Pressure-induced phenomena in single-walled carbon nanotubes

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1 Introduction

Single-walled carbon nanotubes (SWNTs) attract much interest not only because of their numerous possible applications, but also since they are model systems for one-dimensional physics. The investigation of SWNTs under high pressure is particularly interesting as one can induce structural deformations of the SWNTs and study their effect on the electronic, vibrational, and mechanical properties. Furthermore, one can tune the distance between the SWNTs by the application of pressure and hence study the influence of intertube interactions. In a previous pressure-dependent study it was found that the absorption spectra of films of unoriented SWNTs are very sensitive to the application of pressure [1]: with increasing pressure up to 4.1 GPa a broadening and reduction in intensity of the absorption features were observed. It could, however, not be clarified, whether these changes are due to an enhanced intertube interaction or a structural deformation of the bundled SWNTs induced by pressure. In an attempt to answer these open questions, we studied the optical response of thin films of both unoriented and oriented SWNTs as a function of pressure up to 8 GPa. From the polarization-dependent optical response of the oriented SWNT films under pressure we could furthermore infer how the anisotropy of the optical properties changes with pressure, and whether a dimensional crossover of this highly anisotropic system from one to two dimensions is induced above a certain pressure.

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2 Experiment

The SWNTs were synthesized by laser ablation and purified to remove impurities and defects [2, 3]. Free-standing films of unoriented SWNTs (tube diameter range 1.2−1.4 nm) were prepared as described in Ref. [2]. For the preparation of aligned films, the SWNTs (average tube diameter 1.4 nm) were embedded in a polyethylene matrix, and the nanotube alignment was achieved by mechanical stretching of the SWNT/polymer composite [3].

The pressure-dependent transmittance measurements were performed at room temperature using a Bruker IFS 66 v/s spectrometer with an infrared microscope (Bruker IRscopeII). Part of the measurements was carried out at the infrared beamline of the synchrotron radiation source ANKA in Karlsruhe. The pressure (up to 8 GPa) was generated by a diamond anvil cell (DAC) and the ruby luminescence method was used for pressure determination [4]. The transmittance spectra were recorded over a broad frequency range, from the infrared up to the visible: A piece of SWNT film with a size of about 100×100 µm was placed inside the DAC, and the DAC was then filled with liquid argon which served as the pressure transmitting medium; the intensity $I_s(\omega)$ of the radiation transmitting the SWNT film was measured [see inset of Fig. 1(b) for the measurement scheme]. For obtaining the reference, the incoming beam was focused next to the SWNT film in the DAC and the intensity $I_r(\omega)$ transmitted by the argon was recorded. The transmittance was then calculated according to $T(\omega) = I_s(\omega)/I_r(\omega)$. The absorbance is given by $A = \log_{10}(1/T)$. For the oriented SWNT films the polarization-dependent transmittance spectra were measured.

3 Results and discussion

The absorbance spectrum in the midinfrared to visible frequency range [see Fig. 1(a)] of the unoriented SWNT film consists of four absorption bands, denoted by S_{11}, S_{22}, M_{11}, and S_{33}, superimposed on a broad $\pi-\pi^*$ absorption feature (centered at ≈ 5 eV) due to the bulk properties of SWNTs [1]. The four absorption bands can be assigned to optical transitions between the Van Hove singularities of the density of states of the SWNTs [5]: The bands denoted by S_{11}, S_{22}, and S_{33} correspond to electronic transitions between the first, second, and third pair of singularities in semiconducting SWNTs, and the band denoted
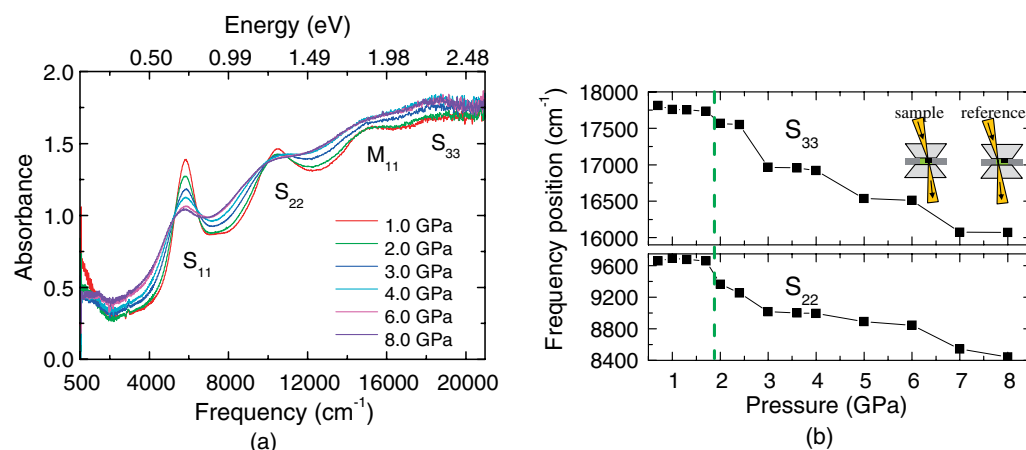

Fig. 1 (online colour at: www.pss-b.com) (a) Absorbance spectra for the film of unoriented SWNTs as a function of pressure. S_{11}, S_{22}, and S_{33} denote the absorption bands corresponding to the optical transitions between the Van Hove singularities of the density of states of semiconducting SWNTs, while M_{11} denotes the corresponding absorption band in metallic SWNTs. (b) Frequency positions of the optical transitions S_{22} and S_{33} as a function of pressure, extracted from the absorbance spectra by Lorentz fitting. The vertical dashed line indicates the pressure of the structural phase transition.

by M_{11} can be assigned to the electronic transition between the first pair of singularities in metallic SWNTs. With increasing pressure the absorption bands shift to lower frequencies and broaden [Fig. 1(a)]. However, they can be clearly observed up to the highest applied pressure (8 GPa), in contrast to Ref. [1]. In order to determine the frequency positions of the bands, a linear background due to the $\pi-\pi*$ absorption was subtracted and the resulting spectra were fitted with Lorentzian functions (more details on the analysis of the data will be published in a forthcoming paper [6]). In Fig. 1(b) we present the frequency positions of the S_{22} and S_{33} optical transitions as a function of pressure, as examples. Up to about 2 GPa the frequency positions are hardly affected by the pressure application. However, above 2 GPa the bands shift to lower frequencies with increasing pressure.

Figure 2(a) shows the absorbance spectra of the oriented SWNT film for the polarization $\boldsymbol{E}$ along and perpendicular to the nanotube axis. The sharp absorption features for both polarizations below 5000 cm^{-1} are due to vibrational excitations in polyethylene and no intrinsic property of the SWNTs. In accordance to our findings for the unoriented SWNT film, the three absorption bands for the polarization $\boldsymbol{E} \parallel$ tubes are attributed to the optical transitions in semiconducting (S_{11}, S_{22}) and metallic (M_{11}) SWNTs. For $\boldsymbol{E} \perp$ tubes these transitions are suppressed, in agreement with the selection rules [7−9]. Each absorption band is split into two components, which might be due to the diameter distribution of the SWNTs in the film. A similar splitting, however less obvious, is also found for the unoriented SWNT film [6]. Like for the unoriented SWNT film, the absorption bands of the oriented SWNTs shift to lower frequencies and broaden with increasing pressure. The pressure dependence of the frequency positions of the bands is shown in Fig. 2(b). For the components of the S_{11} band one observes an anomaly at around 2 GPa. For
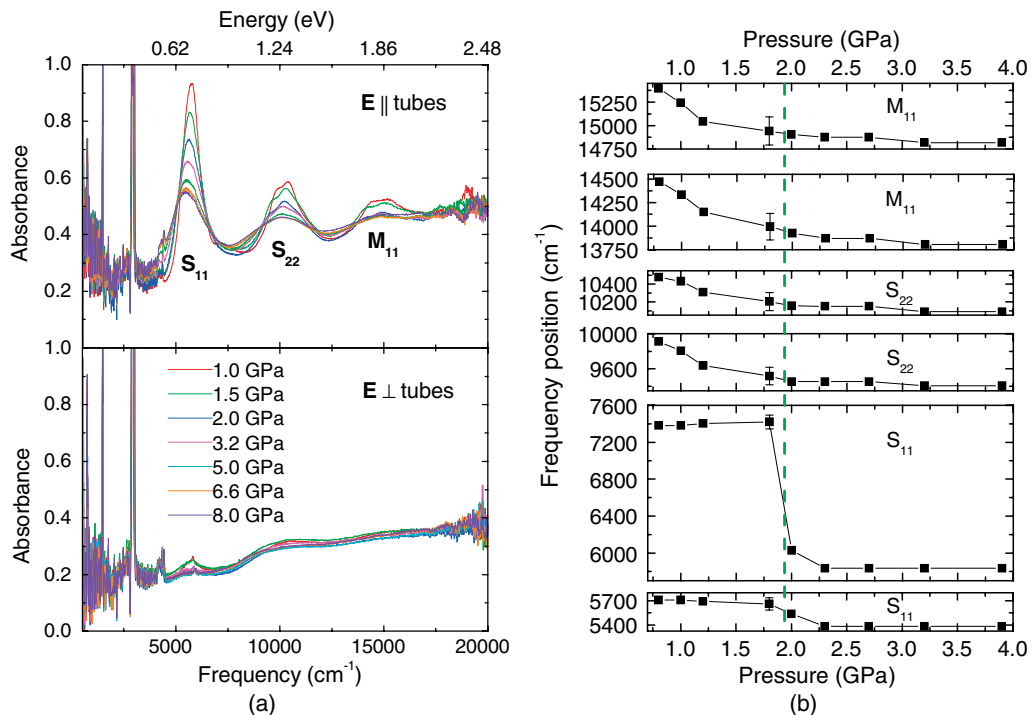

Fig. 2 (online colour at: www.pss-b.com)   (a) Polarization-dependent absorbance spectra for the film of oriented SWNTs as a function of pressure. S_{11} and S_{22} denote the optical transitions between the Van Hove singularities of the density of states of semiconducting SWNTs, while M_{11} denotes the corresponding optical transition in metallic SWNTs. (b) Frequency positions of the optical transitions for the polarization $\boldsymbol{E} \parallel$ tubes as a function of pressure, extracted from the absorbance spectra by Lorentz fitting. The vertical dashed line indicates the pressure of the structural phase transition.

the other bands an anomaly in the frequency position is less obvious. In summary, one finds an overall agreement in the pressure dependence of the electronic structure for films of oriented and unoriented SWNTs.

The expected pressure-induced changes in the properties of SWNTs are (i) a decreasing distance between the SWNTs and thus an increasing intertube interaction, and (ii) a deformation of the cross-section of the SWNTs [10]. Pressure-dependent Raman experiments [11, 12] found anomalies in the Raman shifts of the radial breathing mode and the tangential modes of SWNTs at around 2 GPa. These were attributed to a structural phase transition, in agreement with theoretical calculations [10, 11]. Our observation of anomalies in the pressure dependence of the optical transitions at the same pressure (≈ 2 GPa) therefore evidences that the structural phase transition significantly affects not only the lattice dynamics but also the electronic properties of SWNTs. The pressure-induced changes of the absorption bands (shift to lower frequencies, broadening) resemble those observed for debundled SWNTs studied for low pressures (<1.1 GPa) [13] and could therefore be attributed to the structural deformation of the SWNTs, at least in the low-pressure range [6]. In the case of aligned SWNTs, one expects the occurrence of a pressure-induced crossover from a one-dimensional to a two-dimensional character, which should strongly alter the polarization-dependent optical response of this highly anisotropic system. In contrast, our results on the oriented SWNT film clearly demonstrate that the material keeps its one-dimensional electronic character up to the highest applied pressure (8 GPa), and no indication of a dimensional crossover is found.

4 Conclusions

In conclusion, our pressure-dependent study of the absorbance spectra of unoriented and oriented SWNT films confirm the occurrence of a structural phase transition at around 2 GPa. The absorption bands of semiconducting and metallic SWNTs shift to lower frequencies and broaden with increasing pressure, which could be attributed to the structural deformation of the SWNTs, at least in the low-pressure (<1.1 GPa) range. The polarization-dependent results of the oriented SWNT film show no indication of a dimensional crossover induced by pressure.

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