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K. P. Meletov ^a

^a Institute of Solid State Physics of RAS, Moscow region, Russia

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Intertubular Interaction in Bundled Single-Walled Carbon Nanotubes Studied by Raman Scattering at a High Pressure and Temperature

K. P. MELETOV

Institute of Solid State Physics of RAS, Moscow region, Russia

Raman spectra of bundled single-walled carbon nanotubes (SWCNTs) were measured at temperatures up to 730 K and pressures up to 7 GPa. The temperature- and pressure-induced shifts of Raman G_+ and G_- bands are reversible while the dependence of the relative to the ambient conditions frequency Ω/Ω_0 versus the inverse relative variation of the triangular lattice constant A_0/A shows that the dilatation constant is not compatible with the compressibility constant.

Keywords Carbon nanotubes, high pressure, Raman scattering

Introduction

The temperature dependence of the nanotube diameter and the expansion of the triangular bundle lattice were studied by X-ray diffraction. The thermal expansion coefficient for the tube diameter is negligibly small, while the expansion coefficient of the bundle lattice is larger than that of graphite in the c-axis direction (1). The *in-situ* X-ray diffraction study of bundled single-walled carbon nanotubes (SWCNTs) at high pressure up to 13 GPa has shown that the triangular bundle lattice continues to persist at least up to ~ 10 GPa as well as the reversibility of the two-dimensional lattice symmetry after pressure release (2). The variation of the two-dimensional triangular bundle lattice parameter A with pressure can be fitted to the one-dimensional analogue of the Murnaghan equation:

$$A/A_0 = \{(\beta/\beta_0)P + 1\}^{-1/\beta'} \quad (1)$$

where $\beta_0 = (43 \pm 4)$ GPa is the bulk modulus and $\beta' = 33 \pm 3$ is its pressure derivative (2). These values are close to the first-principles calculations of the bulk modulus of bundled SWCNTs (3).

The Raman study and molecular dynamics simulations of bundled SWCNTs have shown the important role of the van der Waals interaction in the softening of the G band at high temperature, while the radial expansion of tubules is negligible (4). The Raman study of bundled SWCNTs at high pressure up to 40 GPa has shown a reversible sub-linear pressure shift of the G-band (5). Earlier Raman studies at high pressure have shown the change in the linear pressure shift of the G-band near ~ 2 GPa that was interpreted as a possible phase transition of the bundle lattice (6,7). In the present paper, we have measured

Address correspondence to K. P. Meletov, Institute of Solid State Physics of RAS, 142432 Chernogolovka, Moscow region, Russia.

the Raman spectra of bundled SWCNTs at temperatures up to 730 K and pressures up to 7 GPa in order to compare the G-mode shift under lattice expansion/contraction and to study the van der Waals inter-tubular interaction.

Experimental Details

The starting SWCNT material was synthesized by the arc discharge evaporation method in helium atmosphere at a pressure of 0.86 bar using a metallic Ni/Y catalyst. A purification method, based on the multi-step oxidation in air and reflux in HCl, resulted in a ~ 90 wt% content of SWCNTs. No surfactants were applied during the purification procedure. The main impurities were graphite particles of the order of 2–4 μm , and the total content of metal impurities was $\sim 1.3\%$. The purified SWCNTs were annealed in vacuum at 873 K for 5 hours. The average diameter of the nanotubes was 1.5 nm, as it follows from the preparation method, the TEM and Raman characterization. Raman spectra at high pressure and high temperature were recorded using spectrograph Acton SpectraPro-2500i equipped with the CCD Pixis2K cooled down to -75°C . The 514.5 nm line of an Ar^+ laser was focused on the sample by means of a fiber and an Olympus 50 \times objective in a spot of ~ 10 μm diameter, the scattered laser line was suppressed by super-notch filter with suppression efficiency $\text{OD} = 6$ and bandwidth ~ 160 cm^{-1} , while the beam intensity before the sample was ~ 5 mW. The measurements at high pressure were performed by the use of a diamond anvil cell (DAC) of Mao–Bell type, and the 4:1 methanol/ethanol mixture was used as the pressure-transmitting medium. For the high temperature measurements, a homemade high temperature cell was used with a temperature controller that maintained temperatures up to 750 K with an accuracy of ± 2 K.

Results and Discussion

The main bands in the Raman spectrum of SWCNTs at ambient conditions are the radial breathing modes (RBM) and the tangential C–C stretching vibrations mode that splits to the G_- (circumferential for a semiconducting tube component, 1568 cm^{-1}) and to the G_+ (axial for a semiconducting tube component, 1591 cm^{-1}) bands. The G_- mode frequency refers to tubes of ~ 1.5 nm in diameter. The frequency of this band becomes slightly smaller when the tube diameter decreases significantly whereas the G_+ mode frequency does not depend on the tube diameter. Figure 1 depicts the Raman spectra of bundled SWCNTs in the region of the G_+ and G_- modes at high temperature up to 730 K (a) and high pressure up to 7 GPa (b).

The temperature and pressure dependencies of the G_- and G_+ mode frequencies, obtained by fitting Voigt functions to the experimental Raman spectra of bundled SWCNTs, are shown in Figures 2a and 2b, respectively. Open (closed) symbols show data for the increase (decrease) of temperature or pressure. The temperature dependence is reversible; the data for both temperature runs coincide within experimental error. As is expected from the anharmonic nature of the van der Waals interaction, the temperature shift dE/dT is negative and is practically the same for the G_- ($dE/dT = -0.0230 \pm 0.0007$ cm^{-1}/K) and G_+ ($dE/dT = -0.0229 \pm 0.0002$ cm^{-1}/K) bands. These data indicate that there are no detectable changes in the tube diameter upon heating of SWCNT bundles, as the difference of the G_+ and G_- band frequencies does not change with temperature. The pressure shift dE/dP is positive and reversible for both bands. The pressure shift is linear up to ~ 3 GPa; at higher pressure some deviation from the linear dependence is observed. The pressure coefficients of the linear shift dE/dP are 7.11 ± 0.29 $\text{cm}^{-1}/\text{GPa}$ for the G_- band and 6.65 ± 0.22 $\text{cm}^{-1}/\text{GPa}$ for the G_+ band.

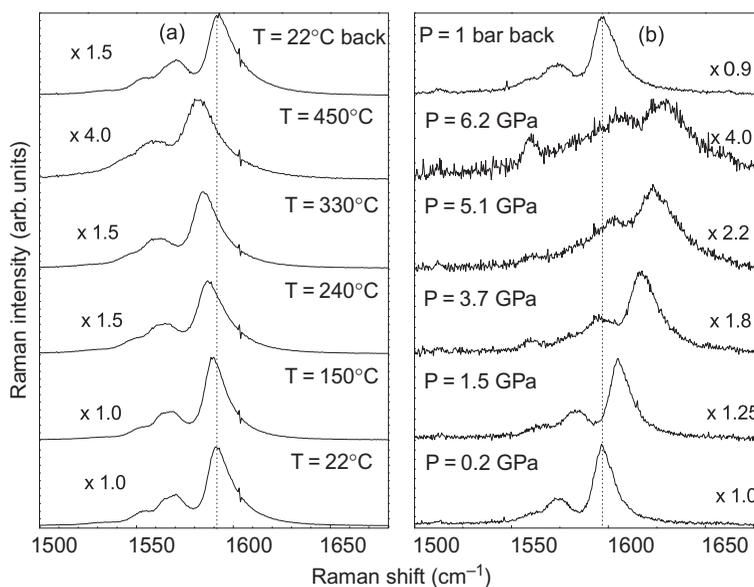


Figure 1. Raman spectra of bundled SWCNTs in the region of the G_+ and G_- bands at high temperature (a) and high pressure (b). Vertical lines show the position of the G_+ band at ambient conditions.

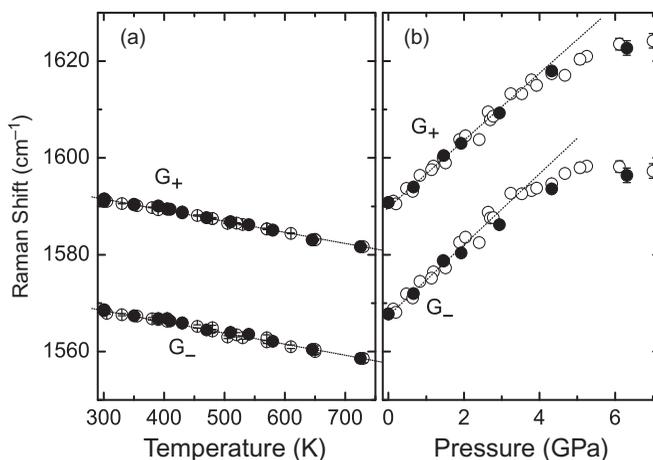


Figure 2. (a) Temperature dependence of the G_+ and G_- band frequencies at ambient pressure. (b) Pressure dependence of the G_+ and G_- band frequencies at room temperature. Open (closed) symbols show the increase (decrease) temperature or pressure runs.

Similar changes in the slope of the linear pressure shift were observed near 2 GPa in (6,7), whereas the measurements in the extended pressure range up to 40 GPa have shown a smooth sub-linear dependence. It is interesting to note that near 3 GPa the G_- and G_+ bands broaden considerably, making the accurate determination of their position rather difficult. In addition, SWCNT bundles under compression show a marginal decrease in the frequency difference between the G_+ and G_- bands, whereas possible pressure-induced decrease of the tube diameter should result in an increase of this difference.

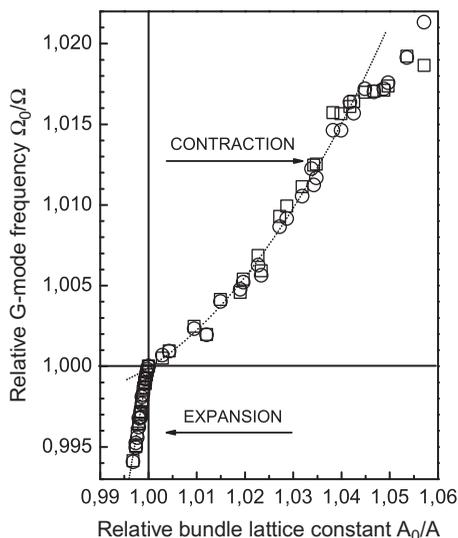


Figure 3. The dependence of the relative to ambient conditions frequency Ω/Ω_0 for the G_- (squares) and G_+ (circles) bands on the inverse relative triangular lattice constant A_0/A . Lower left part – expansion, upper right part – compression of the bundle lattice.

Based on our Raman data and using the linear compression and dilatation constants, obtained by X-ray diffraction (1,2), we have calculated the dependence of the relative to ambient conditions frequency Ω/Ω_0 for the G_- and G_+ bands on the inverse relative triangular lattice constant A_0/A . These results are shown in Figure 3, where the left lower part refers to the heating run and the right upper part refers to the compression run. The squares and circles denote G_- and G_+ band frequencies, respectively. Note that the slope of the linear dependence for the heating run is quite different from the slope of the linear dependence for the compression run. This suggests that the dilatation constant determined by the X-ray diffraction measurements at high temperature (1) is underestimated and not compatible with the compressibility constant (2). The compressibility data (2) appear more reliable as they were confirmed by independent X-ray diffraction measurements and numerical calculations (3). Finally, the dependence of the G mode relative frequency on the inverse relative triangular lattice constant is super-linear, in agreement with the nature of the van der Waals inter-tubular interaction.

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