4]. Other experiments have examined the effect of strain induced by the surrounding environment at low temperatures and the effect of hydrostatic pressure on the band gap of carbon nanotubes [5,6]. In order to ensure that the observed effects are solely due to the effect of temperature on the electronic band gap of the carbon nanotubes and not related to the surrounding environment, we take a different approach in the sample preparation. We carefully examine the temperature dependence of the band gap for ten different carbon nanotube species, and use these results to remove the temperature dependence and study purely the extrinsic effect of strain in a different environment.

Using a method similar to one previously reported in [7], the as-produced HiPco SWNTs (Carbon Nanotechnologies) were suspended in aqueous (D_2O) sodium dodecyl sulfate (SDS). In order to lower the freezing temperature down to 190 K, the aqueous suspension of SWNTs was mixed with glycerol (1:2 v/v). A second solution mixture was prepared using a different surfactant, namely, dodecylbenzenesulfonic acid (DDBS). An aliquot of the DDBS surfactant stabilized SWNTs was added to an Eastman *AQ*55 polymer solution (Eastman Chemical Company). The mixture was stirred and lyophilized resulting in a gray SWNT-*AQ*55 powder. The solution mixture or the polymer powder containing the nanotubes were mounted inside a variable temperature cryostat. The PL spectra were recorded using a grating spectrometer, equipped with a liquid nitrogen cooled InGaAs array detector. Several excitation energies were used, starting with 730 nm from a tunable continuous-wave Ti:sapphire laser, and 590 and 650 nm from tunable dye lasers. In order to identify the nanotube species present in the solution and the polymer, room temperature PL excitation (PLE) spectra were taken [8]. The PLE maps were collected using a tunable excitation source, a broad band tungsten lamp dispersed in a grating spectrometer, and the PL was detected using a Fourier-transform infrared spectrometer, equipped with a liquid nitrogen cooled germanium detector. The PLE spectra looked very similar in both the solution and the polymer. An energy shift was observed for the nanotube species between the two environments, most likely due to the change of the surrounding dielectric constant. The PLE maps revealed the excitation wavelengths needed to resonantly excite most of the nanotube species in order to increase their emission efficiency and avoid off-resonance effects.

Photoluminescence spectra from the SDS nanotube solution mixture with glycerol were recorded, starting at 297 K, and gradually cooling down to liquid helium temperature 4.2 K. Small blueshifts in the PL from the nanotube species were observed. These energy shifts are slightly different for different species, and they are reproducible after cooling down to 4.2 K and heating the solution back to room temperature. After decreasing the temperature below the freezing point of the solution, an abrupt shift in the PL energies could be observed as in-

dicated by the vertical lines in Fig. 1. The horizontal black arrow marked the point of the phase transition. The PL from the (7,5) species belonging to the $\nu = (n - m)\mathrm{mod}3 = 2$ family shifts stronger to higher energy with decreasing temperature, whereas for the (7,6) species, belonging to the $\nu = 1$ family, the shift reverses direction. The opposite shift of the two families has been attributed to the effect of strain on the nanotubes [5,9,10], and, in fact, the contraction induced by the ice phase transition could lead to uniaxial tensile strain. While the effect of strain will be discussed in more detail at a later point in this manuscript, the fact that no strain effect was observable at temperatures above 190 K, suggests that the energy shifts are most likely due to the shift of the electronic band gap with temperature. In order to exclude effects originating from the environment contacting the nanotube, a second solution with a different surfactant, namely, the DDBS surfactant mixed with glycerol, was studied under the same conditions. There is a constant energy shift in the emission lines due to the change of the dielectric constant of the surrounding surfactant, but the relative energy shifts with temperature were identical. Therefore, it appears that up to the freezing point of the solution, the environment does not affect the temperature dependence of the emission
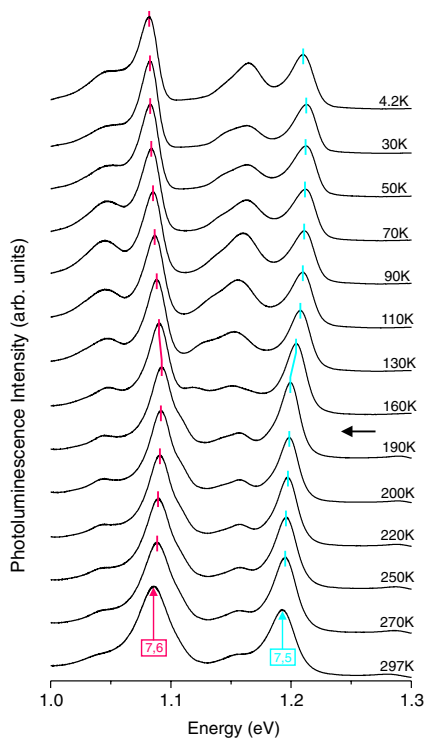

FIG. 1 (color online). Photoluminescence spectra of the carbon nanotubes in the SDS solution mixture for different temperatures from 4.2 to 297 K excited with the 650 nm source, resonantly with the (7,6) and (7,5) species. The nanotube species have been identified using the PLE spectra as described in Ref. [8]. The black arrow indicates the temperature range at which the ice phase transition occurs.

of the nanotubes. A substantial narrowing of the linewidths with decreasing temperature can be observed that, most surprisingly, persists beyond the ice phase transition of the solution all the way to 4.2 K. The largest line narrowing at low temperature is observed for the (7,6) tube. The full width at half maximum of 35.4 meV at 297 K is reduced by 48% to 20.6 meV at 4.2 K. This behavior indicates a very uniformly induced strain by the ice matrix, since random strains have the opposite effect leading to line broadening. In order to explain the temperature shifts of the photoluminescence transitions we follow the model introduced in Ref. [2]. The temperature dependence of the band gap at constant pressure can be separated into harmonic and anharmonic contributions: $(\partial E_g / \partial T) = (\partial E_g / \partial T)_{\mathrm{har}} + (\partial E_g / \partial T)_{\mathrm{anhar}}$. The harmonic term arises from the electron-phonon interaction, while the anharmonic term is due to the thermal expansion [11,12]. The contribution from the thermal expansion is smaller and can be neglected in the first approximation. The temperature dependence of the band gap can be obtained to first approximation by evaluating the harmonic term. The evaluation of the harmonic term is quite challenging, therefore, approximate models have been shown to be very useful tools in the evaluation of the temperature dependence of the band gap of solids [13].

We use an approximate model for E_g of semiconducting SWNT's in the temperature range of $T < 400$ K based on a two-phonon model introduced by Viña, Logothetidis, and Cardona [13] and successfully adopted to carbon nanotubes in Ref. [2], such that the parameters include diameter and chirality effects. This model provided an excellent fit to the simulations obtained by fully evaluating the harmonic term and the fitting parameters were listed. The same parameters are used to produce the theoretical curves for our experimental data. The theoretical curves together with the experimental measured values are shown in Fig. 2. For clarity, the carbon nanotube species are divided in two groups depending on their chiral angle θ. In Fig. 2(a) the carbon nanotube species with small and large chiral angles have been plotted together, whereas in Fig. 1 (b) those with intermediate chiral angles are shown. The magnitude of the shifts is larger than the previously reported values [4,14] and only a moderate chirality dependence was observed. It should be pointed out here that the temperature dependence of the band gap could be measured only between 200 K and room temperature. As a result, we have no experimental knowledge of the zero-Kelvin energy positions of the carbon nanotube species. The zero-Kelvin energy positions have been chosen arbitrarily such that the experimental data is aligned with the theoretical curves. The experimental points follow the theoretical curves reasonably well; i.e., the relative shift within this temperature range is well described by the theoretical curves. The large linewidths of the PL spectra, the overlap of different nanotube species, and the relative small shifts with temperature,
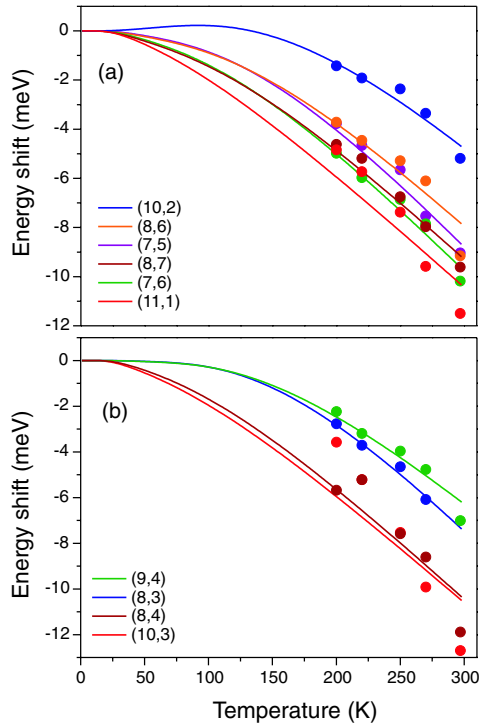
FIG. 2 (color online). Energy shift of the band gap of different nanotube species as a function of temperature. Lines are the energy positions calculated using the method introduced in Ref. [2] and dots are the experimental values. The carbon nanotube species have been divided in two groups: (a) nanotubes with large and small chiral angles, and (b) nanotubes with intermediate chiral angles.
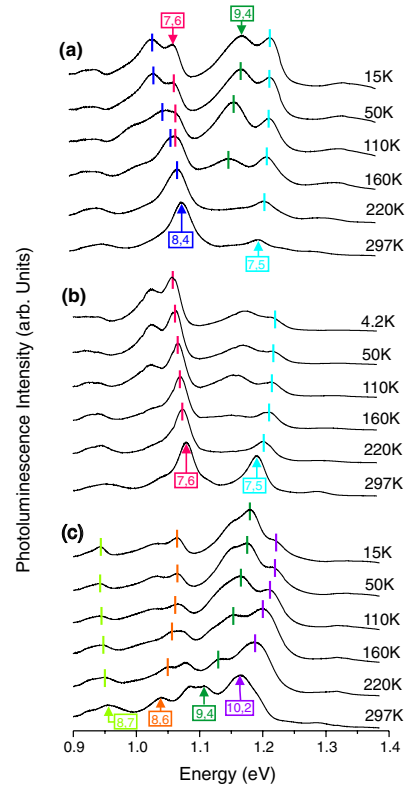

FIG. 3 (color online). Selected photoluminescence spectra of the polymer dispersed carbon nanotubes for three excitation wavelengths, (a) 590, (b) 650, and (c) 755 nm, resonant for specific tube species. The equally colored vertical lines mark the spectral position of the different nanotube species at different temperatures.

make it challenging to accurately determine the line position. Moreover, the ability to accurately control the temperature of the liquid is an additional factor leading to some experimental uncertainty.

In order to gain deeper insight into the intrinsic and extrinsic effects of temperature on the carbon nanotubes, we examined their behavior in a different environment. Selected PL spectra of the polymer dispersed nanotubes are plotted in Fig. 3 for the three excitation wavelengths. The spectra were collected in the temperature range of 1.8 up to 380 K and show significantly larger temperature shifts than the previous ones indicating a different mechanism. The energy shifts of the different species with temperature have been plotted in Fig. 4 where the low temperature end has been chosen as a reference. In order to be able to plot all species together and to highlight the behavior of each species, the low temperature (1.8 or 4.2 K) energy position has been subtracted and the energy shifts have been plotted as a function of increasing temperature. Different behaviors can be observed for the two nanotube families, similar to the behavior observed in the solution below the freezing temperature. While the $\nu = 1$ family shifts up in energy with increasing temperature, the $\nu = 2$ shifts down. This is a clear signature of strain, which

discriminates between the two nanotube families [9,10,15]. Previous studies on the stress dependence induced by cooling polymer wrapped carbon nanotubes have neglected the intrinsic temperature effect on the band gap of the nanotubes [5]. Here we used the calculated curves shown in Fig. 2 to obtain the energy shifts for the entire temperature range, and have subtracted these values in order to obtain the pure strain behavior. In Fig. 4 we show for the (7,6) and (8,6) tubes the shifts without removing the temperature dependence of the band gap (squares) and pure strain shifts (dots), marked by the lateral green arrows. After removing the temperature dependence of the band gap, the nanotube species are distributed symmetrically around the reference point (0 meV) as predicted by theory [9,15] and approach the expected linear behavior, giving additional support to the theoretical calculations of Ref. [2] for the entire temperature range. Moreover, within each family we have divided the nanotube species into two groups, labeled as A1, B1, A2, and B2, according to the magnitude of their band gap shift with strain. In both families it appears that larger chiral angle tubes, belonging to A1 and A2, are less affected by strain than the smaller chiral angle tubes, belonging to B1 and
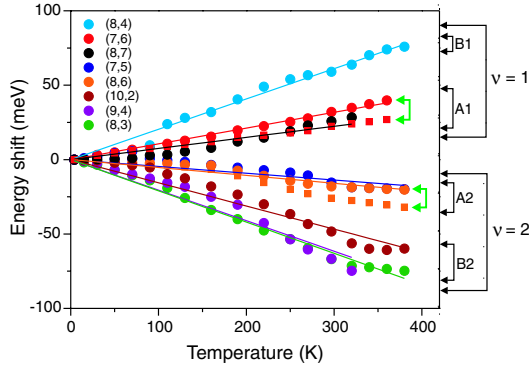
PHYSICAL REVIEW LETTERS

FIG. 4 (color online). Energy shift of the polymer dispersed carbon nanotube species with temperature. The behavior of the two nanotube families, $\nu = 1$ and 2, indicates strain induced by the wrapping polymer. The dots are the experimental line positions after removing the temperature shift of the band gap, the squares represent the line positions without removing the temperature shift, and the lines show the best fits to the experimental data.

B2. In order to understand the behavior of the different nanotube species under strain, we follow the theory of Yang and Han [9]. The band gap change under small strains is given by

$$\Delta E_g = \text{sgn}(2p + 1)3t_0[(1 + \eta)\sigma\cos(3\theta) + \gamma\sin(3\theta)],$$
(1)

where $p = -1$ for the $\nu = 2$ and $p = 1$ for the $\nu = 1$ family. t_0 and η are the carbon-carbon transfer integral and Poisson's ratio. Following the previous studies of carbon nanotubes under strain [5,9], $t_0 = 3.0$ eV and $\eta = 0.2$. σ and γ are the strains along the tube axis and circumference, corresponding to uniaxial and torsional strains on the nanotubes. The cosine factor ($0 < \theta < 30°$) in the uniaxial component of the energy shift leads to a decrease of the energy shift induced by the strain with increasing chiral angle θ. This indicates that the strain responsible for the shifts observed here is mostly uniaxial. Increasing tension or decreasing compression with increasing temperature are equivalent in Eq. (1), however, due to the expansion of the polymer with increasing temperature, increasing tension ($\sigma > 0$) is the most likely cause. It would be interesting to explore the effect of the torsional component of the strain, which due to the sine factor has a larger effect on the nanotubes with larger chiral angles, compensating to some degree the effect of the uniaxial component. An attempt to fit the data using fixed values for $\sigma = 1.979 \times 10^{-3}$ %/K and $\gamma = 0.453 \times 10^{-3}$ %/K lead to a relatively large error, although it improved the fit compared to using only the uniaxial component σ. An excellent fit was achieved using a constant uniaxial strain component $\sigma = 1.158 \times 10^{-3}$ %/K for all nanotube species and by varying the torsional component γ from 0.116×10^{-3} to 1.895×10^{-3} %/K. The values of γ obtained by the best

fits show a clear chiral angle dependence. They are larger for the smaller chiral angle nanotubes and are smaller for the large θ tubes, although the chiral angle dependence of the torsional component should be entirely expressed by the $\sin(3\theta)$ factor of Eq. (1). More elaborate theoretical models may be needed to better reproduce the strain behavior of the emission lines. Recent calculations [15] predict a (n-m) dependence with strain, which can be observed in our experimental data (Fig. 4) for the nanotube species (7,6) and (8,7), (7,5), and (8,6), and (9,4), and (8,3).

In conclusion, the temperature dependence of the band gap of semiconducting carbon nanotubes was measured in the range of 200 K to room temperature. Small and reproducible blueshifts of the emission lines with decreasing temperature were observed, showing only a moderate chirality dependence, in good agreement with the calculations presented in Ref. [2]. In addition to the energy shift, a substantial line narrowing was observed, that persisted all the way to 4.2 K. The effect of the temperature on the band gap was removed in order to examine the pure effect of strain on polymer wrapped nanotubes and a clear chirality dependence is observed, in agreement with the theory [9,15].

---

*Electronic address: Denis_Karaiskaj@nrel.gov
[1] C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, Phys. Rev. Lett. **92**, 077402 (2004).
[2] R. B. Capaz, C. D. Spataru, P. Tangney, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **94**, 036801 (2005).
[3] J. Lefebvre, P. Finnie, and Y. Homma, Phys. Rev. B **70**, 045419 (2004).
[4] P. Finnie, Y. Homma, and J. Lefebvre, Phys. Rev. Lett. **94**, 247401 (2005).
[5] L.-J. Li, R. J. Nicholas, R. S. Deacon, and P. A. Shields, Phys. Rev. Lett. **93**, 156104 (2004).
[6] J. Wu *et al.*, Phys. Rev. Lett. **93**, 017404 (2004).
[7] M. J. O'Connell *et al.*, Science **297**, 593 (2002).
[8] S. M. Bachilo *et al.*, Science **298**, 2361 (2002).
[9] L. Yang and J. Han, Phys. Rev. Lett. **85**, 154 (2000).
[10] L. Yang, M. P. Anantram, J. Han, and J. P. Lu, Phys. Rev. B **60**, 13 874 (1999).
[11] P. B. Allen and M. Cardona, Phys. Rev. B **23**, 1495 (1981).
[12] P. B. Allen and M. Cardona, Phys. Rev. B **27**, 4760 (1983).
[13] L. Viña, S. Logothetidis, and M. Cardona, Phys. Rev. B **30**, 1979 (1984).
[14] H. Htoon, M. J. O'Connell, P. J. Cox, S. K. Doorn, and V. I. Klimov, Phys. Rev. Lett. **93**, 027401 (2004).
[15] R. B. Capaz *et al.*, Phys. Status Solidi B **241**, 3352 (2004).