

Far- and mid-infrared anisotropy of magnetically aligned single-wall carbon nanotubes studied with synchrotron radiation

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Abstract

We performed polarized infrared reflectivity measurements on magnetically oriented carbon nanotubes using conventional light sources as well as synchrotron radiation. A strong anisotropy in the far-infrared spectral range was found, indicating preferred orientation of metallic tubes. Much less effect is seen in the spectral region typical of semiconducting tubes. We propose an explanation based on preferred orientation of metallic tubes, polarization-dependent dipole selection rules, and possible doping effects in these materials. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Carbon nanotubes are special rolled-up graphene sheets with typical diameter of 1–2 nm and length of several micrometers to centimeters. Their one-dimensional structure should manifest itself in their optical properties as well. However, the measurement of optical anisotropy on macroscopic samples has proven extremely difficult. Raman data [1] and optical absorption measurements on oriented macroscopic networks above 1 eV [2–4] showed some anisotropy. Anisotropy effects have also been reported below 2 THz by opto-electronic methods [5]. At intermediate frequencies, however, measurements are hin-

dered by small intensities and the lack of oriented samples. The microscopic analogue, low-bias tunneling spectra on isolated tubes, also reflect the configuration with current flowing along the nanotube axis.

We report on an optical study of single-wall carbon nanotube networks (“buckypapers”) aligned in magnetic field. Polarized Raman spectroscopy proved the degree of orientation to be about 70%. Microreflectance infrared spectra (100–8000 cm⁻¹) on these buckypapers were measured at the University of Stuttgart and at the ANKA infrared beamline, combining IR microscopy with high flux of infrared radiation.

The optical properties of carbon nanotubes are determined by their one-dimensional structure. Depending on the exact way of how a particular nanotube is derived by rolling up a graphene sheet, these tubes can be either metallic or semiconducting. The most striking features are absorption peaks corresponding to transitions between Van Hove singularities in the density of states [6]. These

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transitions are diameter-dependent; for an assembly of tubes like the one we investigated, the first such peak for semiconducting tubes occurs around 6000 cm^{-1} (with a distribution reflecting that of the diameters in the network), and for metallic tubes at 15000 cm^{-1} . In addition, metallic tubes exhibit a Drude peak caused by free-carrier absorption. Thus, two distinct spectral regions are of special interest: in the far- to mid-infrared range ($\omega \leq 3600\text{ cm}^{-1}$) only metallic nanotubes are detectable, and in the mid- to near-infrared ($3600\text{ cm}^{-1} \leq \omega \leq 10000\text{ cm}^{-1}$) the same is true for semiconducting nanotubes. The spectrum of a random assembly of metallic and semiconducting tubes (estimated, in the ideal case, to contain 1/3 metallic and 2/3 semiconducting species) is given by the sum of these two spectral features.

For the polarization of the incident radiation along the tube axes as compared to the perpendicular direction we obtained a distinct enhancement in the free-carrier plasma frequency (which is a measure of carrier concentration due to metallic nanotubes), but almost no intensity difference around the first interband transition of semiconducting tubes. We suggest some explanations for this phenomenon: preferred alignment of metallic compared to semiconducting tubes, accidental degeneracy of dipole-allowed transitions in the parallel and perpendicular directions, or increase of dimensionality due to doping.

2. Experimental

The alignment of laser-oven produced carbon nanotubes in a magnetic field of 25 T has been described in detail in

Ref. [7]. The tube diameter distribution was determined from Raman spectroscopy [8] yielding $d = 1.34\text{ nm}$ and $\sigma = 0.10\text{ nm}$ for the mean diameter and the variance of the Gaussian distribution, respectively. The samples were in the form of shiny black films on a nylon membrane filter. Although we have no data on film thickness, they were thicker than the penetration depth (proven by the fact that the intense infrared features of the nylon filter were not visible) and therefore can be regarded as semi-infinite from the point of view of infrared spectroscopy. Buckypaper samples usually consist of intertwined bundles of nanotubes; during the orientation procedure, the bundles are thought to arrange themselves in a more or less ordered fashion, aligning the bundle axis (and thus the tube axes) in the magnetic field direction. Raman spectra taken with 488 nm excitation showed similar anisotropy as previous measurements [7] (Fig. 1), from which we estimate the degree of orientation to be about 70%.

Infrared reflectance measurements at room temperature have been carried out on two separate Bruker infrared spectrometers, both equipped with a Hyperion infrared microscope. For the mid- and near-infrared (at the University of Stuttgart), we used conventional sources (Globar and tungsten source). Far-infrared spectra were taken at the IR-beamline of the Angströmquelle Karlsruhe (ANKA) of the Forschungszentrum Karlsruhe. We measured polarized reflectance down to 100 cm^{-1} in the preferred orientation direction and to 400 cm^{-1} in the perpendicular direction, where the signal-to-noise ratio became much worse. Typical aperture size was 0.75 mm with a 15 \times objective, which gives a spot size on the sample

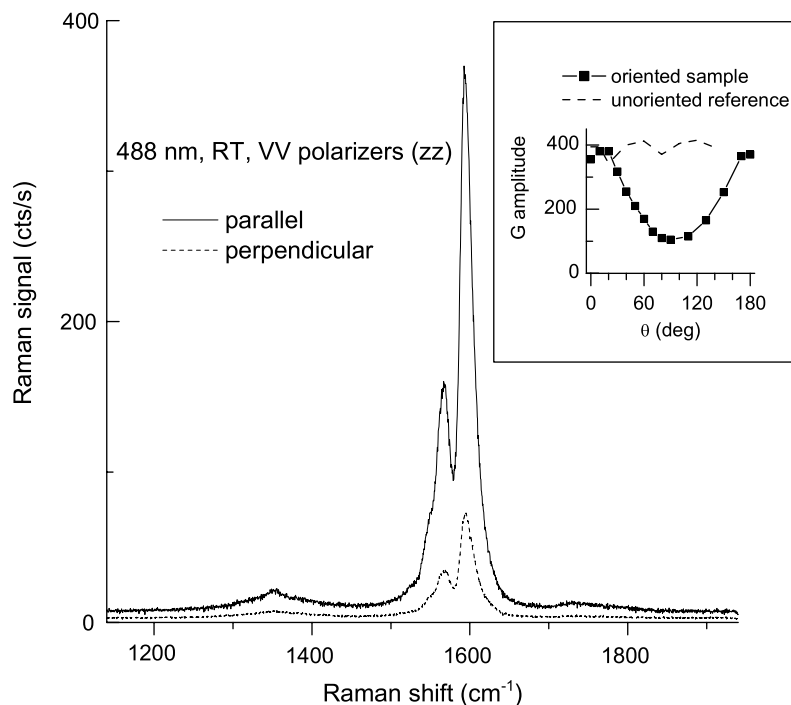


Fig. 1. Raman spectra of oriented single-walled carbon nanotubes at room temperature with the polarization parallel and perpendicular to the bundle axes. Inset: Dependence of the 1600 cm^{-1} nanotube G-band amplitude on θ (the angle between the polarization of the exciting field and the bundle axis).

of 50 μm . Spectral resolution was 2 cm^{-1} . The shape of the reflectivity was fully reproducible between different spots, but the intensity showed considerable scatter due to inhomogeneities on the sample surface. We chose the spectra for further analysis which showed the best overlap between different spectral ranges. An aluminum mirror was used as reference. The spectra were further analyzed by Kramers–Kronig transformation to extract the optical conductivity and the spectral weight. For the low-frequency extrapolation we used a Hagen–Rubens fit to the lowest frequency data and for high frequencies a power-law extrapolation to the reflectivity. The exact form of the latter was determined such that the Drude–Lorentz fit of the reflectance and the conductivity remain Kramers–Kronig consistent.

3. Results and discussion

Our results are summarized in Fig. 2. The measured spectral range comprises the free-carrier absorption of the metallic tubes in the far infrared (M_{00}), and the first interband transition of the semiconducting tubes in the near infrared (S_{11}). The two regions are clearly distinguishable (see the dotted line separating them at around 3600 cm^{-1}), yielding the advantage that the anisotropy of metallic and semiconducting tubes can be studied separately.

Interestingly, while the low-frequency reflectance is highly anisotropic, the anisotropy is almost absent at higher frequencies. The lower panel of Fig. 2 shows the optical conductivity calculated from the reflectance by Kramers–Kronig transformation. The ratio of the spectral weights along and perpendicular to the tube axis amounts to 1.71:1 below 3600 cm^{-1} and 1.04:1 between 3600 and 8000 cm^{-1} .

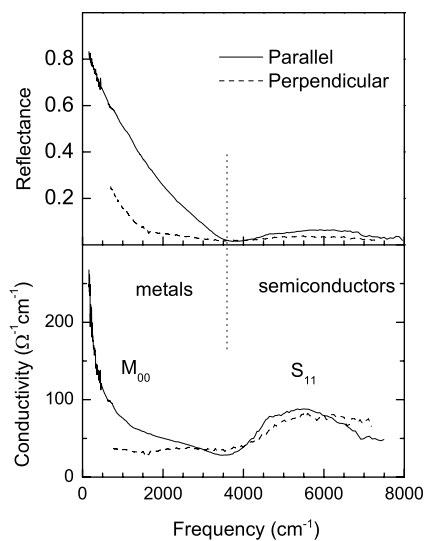


Fig. 2. Infrared reflectance and conductivity of oriented single-walled carbon nanotubes at room temperature for the polarization of the incident radiation parallel and perpendicular to the bundle axes. The dotted bar separates the region of absorption of metallic and semiconducting nanotubes.

In Ref. [7] the angular dependence of the transmission of a suspension of nanotubes in magnetic field was studied, showing a strong modulation at high field when changing the polarization direction of a HeNe laser. The wavelength of this excitation corresponds to the first interband transition of metallic tubes M_{11} ; it thus probes preferentially metallic tubes, corroborating our findings for the free-carrier absorption.

The apparent lack of anisotropy in the region between 0.5 and 1 eV (4000 and 8000 cm^{-1}) demands careful consideration. Calculations [9] predict that metallic tubes are paramagnetic in the axis direction, while semiconducting tubes are diamagnetic. The absolute value of the magnetic susceptibility for metallic tubes was estimated to be about a factor of ten larger than that of semiconducting tubes. Thus the simplest explanation would be that while the applied magnetic field was strong enough to align metallic tubes, semiconducting tubes remained disordered. This would also mean that aligned bundles consist predominantly of metallic tubes, for which there is no independent evidence. We also have to take into account that selection rules are quite different for polarization along and perpendicular to the tube axis [10–12]. For parallel polarization, the well-known symmetry selection rules are valid (S_{11} , S_{22} etc.), but for transverse polarization the allowed principal transitions are S_{21} and S_{12} . Recent resonance Raman experiments on oriented nanotubes [13,14] present experimental evidence for such transitions (S_{21} , S_{12}) polarized perpendicular to the tube axis. These transitions are observed in the frequency range between the S_{11} and S_{22} peaks for an individual nanotube. In a macroscopic sample with considerable diameter distribution, it is possible that the overlap of S_{21} and S_{12} peaks from tubes in the perpendicular orientation and the S_{11} peak from tubes in the parallel orientation is simply perceived as a broadening of the original S_{11} peak. Another fact worth considering is that the buckypaper was purified by nitric acid prior to treatment, a procedure known as strongly p-doping the material. Doping causes an increase in the free-carrier absorption and decreases the intensity of the interband transitions [15]. Both the position of the reflectance minimum and the ratio of the low- and high-frequency reflectance in our samples indicate moderate doping when compared to spectra of pristine material [16]. Assuming that the conductivity retains its one-dimensional character after doping, the reduced anisotropy of the near-infrared transition would simply reflect the reduced number of occupied states in the valence band of the one-dimensional band structure. It has been suggested previously, however, that doping reduces the anisotropy of nanotubes [17,18]. As a consequence, the one-dimensional Van Hove singularities would disappear, causing the S_{11} transition to smear out, similarly to what has been observed in photoemission experiments [18]. The free-carrier part in the doped case is a complicated matter: both metallic and doped semiconducting tubes contribute to the low-frequency absorption. Both types can behave as a three-dimensional but anisotropic

metal, with intertube interactions and misalignment further complicating the picture. Careful investigations in a wider frequency range and as a function of doping are necessary to be able to establish the role of the above mentioned factors.

4. Conclusions

We have measured the anisotropy of magnetically oriented carbon nanotube bundles in the far- to near-infrared frequency range. Our results show strong polarization in the range of free-carrier absorption of metallic nanotubes, but much less in the interband transition region due to semiconducting tubes. Possible explanations include the preferred orientation of metallic nanotubes, the appearance of cross-polarized transitions with different selection rules, and doping effects. The complete explanation of this phenomenon requires further studies, but the remarkable difference in reflectance for different polarizations is also important for future applications.

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