Infrared microreflectance study of the pressure effect on the structural properties of magnetically aligned single-wall carbon nanotubes

C. A. Kuntscher[1,*], K. Thirunavukkuarasu[1], K. Kamarás[2], F. Simon[3,4], and D. A. Walters[5]

[1] Experimentalphysik II, Universität Augsburg, 86159 Augsburg, Germany
[2] Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O. Box 49, 1525 Budapest, Hungary
[3] Budapest University of Technology and Economics, Institute of Physics and Solids in Magnetic Fields Research Group, Hungarian Academy of Sciences, P.O. Box 91, 1521 Budapest, Hungary
[4] University of Vienna, Faculty of Physics, Strudlhofgasse 4, 1090 Wien, Austria
[5] Department of Chemistry, Rice University, Houston, TX 77005, USA

[*] Corresponding author: e-mail christine.kuntscher@physik.uni-augsburg.de, Phone: +49-821-598-3315, Fax: +49-821-598-3411

1 Introduction A single-wall carbon nanotube (SWCNT) shows a strong anisotropy in its optical response, since it is the prototype of a one-dimensional system [1]. One therefore expects that a macroscopic sample of aligned SWCNT bundles reveals large changes in its reflectance or transmittance spectrum depending on the polarization of the incident radiation with respect to the nanotube axis. This theoretical prediction was proven by numerous experimental works. In a recent paper we could demonstrate that the anisotropy in the optical response of a film of aligned SWCNT bundles is rather robust against the application of hydrostatic pressure [2]. Here we investigate the pressure dependence of the anisotropic optical properties of a free-standing thick film of aligned SWCNT bundles, on which reflectance measurements could be conducted.

2 Experiment Free-standing films of aligned SWCNTs ("buckypaper") produced by laser ablation were obtained according to Ref. [3]. The alignment of the SWCNT bundles was achieved with a high magnetic field of 25 T. Because of the anisotropic magnetic susceptibility of the SWCNTs, the bundles of SWCNTs arrange themselves in such a way that the bundle axes and thus the SWCNT axes are parallel to the magnetic field direction. Raman spectroscopy yields a degree of orientation of about 70% [3, 4]. The SWCNTs have a mean nanotube diameter of $d = 1.4$ nm or $d = 1.36$ nm according to transmission electron microscopy and x-ray diffraction, respectively [5].

The ambient-pressure and high-pressure reflectance measurements were performed at room temperature using a Bruker IFS 66v/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. For the ambient-pressure reflectivity of the sample the intensity reflected from an Al mirror served as reference. For pressure generation (up to 8 GPa) a clamp diamond anvil cell (Diacell cryoDAC-Mega) was used, and the ruby luminescence method was applied for pressure determination [6]. The reflectance spectra were recorded over a broad frequency range, from the infrared up to the visible. A piece of buckypaper with a size of about 100 µm × 100 µm was placed inside the diamond anvil cell (DAC), and the DAC was then filled with finely ground CsI salt which served as pressure transmitting medium; the use of a salt as pressure medium ensured the direct contact of the sample with the diamond anvil surface. Reflectance spectra, $R_{\mathrm{s-d}}$, of the sample with respect to diamond were obtained by measuring the intensity $I_{\mathrm{s-dia}}(\omega)$ reflected at the interface between the sample and the diamond anvil. As reference, the intensity $I_{\mathrm{dia}}(\omega)$ reflected from the inner diamond-air interface of the empty DAC was used. The reflectance spectra were calculated according to $R_{\mathrm{s-d}}(\omega) = R_{\mathrm{dia}} \cdot I_{\mathrm{s-dia}}(\omega)/I_{\mathrm{dia}}(\omega)$, where R_{dia} is the reflectance of diamond with respect to air. R_{dia} was estimated from the refractive index of diamond n_{dia} to 0.167 and assumed to be independent of pressure [7, 8].

3 Results and discussion The polarization-dependent reflectance spectra at ambient conditions [see Fig. 1(a)] reveal the anisotropy of the buckypaper. For the polarization of the incident radiation pointing along the orientation direction, denoted as E ∥ tubes, one finds a high reflectance at low energies and a sharp drop above ≈1500 cm^{-1}. Since the degree of orientation of the nanotubes is only 70 % and thus deviates considerably from 100 %, the reflectance spectrum for E ⊥ tubes [Fig. 1(a)] looks qualitatively similar; however, the reflectance level at low frequency is lower and the drop in reflectance occurs at smaller energies. The excitations in the material can be directly seen in the real part of the optical conductivity, obtained by Kramers-Kronig analysis of the reflectance data, and is shown in Fig. 1(b). For E ∥ tubes the optical conductivity spectrum $\sigma_1(\omega)$ is dominated in the low-energy range ($\omega \lesssim 3500$ cm^{-1}) by a relatively strong, broad peak. Several explanations were proposed for this infrared peak, including (i) the curvature-induced energy gap [9] and (ii) the dielectric function of an heterogeneous medium described by the Maxwell-Garnett effective medium model [10]. Within this model the sample is described as an effective medium consisting of the SWCNTs within a dielectric medium with a known dielectric function (in our case air). According to our results, the energy position of the infrared peak appears to be robust against pressure (not shown), and thus an interpretation in terms of the effective medium model seems to be more appropriate. A detailed analysis of our ambient- and high-pressure reflectance data using both approaches (i.e., curvature-induced energy gap and Maxwell-Garnett effective medium model) will be given in a forthcoming publication. Here, we want to concentrate on the higher-frequency range, above approx. 3500 cm^{-1}, where the optical transitions are located.

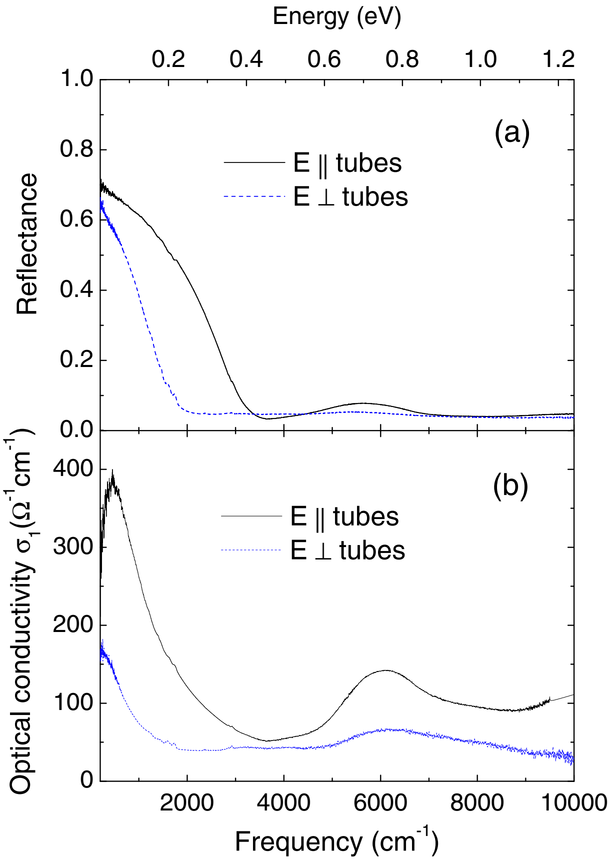

Figure 1 (a) Reflectance spectrum of the free-standing buckypaper for the polarization E of the incident radiation parallel and perpendicular to the nanotube axis. (b) Real part of the optical conductivity, σ_1, for the polarization E of the incident radiation parallel and perpendicular to the nanotube axis, obtained from the reflectance spectra by Kramers-Kronig analysis.

Our reflectance spectra R_{s-d} of the buckypaper under pressure cover three optical transitions of semiconducting (denoted as S_{11} and S_{22}) and metallic (denoted as M_{11}) SWCNTs. Each optical transition is described by at least two Lorentzian functions, in agreement with a certain diameter distribution of the studied nanotube sample. The frequencies of the optical transitions for the polarization E ∥ tubes, as obtained by the fitting with Lorentzian functions, are plotted as a function of pressure in Fig. 2(b). One finds a change in the pressure-induced shift of the optical transitions at a pressure of P_c≈2.7 GPa, which can be assigned to the critical pressure of a structural phase transition. This value of P_c is in good agreement with *ab initio* calculations for crystalline SWCNT bundles, predicting P_c≈2.7 GPa for a bundle of (10,10) tubes with tube diameter $d = 1.36$ nm [11]; it also agrees well with earlier experimental results [13]. According to theoretical predic-

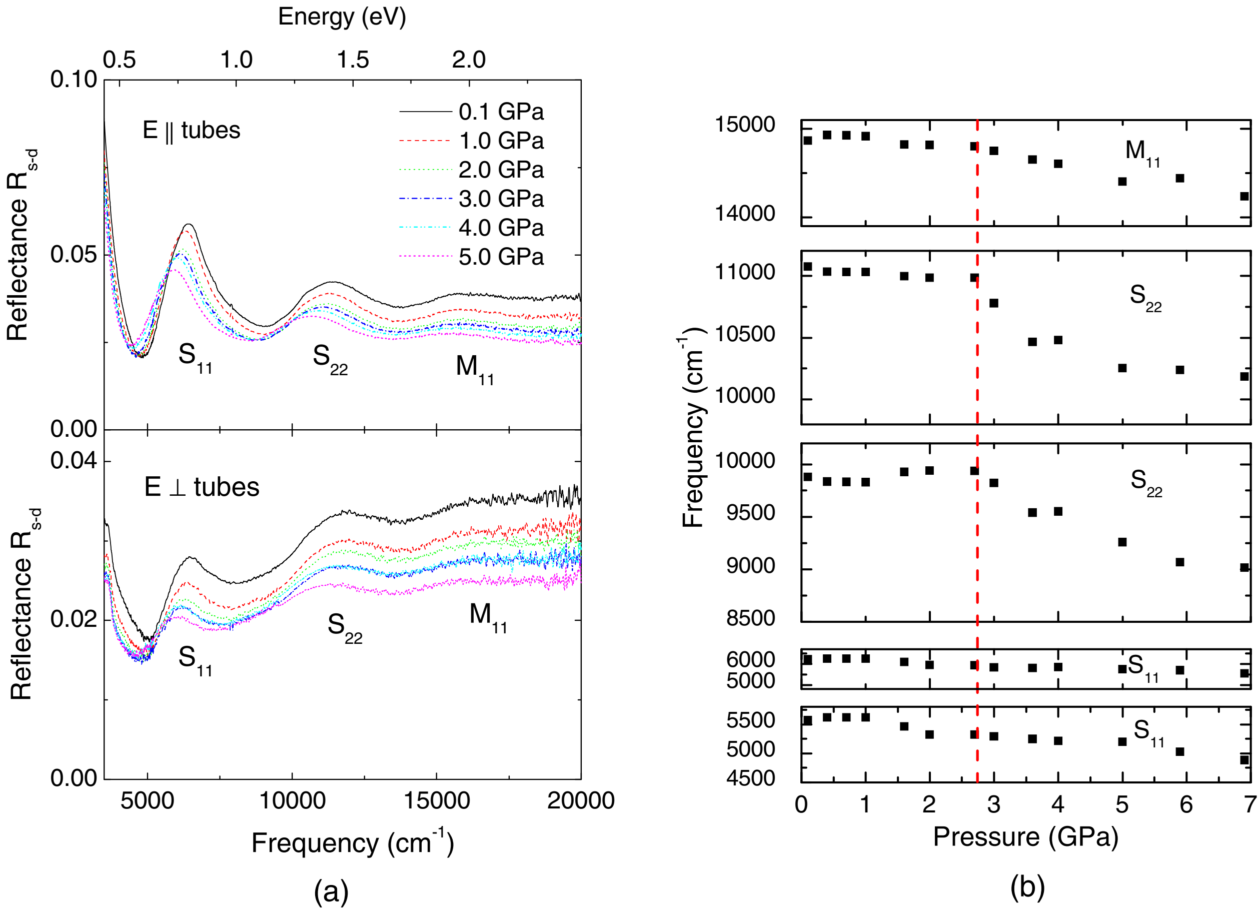

Figure 2 (a) Polarization-dependent reflectance R_{s-d} spectra for buckypaper as a function of pressure. S_{11} and S_{22} denote the optical transitions in semiconducting SWCNTs, while M_{11} denotes the lowest optical transition in metallic SWCNTs. (b) Frequencies of the optical transitions for the polarization E||tubes as a function of pressure, extracted from the reflectance spectra by Drude-Lorentz fitting. The vertical dashed line indicates the critical pressure of the structural phase transition.

tions [11, 12] we interpret this structural phase transition in terms of a circular-to-oval deformation of the SWCNTs.

4 Conclusions In conclusion, we studied the polarization-dependent optical properties of buckypaper of aligned SWCNTs at ambient and high pressure by reflectance measurements, covering the infrared and visible frequency range. The optical properties are anisotropic and show the characteristic excitations, namely a broad peak in the infrared range followed by optical transitions. The pressure-induced shift of the optical transitions reveals an anomaly at the critical pressure $P_c \approx 2.7$ GPa, which can be attributed to the circular-to-oval structural phase transition in the SWCNTs.

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