POLARIZED RAMAN MEASUREMENTS IN ZEOLITE-GROWN SINGLE-WALL CARBON NANOTUBES

J. Maultzsch*, P. M. Rafailov, M. Machón, S. Reich, and C. Thomsen

Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin,
E-Mail: janina@physik.tu-berlin.de

The Raman spectra of carbon nanotubes are still being controversely discussed, despite the numerous studies in this field. Tubes with similar diameter but different chirality can have significantly different electronic and vibrational properties. Therefore, Raman measurements on tubes with known chirality and diameter are desirable. Tang *et al.* were able to grow carbon nanotubes inside the channels of an $AlPO_4$ zeolite crystal [1]. The directions of the tube axes are well defined by the parallel alignment of the zeolite channels. The diameter of the tubes is approximately 0.4 nm, which restricts the number of possible chiralities to three: (3,3), (5,0), and (4,2).

We performed polarization dependent Raman experiments at different laser wavelengths on the zeolite-grown nanotubes. In addition, we calculated the electronic band structure, the optical absorption, and the phonon dispersion relations of the three tubes by first principles calculations.

The structure and the electronic dispersion of the (3,3), (5,0), and (4,2) nanotube we calculated within the local density approximation to density functional theory as implemented in the SIESTA *ab initio* packet [2]. For the valence electrons we used a double-ξ, singly polarized basis set of atomic-like orbitals with cutoff radii around 5 a.u.; grid integrations were performed with a cutoff of 270 Ry. The phonon dispersion we obtained from a finite difference approach, i.e., by successively displacing the carbon atoms in the unit cell within an 1x1x5 supercell and setting up the dynamical matrix from the induced forces. The frequencies of the Γ point vibrations are strongly shifted to lower frequencies (by at least 50 cm^{-1}) when compared to graphene (1630 cm^{-1} in our calculation). This trend—a softening of the force constants by curvature in the $d \approx 0.4$ nm tubes—is expected both from second order Raman experiments and from other *ab initio* calculations [3,4]. The strongest red shift we found for the (3,3) nanotube where the circumferential A_{1g} and the axial A_{1u} phonon mode are at 1492 and 1460 cm^{-1}, respectively (see Fig. 1). In contrast, the high-energy peaks in the experimental spectrum are around 1610 cm^{-1}, i.e., well above the energy of the graphite optical mode and even higher than in standard nanotube samples with diameters between 1 and 1.5 nm.

We compare the results of the experiments with our calculations in terms of (double) resonant Raman scattering. The measured Raman intensity as a function of laser energy reflects the calculated optical absorption profile. Corresponding to the high optical absorption for light polarized parallel to the tube axis, we find the strongest Raman signal for a scattering configuration with both incoming and outgoing light polarized parallel to the tube axis. Due to a double-resonant scattering process, the observed Raman frequencies correspond to a convolution of the phonon dispersion relation with the electronic band structure. Moreover, phonon wave vectors, which are larger when compared to the wave vector of the incoming and outgoing light are involved in the double resonant process. The measured high-energy modes between 1580 and 1610 cm^{-1} are in excellent agreement with the highest values of the calculated $A_{1(g)}$ phonon frequencies – in part inside the Brillouin zone.

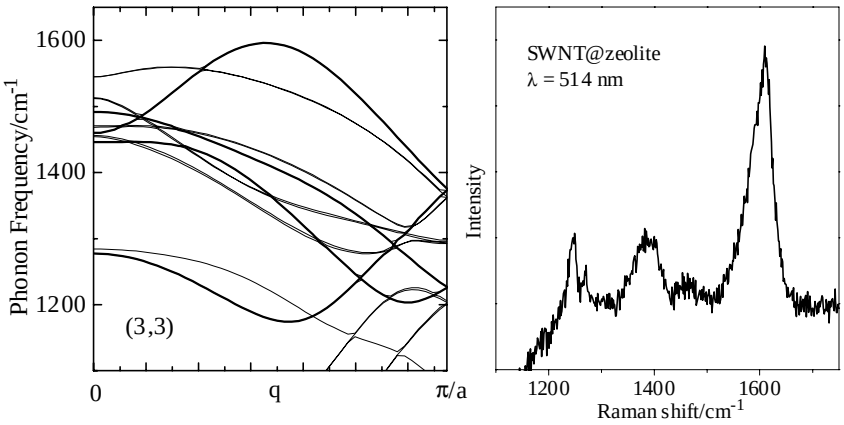

Fig.1: Calculated phonon dispersion relation of the (3,3) tube (*left*). The two non-degenerate optical branches are indicated by the bold lines. The Γ-point frequency of the vibration along the tube axis is at 1460 cm^{-1}, leading to a strong overbending of the branch up to 1600 cm^{-1}. *Right:* High-energy Raman spectra of zeolite-grown carbon nanotubes with the incoming and outgoing light polarized parallel to the tube axis.

1. Z.K. Tang, H. D. Sun, J. Wang, J. Chen, and G. Li, Appl. Phys. Lett. **73** (16), 2287 (1998).
2. D. Sánchez-Portal, P. Ordejón, E. Artacho, and J. M. Soler, Int. J. Quantum Chemistry **65**, 453 (1997).
3. C. Thomsen, Phys. Rev. B **61**, 4542 (2000).
4. D. Sánchez-Portal, E. Artacho, J. M: Soler, A. Rubio, and P. Ordejón, Phys. Rev. B **59**, 12687 (1999).