

Pressure and polarization-angle dependent Raman spectra of aligned single-wall carbon nanotubes in AlPO_4 -5 crystal channels

P. M. Rafailov*, J. Maultzsch*, M. Machón*, S. Reich*, C. Thomsen*,
Z. K. Tang†, Z. M. Li† and I. L. Li†

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

†*Department of Physics and Institute of Nano Science and Technology, Hong Kong University of
Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China*

Abstract. We investigated aligned single-wall carbon nanotubes (SWNTs) with small diameters ($\approx 4 \text{ \AA}$) grown in AlPO_4 -5 crystal channels. The phonon frequencies of the band at $\approx 1600 \text{ cm}^{-1}$ were studied as a function of applied external pressure. We analyze the obtained pressure dependences in terms of the elastic continuum model. Polarized Raman spectra at different wavelengths were taken at different angles of the electric field polarization vector with respect to the nanotube axis. We found the scattering intensity to be at maximum for laser light polarized parallel to the channel direction while it is highly suppressed for polarization perpendicular to the channels. This is consistent with a resonant absorption as a first step in the Raman scattering process and only $A_{1(g)}$ symmetry scattering.

Introduction. The synthesis of SWNTs within zeolite crystals (SWNT@Zeolite) created a new opportunity to fabricate samples of aligned nanotubes with controlled diameters [1, 2]. That is why Raman spectroscopy is a highly appropriate tool for their investigation as aligned and mono-sized free-standing nanotubes are still difficult to obtain. On the other hand, most of the established results on SWNT@Zeolite, especially the polarization properties, will still be valid for free-standing SWNTs with bigger diameters thus offering a useful criterion for comparison.

In this work we examined the high-energy (bond-stretching) Raman band in SWNTs with applying hydrostatic pressure and in different polarization geometries. The measured SWNTs were grown in the $\approx 1 \text{ nm}$ - sized channels of an AlPO_4 -5 single crystal (AFI) by pyrolysis of tripropylamine (TPA) [1]. For the pressure measurements a small piece ($\approx 80 \times 50 \times 30 \text{ \mu m}$) of an AFI crystal containing SWNTs was put into a gasketed diamond-anvil cell [3]. Using a 4:1 methanol-ethanol mixture as pressure medium we obtained pressures up to 8 GPa as determined by the ruby-luminescence method. The Raman spectra were recorded with a DILOR triple grating spectrometer equipped with a CCD detector. The 488 and 514.5 nm lines of an Ar^+/Kr^+ laser were used for excitation, the spectral resolution was 6 cm^{-1} .

The effect of pressure. Figure 1 shows the shift of the bond-stretching Raman band upon external hydrostatic pressure. The band can be well fitted with two Voigt peaks.

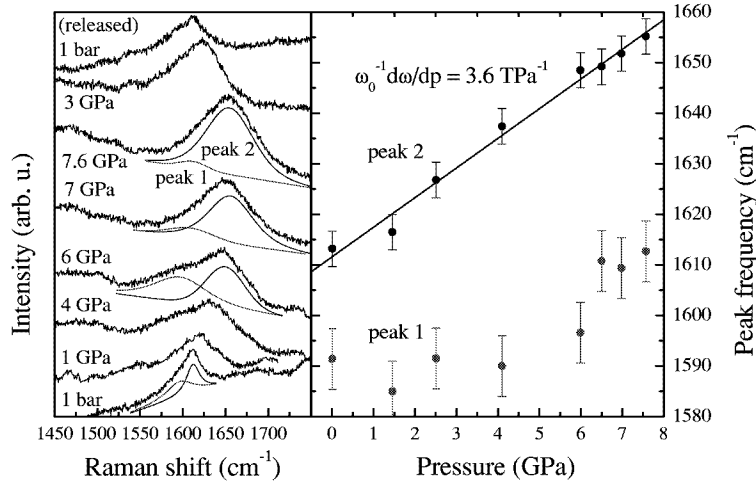


FIGURE 1. The bond-stretching Raman band fitted with two Voigt peaks as measured at several hydrostatic pressures (*left*) and the pressure dependence of the two components (*right*)

Only peak 2 exhibits a well-defined linear pressure dependence of $\omega_0^{-1}d\omega/dp = 3.6$ TPa^{-1} . This is close to the value measured for the main peak at 1593 cm^{-1} in the high-energy band of free-standing SWNTs (3.8 TPa^{-1})[4] which has been assigned to semiconducting tubes. Both peak 1 and 2 show significant broadening and peak 1 loses its intensity with increasing pressure unlike the peaks at the low-frequency flank in the high-energy band of free-standing SWNTs which preserve their intensity up to 10 GPa.

We analyse this pressure dependence with our elastic continuum model previously developed to describe the behavior of free-standing SWNTs upon applied hydrostatic pressure. In the present case however this is only a rough approximation because the external hydrostatic pressure is not uniformly transferred to the nanotubes due to the AFI anisotropy. The AFI channels themselves are strained more in circumferential than in axial direction. Thus the circumferential strain of a nanotube will increase more in comparison to the axial one.

For a homogeneous deformation the expected dependence of the phonon frequency on the strain (ω_0 at ambient pressure) is [4]:

$$\frac{p}{\omega_0} \frac{d\omega}{dp} = \gamma(\epsilon_{zz} + \epsilon_{\theta\theta}) \pm \frac{1}{2}SDP(\epsilon_{zz} - \epsilon_{\theta\theta}), \quad (1)$$

where γ is the Grüneisen parameter and SDP is the shear deformation potential.

The elastic continuum model reveals the strains ϵ_{zz} in axial and $\epsilon_{\theta\theta}$ in circumferential direction as expressed by the inner and outer radii R_i and R_o of the nanotube, Poisson's ratio ν , Young modulus E and the applied pressure p [5]:

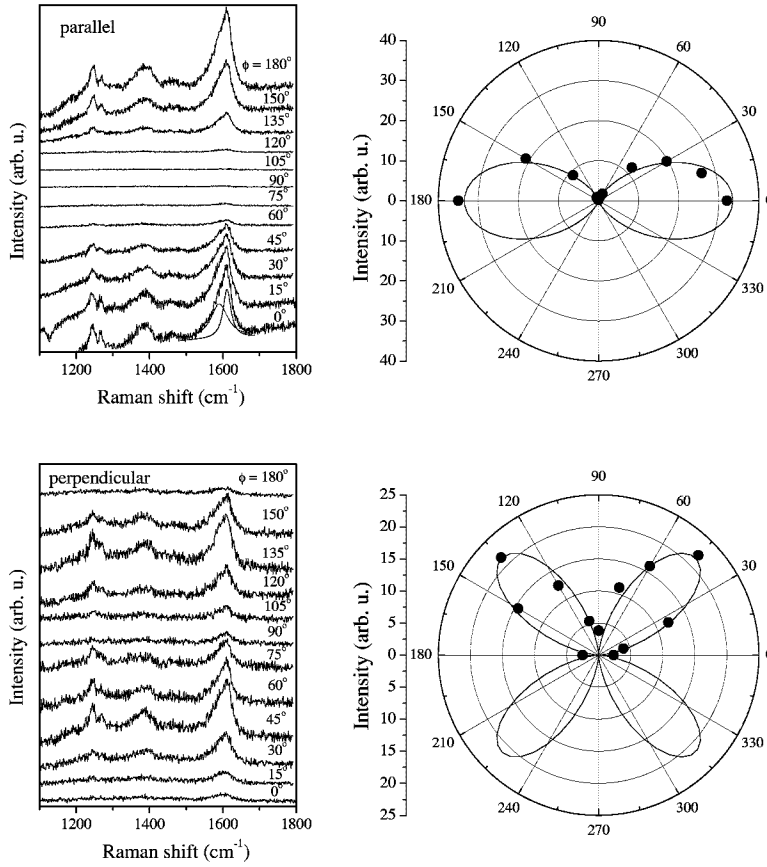


FIGURE 2. Upper panel: Raman spectra for parallel polarization of incoming and outgoing light at different angles ϕ between the polarization direction and the tube axis (*left*) and a polar graph of the Raman intensity as a function of ϕ . The solid line is proportional to $\cos^4(\phi)$ (*right*). **Lower panel:** Same as above, but for crossed polarization of the incoming and outgoing light. The solid line is proportional to $\cos^2(\phi) \sin^2(\phi)$.

$$\epsilon_{\theta\theta} = -\frac{pA v^-}{E} \left(1 + \frac{v^+ R_i^2}{v^- r^2} \right) \quad \text{and} \quad \epsilon_{zz} = -\frac{pA v^-}{E}$$

with $A = R_o^2 / (R_o^2 - R_i^2)$, $v^+ = 1 + v$ and $v^- = 1 - 2v$

Using $r = 4.1 \text{ \AA}$ [2], $\omega_0^{-1} d\omega/dp$ of peak 2 and assuming a nanotube wall thickness of 3.4 \AA we obtain $\gamma \approx 1.4$. This is consistent with the value 1.24 for 1 nm - diameter SWNTs and graphene (1.59) [4].

Polarized Raman measurements. Figure 2 shows the Raman intensity as function of the angle ϕ between the excitation polarization direction and the tube axis. It is

obvious that the intensity of the Raman scattering follows a \cos^4 -dependence on ϕ in the parallel polarization and a $\cos^2(\phi)\sin^2(\phi)$ -dependence in the perpendicular one. This holds not only for the graphitic bond-stretching band at $\approx 1600\text{ cm}^{-1}$, but also for the bands at $\approx 1400\text{ cm}^{-1}$ and 1250 cm^{-1} , the latter being associated with the graphitic disorder (D) mode. Actually, these modes originate from quite different regions of the SWNT 1D Brillouin zone. The same polarization-angle dependences were established by Gommans *et al.* [8] for free-standing aligned SWNT ropes. On the other hand, a \cos^2 -dependence of the optical absorption was recently measured by Li *et al.* [7] for small diameter SWNT in AFI crystals. Consequently the Raman intensity follows the optical absorption profile which is consistent with a resonant scattering process and a Raman tensor of $A_{1(g)}$ symmetry with zz being the only non-vanishing component [8, 9] for all of the observed Raman modes.

In summary, we performed pressure and polarization-angle dependent Raman measurements on aligned SWNT of $\approx 4\text{ \AA}$ in diameter confined in AFI crystal channels. From the overall hydrostatic shift of the frequency of the high-energy band under pressure we estimated a Grüneisen parameter of ≈ 1.4 in good agreement with values obtained for free standing SWNTs and graphite. Our polarization dependent measurements show that the Raman intensity reflects the optical absorption profile. This is consistent with a resonant Raman process as well as with an $A_{1(g)}$ symmetry of the observed Raman modes.

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