

# An electron energy-loss study of the structural and electronic properties of magnetically aligned single wall carbon nanotubes

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## Abstract

We have performed momentum-dependent electron energy-loss studies of magnetically aligned bundles of single wall carbon nanotubes. Our experiment directly shows the anisotropy in the electron diffraction and C1s absorption spectra. We do not observe any anisotropy for the low energy interband transitions related to the van Hove singularities in the nanotube density of states although we observe a strong anisotropy for the  $\pi$  plasmon.

**Key words:** Single wall carbon nanotubes, Electron energy-loss spectroscopy

## 1. Introduction

Carbon nanostructures are a promising new member of the growing family of novel fullerene-based materials, and represent model building blocks for nanoengineering as a result of their special electronic [1] and mechanical [2] properties. Especially single wall carbon nanotubes (SWCNTs) can be envisaged as rolled-up graphene sheets which are capped with fullerene-like structures. Their electronic properties are predicted to vary depending upon the wrapping angle and diameter of the graphene sheet, thus giving either metallic or semiconducting behavior [3].

However, in macroscopic SWCNTs samples generally form bundles which contain a distribution of tubes with different diameters and chiralities. Furthermore, the bundles are randomly oriented in bulk samples. Thus the experimentalist measures an averaged picture of their properties. Therefore most of the work has been performed on individual nanostructures. The optical properties have been analysed using spatially-resolved electron energy-loss spectroscopy (EELS) of individual single bun-

dle of SWCNTs [4]. However, these measurements with high spatial resolution are hindered by having low energy and momentum resolution. Therefore, measurements of purified SWCNTs using high resolution EELS in transmission have been performed and allowed for the first time the identification and assignment of the low energy excitations in a bulk SWCNT samples [5]. However, a detailed analysis of the intrinsic properties of these perfect one dimensional systems parallel and perpendicular to the tube axis was still hindered by the polycrystallinity of the samples. Thus macroscopically oriented arrays of SWCNTs will offer many advantages in such investigations.

In this contribution we present our first results on the structural and electronic properties of magnetically aligned SWCNTs using electron energy-loss spectroscopy in transmission. Their anisotropic properties are clearly observed.

## 2. Experimental

The production of magnetically aligned SWCNT has been described previously [6,7]. Thick films of so-called "buckypaper" [8] with an effective thick-

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ness of about  $7 \mu\text{m}$  [9] have been produced by deposition of SWCNT bundles onto a cylindrical filter of 33 mm diameter in a 25 Tesla DC resistive selenoid.

Thin films of an effective thickness of about 1000 Å were prepared by peeling off a surface layer with a sticky tape. After dissolving the tape in chloroform the films were transferred to a standard 200 mesh platinum electron microscopy grid and heated for 6 h in ultra high vacuum to 700 °C, which has been shown to improve crystallinity of the SWCNT bundles [8].

The EELS measurements were carried out using a 170 keV spectrometer described elsewhere [10]. The energy and momentum resolution were chosen to be 100 meV and  $0.02 \text{ Å}^{-1}$  for the electron diffraction experiments and for the measurements of the low energy loss function in the region of the valence band excitations, respectively. For the C1s absorption measurements the same energy resolution but a slightly reduced momentum resolution of  $0.1 \text{ Å}^{-1}$  was chosen. The loss function  $\text{Im}(-1/\epsilon(\mathbf{q}, \omega))$ , which is proportional to the dynamic structure factor  $S(\mathbf{q}, \omega)$ , has been measured for various momentum transfers,  $q$ .

### 3. Results and discussion

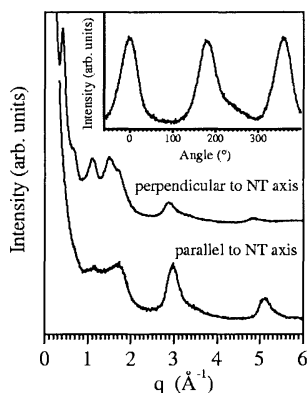


Fig. 1. Electron diffraction intensity profile of a magnetically aligned film of SWCNT bundles measured parallel and perpendicular to the alignment direction. The inset shows the mosaic spread as revealed by the first bundle peak at  $0.43 \text{ Å}^{-1}$ .

By setting the energy-loss to zero, we can carry out electron diffraction experiments in-situ in the EELS spectrometer. Fig. 1 shows electron diffraction data for purified magnetically aligned SWCNT bundles for momentum transfer parallel and perpendicular to the tube axis. The data of the

SWCNT bundles perpendicular to the tube axis are consistent with the published x-ray diffraction results which have been interpreted in terms of a triangular lattice formed by the individual SWCNTs in the ropes [8,11].

For parallel orientation these peaks related to the bundles disappear, and the peaks at about  $3 \text{ Å}^{-1}$  ((100) Bragg peak in graphite) and at about  $5.4 \text{ Å}^{-1}$  ((110) Bragg peak in graphite) are strongly enhanced in their relative intensity. This points out that for parallel orientation the SWCNTs have a similar lattice constant to in-plane graphite. The mosaic spread [12] as revealed by the first peak related to the bundle formation at  $0.43 \text{ Å}^{-1}$  is shown in the inset of Fig. 1. From a fit with a Gaussian function we find a full-width at half-maximum of about  $45^\circ$ , which is slightly bigger than the observed  $35^\circ$  observed in x-ray diffraction experiments on similar films [7].

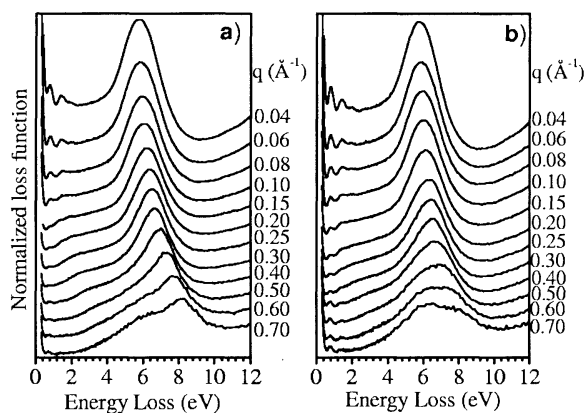


Fig. 2. Loss function of magnetically aligned SWCNT bundles as a function of applied momentum transfer  $q$  for (a)  $q$  parallel to the direction of the alignment and (b)  $q$  perpendicular to the nanotube axis.

In Fig. 2, we show the low energy loss function of a magnetically aligned buckypaper as a function of momentum transfer,  $q$ . In the left panel the momentum transfer is applied parallel to the direction of alignment (axis of the SWCNT bundles), in the right panel perpendicular to the aligned direction, respectively. For the low energy excitations at about 0.8, 1.4 and 2 eV, which correspond to the interband transitions between von Hove singularities in the nanotube density of states (as can be also measured in optical absorption spectrum [13]), we find no anisotropy in the momentum dependence of the loss function. The only significant change is an increase of the intensity of these excitations for momentum transfers higher than  $0.4 \text{ Å}^{-1}$  when measured perpendicular to the SWCNT

axis. This is related to multiple scattering and contribution of the spectra at zero momentum transfer due to the occurrence of the first bundle peak in this direction. However there is a significant change in the dispersion of the  $\pi$  plasmon, which is the collective excitation of the  $\pi$  electrons with SWCNT orientation.

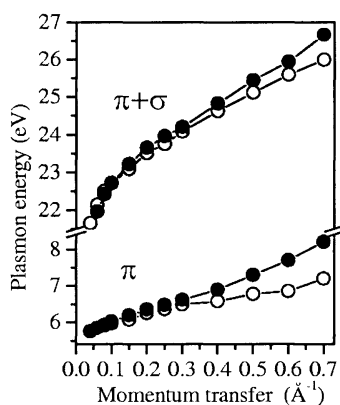


Fig. 3. Plasmon dispersion of the  $\pi$  and  $\pi + \sigma$  plasmons of magnetically aligned SWCNT bundles. The momentum transfer has been applied parallel (●) and perpendicular to the nanotube axis (○), respectively.

The details of this anisotropy of the  $\pi$  plasmon are depicted in Fig. 3 together with the anisotropic dispersion of the  $\pi + \sigma$  plasmon, which arises from collective excitation of all valence electrons. The anisotropy of the  $\pi$  plasmon is found to be much stronger than for the  $\pi + \sigma$  plasmon since the  $\pi$  electron states depend more strongly on the orientation of the SWCNTs with respect to the applied momentum transfer. This anisotropy is in good agreement with the postulated polarization dependent momentum dependence of the  $\pi$  plasmon in unoriented samples of SWCNTs [5]. For transitions between electronic states polarized perpendicular to the SWCNT axis the dispersion was expected to be zero, whereas for polarization parallel to the SWCNT axis one expects a similar dispersion relation as in in-plane graphite. Since the observed plasmon dispersion perpendicular to the SWCNT axis is much weaker this is a good confirmation of this postulation of the SWCNT electronic properties.

The C1s absorption edge is plotted in Fig. 4 as a function of the orientation of the SWCNT bundles. For measuring the orientation dependence of the core edges in strongly anisotropic materials we have used a method described by Leapman *et al.* [14]. For the spectra for perpendicular to the  $\pi^*$  orbitals (momentum transfer parallel to the

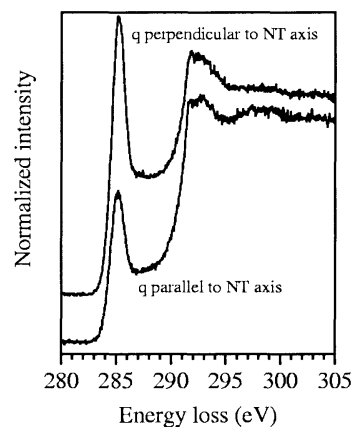


Fig. 4. C1s excitation spectra of pristine samples of magnetically aligned SWCNT bundles for applied momentum transfer parallel and perpendicular to the tube axis, respectively. The absorption spectra have been normalized to the  $\sigma^*$  edge at 291.7 eV.

tube axis), the sample has rotated by  $35^\circ$  with respect to the electron beam and was measured with a transverse momentum transfer of  $0.27 \text{ \AA}^{-1}$ . In general the peak at 285.3 eV can be tentatively identified as the transition from C1s core states to  $\pi^*$  states, meanwhile, the edge at 291.7 eV is to be identified with transition to a broader  $\sigma^*$  state, which confirms the graphitic nature of the electron system in SWCNTs. Normally, the C1s spectra of the pristine unoriented SWCNT bundles [15] strongly resemble that of polycrystalline graphite [16,17]. From the orientation dependent measurements presented here a clear anisotropy is observed. This can be easily seen in Fig. 4 by the about 50 % reduced spectral weight of the  $\pi^*$  density of states in the case of orientation parallel to the tube axis. The fact that which we still see considerable intensity at excitation energies representing excitations into  $\pi^*$  states in the latter case indicates that the alignment of the nanotubes is far from being ideal. In an ideal case, the  $\pi^*$  state intensity should be much smaller. This only partial alignment is in agreement with the results from the electron diffraction data discussed above and in Ref. 7.

#### 4. Summary

We have demonstrated that in magnetically aligned carbon nanotubes a strong anisotropy of both the electronic and the structural properties results. For the low energy interband transitions related to the van Hove singularities in the nanotube density of states we do not observe

any anisotropy whereas we do observe a strong anisotropy for the  $\pi$  plasmon.

### Acknowledgements

We thank the DFG, SMWK and EU for funding. One of us (TP) acknowledges financial support by the ÖAW in form of an APART fellowship.

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