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Pressure effects on unoriented and oriented single-walled carbon nanotube films studied by infrared microscopy

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We present the results of pressure-dependent infrared transmission measurements on films of oriented and unoriented single-walled carbon nanotubes. Up to the highest applied pressure (~9 GPa), the optical response of the oriented single-walled carbon nanotube film is highly anisotropic, with strong absorption bands for the polarization of the radiation along the alignment direction due to optical transitions between the Van Hove singularities in the density of states. With increasing pressure, the optical transitions shift to smaller energies, with an anomaly in the pressure-induced shifts at 2–3 GPa related to the deformation of the nanotubes' cross section. Weak signatures of a second anomaly are found at around 5–6 GPa, probably related to a more drastic deformation of the nanotubes. Different pressure transmitting media change the pressure-induced effects only quantitatively. The results for the oriented nanotube films are very similar to those for the unoriented ones. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4726214]

I. INTRODUCTION

Carbon nanotubes exhibit an extraordinary mechanical strength, which is due to the carbon atom network based on the strong covalent bonds between the sp^2 orbitals. For example, the Young's modulus of single-walled carbon nanotubes (SWCNTs) amounts to ~1 TPa and their tensile strength can reach values up to 50 GPa.[1–3] Despite their high mechanical strength, it is theoretically predicted that the nanotubes undergo severe structural changes above a certain critical pressure p_c, namely a reversible change from the circular cross section to an oval or elliptical shape.[4–7,9,10] The value of p_c decreases with increasing carbon nanotube diameter and follows the relation $p_c \propto 1/d^3$ for both individual SWCNTs[4,8,9,11] and bundled SWCNTs.[4,8–10] For nanotubes grown by the laser ablation technique, with an average diameter of 1.2–1.4 nm, the critical transition pressure is expected to be about 2 GPa.[4,6,7,10,11]

Indeed, the signatures of the above-mentioned pressure-induced structural deformation were observed experimentally, mainly by Raman spectroscopy and x-ray diffraction.[12–16] Recently, it was demonstrated that the deformation of the tubes' cross section can also be detected by transmission measurements in the near-infrared and visible frequency range, where interband transitions are excited. The pressure-induced shifts of the optical transitions between pairs of Van Hove singularities in the density of states (DOS) exhibit an anomaly at around 2–3 GPa,[17,18] which is consistent with the theoretically predicted critical pressure for the structural changes. A comparison of the optical results for different pressure transmitting media furthermore revealed only quantitative differences.[19] For a more hydrostatic pressure transmitting medium, the critical pressure for the onset of the deformation is shifted to slightly higher pressure, $p_c \sim 3$ GPa, compared to a less hydrostatic pressure medium, where $p_c \sim 2$ GPa. According to these results, it seems that the pressure transmitting medium and its eventual penetration in the tubes do not severely influence the pressure effects in SWCNTs, at least in the low-pressure regime. This finding is in contradiction to the interpretation of recent Raman measurements under pressure, where the absence of the signatures of the structural deformation was attributed to the stabilization of the tubes by the argon filling.[21] At higher pressure, around 5–6 GPa, a second anomaly was found in the pressure-induced shifts of the optical transitions,[20] which was interpreted in terms of a more drastic change in the nanotubes' cross section from an ellipse-like to a race-track or peanut-type shape in agreement with earlier Raman studies.[15,16]

A further interesting aspect is the influence of the relative orientation of the nanotubes within an assembly on the mechanical stability. Measurements of the tensile behavior of highly aligned nanocomposite films demonstrated the increase in the elastic modulus of the aligned nanocomposite as compared to the random nanocomposite due to the nanotube orientation.[22] Further studies showed that the improvement of the mechanical properties of aligned SWCNTs is restricted to the alignment direction.[23,24] To address this question, we carried out pressure-dependent optical studies on films of SWCNTs almost perfectly aligned along one direction. By tracing the shifts of the optical transitions as a function of pressure, we obtained the critical pressures for the two structural deformations and compared them to those of unoriented SWCNT films. We will present these results for various pressure transmitting media.

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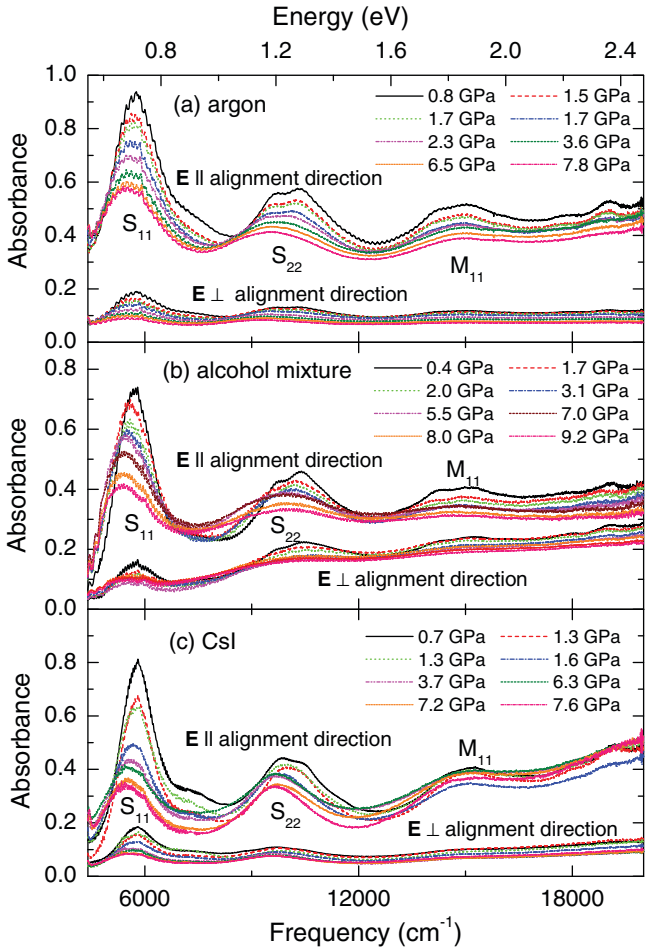

FIG. 1. Background-subtracted absorbance spectra of the oriented SWCNT film as a function of pressure for the polarization of the incident radiation parallel and perpendicular to the alignment direction. Pressure transmitting media used: (a) argon, (b) alcohol mixture, (c) CsI. The labels S_{ii} and M_{ii} denote the optical transitions between pairs of Van Hove singularities in semiconducting and metallic SWCNTs, respectively, where the indices *ii* indicate the energy sequence of the involved Van Hove singularities.

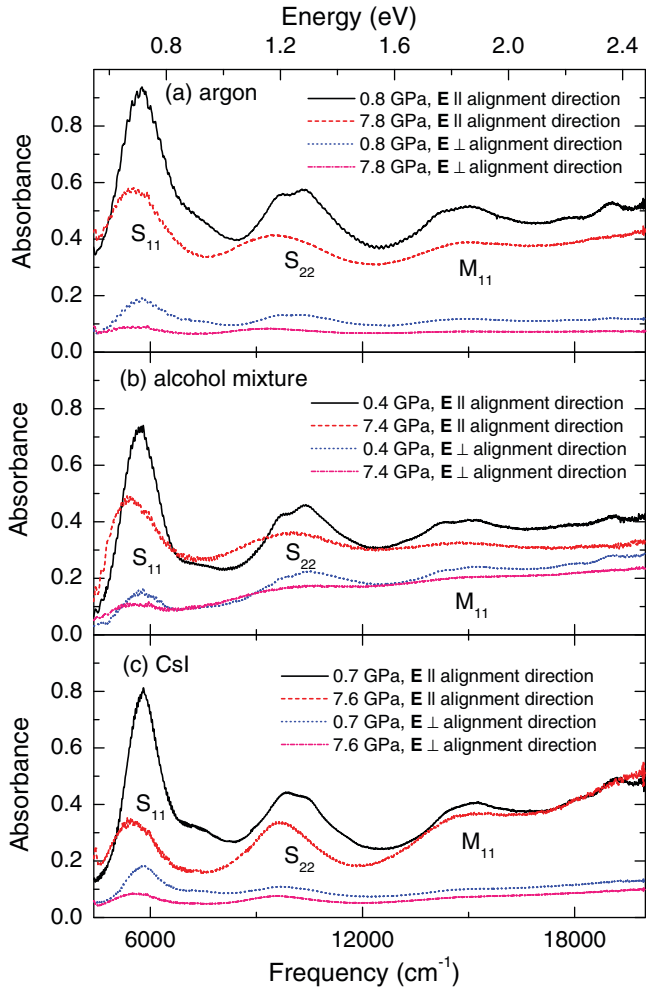

FIG. 2. Background-subtracted absorbance spectra of the oriented SWCNT film for the lowest and highest applied pressure for the polarization of the incident radiation parallel and perpendicular to the alignment direction. Pressure transmitting media used: (a) argon, (b) alcohol mixture, (c) CsI. The labels S_{ii} and M_{ii} denote the optical transitions between pairs of Van Hove singularities in semiconducting and metallic SWCNTs, respectively, where the indices *ii* indicate the energy sequence of the involve Van Hove singularities.

II. METHODS

For the preparation of unoriented and oriented carbon nanotube films, SWCNTs were synthesized by laser ablation and purified for removing impurities and defects.[25,26] For the preparation of the oriented nanotube films,[26] the SWCNTs were mixed with toluene and sonicated for 3 h for dispersion. The dispersed nanotubes were blended with polyethylene/toluene mixture at 160 °C and stirred until the toluene solvent evaporated. The heated composite was mechanically stretched with a drawing rate of 10–20 s and instantly cooled, resulting in free-standing films with a thickness of 10–30 μm.[26] Due to the stretching, a high degree of alignment of the nanotubes in the polyethylene matrix is obtained, with ~90% of the SWCNTs within 25° of the stretching direction. The average tube diameter in the oriented SWCNT films is 1.4 nm. The film of unoriented SWCNTs with the diameter range 1.2–1.4 nm was prepared as described in Ref. 25.

The pressure-dependent transmittance was measured at room temperature in the energy range 2500–20 000 cm^{-1} using a Bruker IFS 66v/S Fourier transform infrared spectrometer coupled with a Bruker IR Scope II infrared microscope with a 15× magnification objective. For the generation of quasi-hydrostatic pressures up to ~9 GPa, two types of diamond anvil cells (DACs), namely Syassen-Holzapfel type[27] and Cryo DAC Mega from Diacell, equipped with type IIA diamonds. Argon, CsI, and 4:1 methanol-ethanol alcohol mixture served as pressure transmitting medium. The intensity $I_{sample}(\omega)$ of the radiation transmitted through the sample placed in the DAC and the intensity $I_{ref}(\omega)$ of the radiation transmitted through the pressure transmitting medium in the DAC were measured. From $I_{sample}(\omega)$ and $I_{ref}(\omega)$, the transmittance and absorbance spectra were calculated according to $T(\omega) = I_{sample}(\omega)/I_{ref}(\omega)$ and $A(\omega) = -\log_{10}T(\omega)$, respectively. For the measurements on the oriented SWCNT films, the electric field of the incoming radiation was aligned parallel and perpendicular to the alignment direction of the nanotubes. A linear background

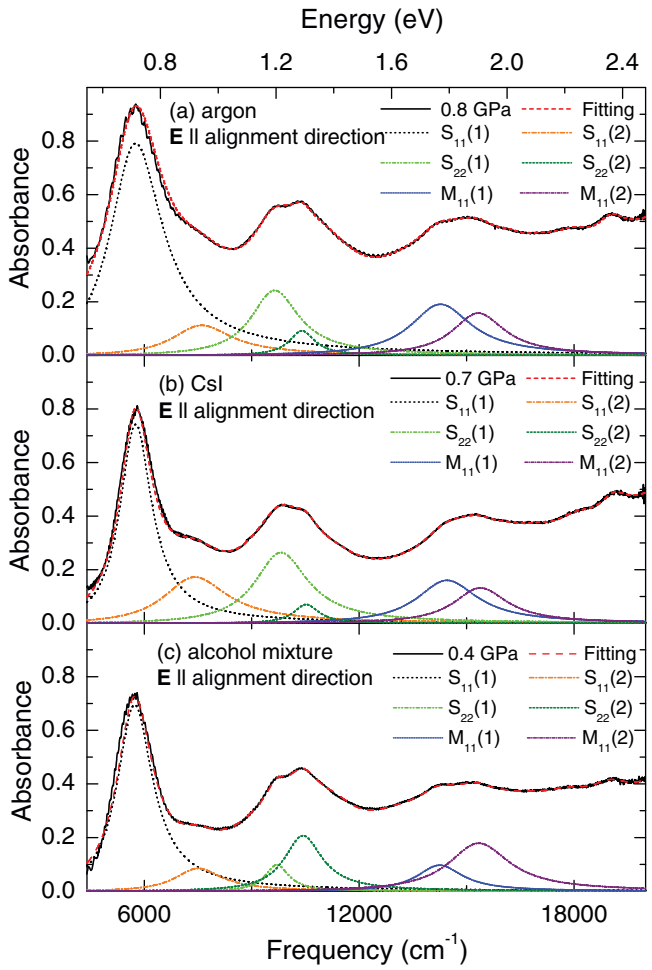

FIG. 3. Fit of the absorbance spectra of the oriented SWCNT film for the lowest applied pressure and for the polarization of the radiation parallel to the alignment direction with Lorentzian functions. Pressure transmitting media: (a) argon, (b) CsI, (c) alcohol mixture.

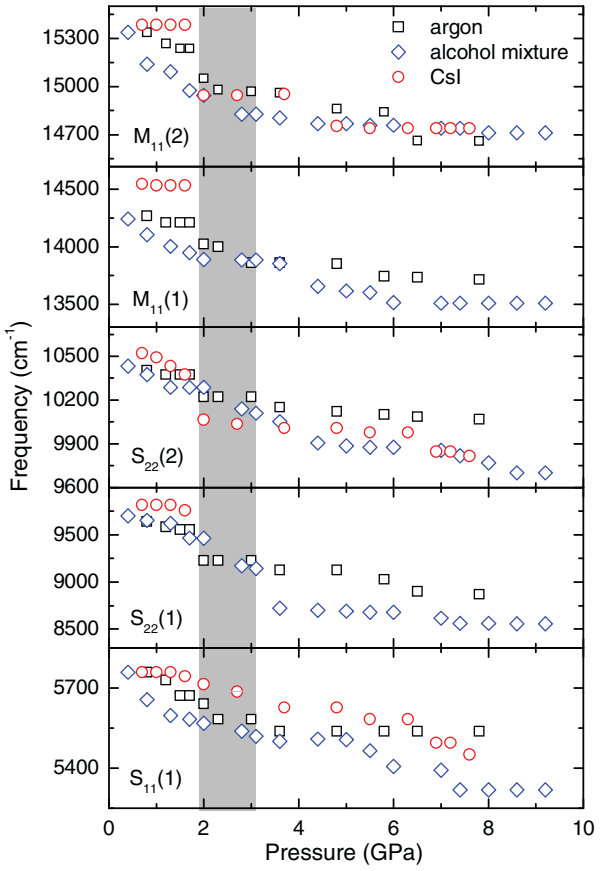

FIG. 4. Pressure-induced frequency shifts of the optical transitions in the oriented SWCNT film for the polarization of the radiation parallel to the alignment direction. Pressure transmitting media used: argon, alcohol mixture, CsI. The gray bar marks the range of the critical pressure p_c of the structural deformation.

due to π–π^* absorption has been subtracted prior to the analysis of the data, as described in Ref. 17.

III. RESULTS AND DISCUSSION

A SWCNT can be viewed as a long and narrow cylinder with a large aspect ratio, and therefore its optical response strongly depends on the polarization of the incident radiation. The optical absorption is strongly suppressed for the electric field **E** perpendicular to the nanotube's axis due to depolarization, which is caused by the charges on the cylinder walls induced by the external electric field.[28] Therefore, as shown in Fig. 1, the absorbance spectrum for **E** parallel to the alignment direction contains pronounced bands due to optical transitions between the Van Hove singularities, whereas for **E** perpendicular to the alignment direction the bands are suppressed. The weak absorption bands for this polarization direction are due to the small misorientation of ~10% of the nanotubes.

The absorption bands (see Fig. 1) labeled S_{11} and S_{22} correspond to optical transitions between the first and second pair, respectively, of Van Hove singularities in the DOS of semiconducting SWCNTs, whereas the M_{11} band corresponds to optical transitions between the first pair of Van Hove singularities in the DOS of metallic SWCNTs.[29] With increasing pressure, the absorption bands shift to lower energy and broaden, similar to the results for unoriented SWCNT films.[17,18] Interestingly, the pronounced anisotropy in the optical spectra is maintained up to the highest applied pressure. This is illustrated in Fig. 2 where the polarization-dependent absorbance spectra are presented for the lowest and highest pressure studied. Thus, the one-dimensional character of the SWCNTs is preserved up to at least 8 GPa. Furthermore, no indication of interactions or chemical bonding between the tubes is found.

For a quantitative analysis of the pressure-induced effects, the absorbance spectra for the polarization along the alignment direction were fitted with several Lorentz functions, in order to extract the frequencies of the optical transitions as a function of pressure. As an example, we present in Fig. 3 the fit of the absorbance spectrum at the lowest applied pressure including the various Lorentz contributions. Each of the three absorption bands S_{11}, S_{22}, and M_{11} can be described by two Lorentzian terms reflecting the diameter and chirality distribution in the sample.[29]

The frequencies of the strongest contributions are plotted in Fig. 4 as a function of pressure. With increasing pressure, all contributions shift to lower energy. This redshift can be attributed to the deformation-induced σ^*-π^* hybridization and symmetry lowering of the nanotubes, which lead to a

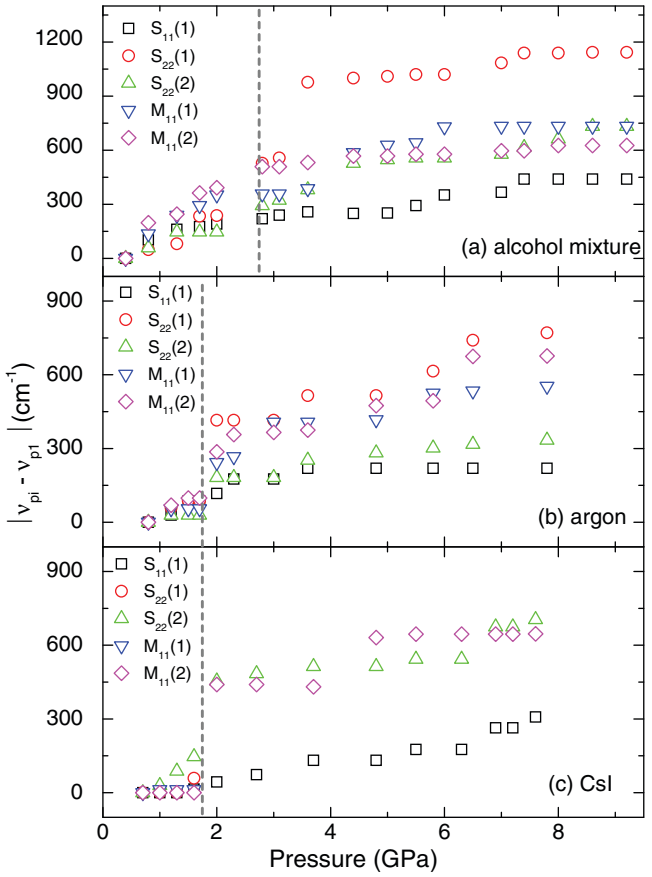

FIG. 5. Pressure-induced relative frequency shifts of the optical transitions in the oriented SWCNT film for various pressure transmitting media: (a) alcohol mixture, (b) argon, (c) CsI. The relative shifts are given with respect to the lowest applied pressure, calculated as the difference between the frequency of the contribution ν_{pi} at a certain pressure pi, and the corresponding frequency ν_{p1} at the lowest pressure $p1$. The vertical gray, dashed line marks the critical pressure of the structural deformation.

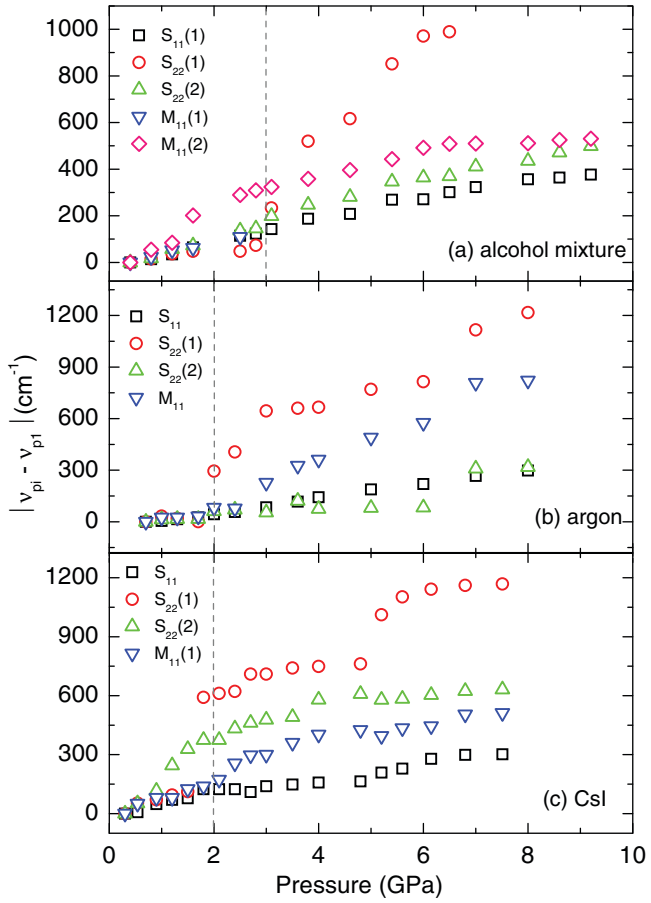

FIG. 6. Pressure-induced relative frequency shifts of the optical transitions in the unoriented SWCNT film for various pressure transmitting media: (a) alcohol mixture, (b) argon, (c) CsI. The relative shifts are given with respect to the lowest applied pressure, calculated as the difference between the frequency of the contribution ν_{pi} at a certain pressure pi, and the corresponding frequency ν_{p1} at the lowest pressure $p1$. The vertical gray, dashed line marks the critical pressure of the structural deformation.

lowering of the conduction-band states towards the Fermi energy.[30,31] A close look at Fig. 4 furthermore reveals an anomaly in the pressure-induced energy shifts within the pressure range 2–3 GPa, marked by the gray bar. In accordance with the theoretical predictions for an average nanotube diameter of ~1.4 nm (Refs. 4, 6, 7, 10, and 11) and the results for unoriented SWCNT films under pressure,[17] we relate this anomaly to the onset of the structural deformation of the nanotubes from the circular to an ellipse-like shape.

The critical pressure p_c of the deformation depends on the degree of hydrostaticity in the DAC. Using CsI salt as pressure transmitting medium provides the least hydrostatic condition in the DAC as compared to alcohol or argon; hence, it leads to the lowest value of p_c, consistent with earlier results on unoriented SWCNTs (Ref. 18) and with the findings in transition-metal oxides.[32,33] It is interesting to note here that the signature of the tube deformation is observed also when argon is used as pressure transmitting medium, despite the expected filling of the nanotubes, presumably opened by the chemical treatment, with argon.

The anomaly in the pressure-induced shifts of the optical transitions at around $p_c = 2$–3 GPa and its dependence on the pressure transmitting medium is further illustrated in Fig. 5, where the relative shifts of the optical transitions with respect to the lowest applied pressure are shown. For argon and CsI as pressure transmitting medium, the anomaly occurs at ~2 GPa, whereas for the alcohol mixture it is found at ~3 GPa.

According to Raman scattering experiments on samples of unoriented SWCNTs, the pressure-induced structural deformations in the nanotubes will lead to two anomalies in the parameters of the Raman-active modes in SWCNTs.[15,16] Both the radial breathing mode as well as the tangential mode showed an anomaly at ~2.5 GPa in the pressure-induced shift or the intensity and full-width-at-half-maximum as a function or pressure. Yet another anomaly was observed at around 9 GPa, namely the onset of a plateau of the pressure-induced shift of the tangential mode. As discussed above, the first anomaly can be interpreted in terms of the deformation of the nanotubes' cross section to an ellipse-like shape. The second anomaly was attributed to a more drastic deformation of the cross section from an ellipse-like to a race-track or peanut-like shape.[15,16] Our pressure-dependent data on the oriented SWCNT film (see Fig. 5) show an abrupt increase in the pressure-induced shifts of the absorption contributions in the range 5–6 GPa, which might be related to the above-mentioned more drastic tubes'

deformation. This anomaly is, however, less obvious than the first anomaly at $p_c \sim 2$–3 GPa.

Finally, we compare our results for the oriented SWCNT films with those obtained for unoriented SWCNT films, presented in Fig. 6. Both films show qualitatively similar results, since two anomalies in the pressure-induced shifts of the optical transitions are observed in both cases. There are quantitative differences, for example, in the absolute values of the energy shifts. These may be related to differences in diameter and chirality distribution of the nanotubes in the two types of films. The qualitative agreement of the results suggests that aligning the SWCNTs along one direction does not enhance the mechanical stability of the tubes, at least not on a microscopic level.

IV. CONCLUSION

In summary, we carried out polarization-dependent transmission measurements on films of oriented SWCNTs as a function of pressure. The observed anisotropy in the optical response with strong absorption bands for the electric field along the alignment direction remains up to the highest pressure studied. This indicates that the one-dimensional nature of the SWCNTs is preserved up to at least 8 GPa. No indication of interactions or chemical bonding between the tubes is found. The pressure-induced shifts of the optical transitions shows an anomaly at 2–3 GPa related to the structural deformation of the nanotubes. There are weak signatures of a second anomaly at around 5–6 GPa, probably related to a more drastic deformation of the nanotubes. The results for the oriented SWCNT films are very similar to those for unoriented SWCNT films under pressure, which suggests that the alignment of the SWCNTs does not enhance their mechanical stability.

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