

Electronic properties of intercalated single-wall carbon nanotubes and C₆₀ peapods

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Electronic properties of intercalated single-wall carbon nanotubes and C₆₀ peapods

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Abstract. This paper reviews recent investigations of the electronic structure and the optical properties of intercalated single-wall carbon nanotubes (SWCNTs) and C₆₀ filled SWCNTs (peapods) using electron energy-loss spectroscopy (EELS) in transmission as a probe. The results from these one-dimensional nanostructures are compared to C₆₀ fullerenes and intercalated graphite, which are well understood prototypes of carbon-based intercalation compounds. In detail, the structural changes were analysed by electron diffraction and the doping level and the matrix element weighted unoccupied density of states (DOS) by an analysis of the C 1s core-level excitations. Regarding the optical properties, the intercalation gives rise to a charge transfer to the peapods (SWCNTs) which leads to the formation of a free charge carrier plasmon in the loss function which is analysed within the framework of an effective Drude–Lorentz model.

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1. Introduction

Right from their discovery by Iijima in 1991 in a transmission electron microscope (TEM) [1] carbon nanotubes have aroused great excitement due to their unique physical properties which span an extremely wide range [2, 3]. Nanotubes are ideal one-dimensional systems which can be envisaged as rolled-up graphene sheets that are capped with fullerene-like structures. For single-wall carbon nanotubes (SWCNTs) the electronic properties vary, depending on the wrapping angle and diameter of the graphene sheet, giving either metallic or semiconducting behaviour [4, 5]. The energy gap of the semiconducting SWCNTs can be continuously changed between 0 eV and about 1 eV by varying the nanotube diameter. In particular, the fact that semiconducting structures exist opens up a wide opportunity for nano-scale device applications such as single molecule transistors. Therefore, SWCNTs are discussed as an ideal building block for nanoelectronic devices [6]. Experimentally, the electronic structure was first investigated for individual SWCNTs using a scanning tunnelling microscope as spectroscopic probe [7, 8]. Such experiments can directly relate structural information to the electronic density of states in the vicinity of the Fermi level of individual single-wall carbon nanotubes. The measured DOS is remarkably similar to the results of tight-binding calculations [5, 9]. The optical and vibronic properties of individual tubes were analysed from their luminescence [10, 11] and Raman response [10, 12], respectively. In addition to the fascinating properties of the individual SWCNTs and their compounds, studies of bulk material are also of great interest as they provide information on the electronic properties of carbon nanotubes on a macroscopic scale and thus complement the knowledge about these new materials. The electronic properties and the optical properties of such bulk samples were first analysed in detail using high energy spectroscopy [13] and optical spectroscopy [14]–[16]. A review of these results can be found in [3], [17]–[19]. In comparison with tight binding and *ab initio* calculations and in agreement with the above-mentioned optical measurements on individual SWCNTs a good correspondance of the calculated DOS with the experimental response has been observed. However, especially regarding the position of the first allowed optical transition and regarding the scaling factor between the first and second optical peak, deviations between theory and experiment are observed, which are due to final state effects of the created electron–hole pairs [10, 16, 20].

A detailed knowledge of the electronic properties in the valence and the conduction bands and the ability to modify them in a controlled way is crucial to design potential devices. For SWCNTs the unique structure allows several different ways to modify their electronic and structural properties in a controlled way. Similar to graphite, the SWCNTs can be doped by adding electron acceptors or donors to the interstitial channels in the SWCNT bundle lattice. This intercalation changes the electronic structure of the SWCNTs without modifying their atomic structure. On the other hand, a substitution of carbon atoms of the SWCNTs by heteroatoms like boron or nitrogen yields a doping which is concomitant with a structural modification. First results of the production and the electronic properties of boron and nitrogen substituted SWCNTs have been reported [21]–[24]. Furthermore, the empty space inside the SWCNT opens up a third and unique way to modify the properties of SWCNT compounds. Similar to fullerenes, carbon nanotubes can be filled by atoms and molecules. SWCNTs have been recently filled by atoms and simple molecules like H, He, S or KI [25], as well as by more complex molecules like chloroform, C₆₀ [26], bigger fullerenes

and metallofullerenes [27]. The fullerene-filled SWCNTs are regularly referred to as peapods. These materials represent a new class of hybrid systems between C_{60} and SWCNTs where the fullerenes form one-dimensional molecular chains within nanotubes and the encapsulated C_{60} peas are van der Waals bonded. In addition, upon application of a high-temperature treatment in vacuum, the peapods act as a carbon source for the creation of double-wall carbon nanotubes [28].

In this paper, a review of recent EELS investigations of the electronic structure of doped SWCNTs and peapods using the method of intercalation is presented. As far as future applications of carbon materials is concerned, the controlled modification of physical properties of these materials by means of intercalation is of particular interest. For instance, the electrochemical reactivity and the porosity make lithium-intercalated SWCNTs attractive in the usage of Li-ion batteries [29]. In the past, doping by intercalation has been studied extensively for the intercalation compounds of fullerenes (FIC) [2] and graphite (GIC) [30]. For the intercalation of SWCNTs, in contrast to FIC and GIC, no distinct intercalation stages have been observed so far. However, in contrast to FIC, SWCNTs are famous for being ambipolar, i.e. electron donors and acceptors occupy the interstitial channels in the SWCNT bundle lattice and lead to a charge transfer to/from the SWCNTs, respectively. Similar to GIC, n-type doping of SWCNT was performed using alkali metals as donors whereas for p-type doping a wide range of electron acceptors like fluorine, bromine, iodine, HNO_3 , H_2SO_4 , or $FeCl_3$ have been used [29], [31]–[36]. From a structural analysis using x-ray diffraction (XRD) and electron diffraction [34]–[36], it has been observed that intercalation caused disorder in the 2D lattice of the pristine SWCNT bundles confirming that the intercalation occurs in between the tubes and increases the intertube distance. For both n- and p-type intercalants, Raman measurements indicated a charge transfer [31] and a strong reduction in the resistance by about two orders of magnitude was observed in transport measurements [32]. The maximum intercalation for potassium doping has been found to be a carbon to alkali metal ratio of ≈ 7 [36, 37]. This value is similar to the highest doping in GIC (KC_8) [30, 38] and FIC (K_6C_{60}) [39]. Regarding the charge transfer and optical properties of intercalated SWCNTs, most of the work was done by EELS [19, 36, 37], optical spectroscopy [33, 40] and Raman spectroscopy [31], [41]–[44]. It was shown that the Fermi level of SWCNTs can be shifted up to 1.3 eV by electron or hole doping. For alkali metal intercalation, EELS revealed a complete charge transfer of the alkali metal s electrons to the SWCNT derived states. This is similar to the charge transfer which can be achieved by performing electrochemical redox reactions between SWCNT thin films and solutions of organic radical anions [45]–[47]. Moreover, the charge transfer to the SWCNTs results in the formation of a charge carrier plasmon below 2 eV, which can be analysed by an effective Drude–Lorentz model [36, 37].

Regarding the intercalation of peapods, Raman studies of potassium intercalation of C_{60} peapods revealed that at high intercalation levels, in addition to a charge transfer to the SWCNT pods, the C_{60} peas are also charged up to $(C_{60})^{6-}$ and form a metallic one-dimensional polymer [48]. At intermediate doping, in contrast to FIC, a continuous charge transfer to the SWCNTs and the C_{60} peas has been observed [49]. This is at variance with results from electrochemical doping which do not show a charge transfer to the C_{60} peas [50] pointing out that a higher doping level can be achieved with potassium intercalation. Recent EELS experiments confirmed that the SWCNTs in the peapods can be doped up to the same level as the empty SWCNTs. Regarding the optical properties of the intercalated peapods,

the charge carrier plasmon is observed at lower energy when compared to the intercalated empty SWCNTs which can be explained by a higher effective screening in these hybrid compounds [51].

2. Experimental details

The pristine SWCNTs used for our studies were produced by laser ablation, purified and filtrated into mats of a bucky paper as described previously [14, 15]. The diameter of the SWCNTs can be determined by electron diffraction and optical absorption spectroscopy. For control experiments, buckypaper of commercially available HiPCO SWCNTs with a mean diameter of 1.07 nm was used. The C₆₀ peapods were produced in a two-step process. The SWCNTs are purified and opened, then they are filled by exposure to a fullerene vapour at high temperature [52]. Measurements of the filling factor using bulk sensitive methods revealed a C₆₀ occupancy of about 92% [52]–[54].

For the analysis of the structural, electronic and optical properties EELS in transmission was used. The quantity measured in an EELS experiment is the loss function, $\text{Im}(-1/\epsilon(q, \omega))$, which provides information on the collective excitations of the electronic system, i.e. the plasmons. For energy-loss below ~ 50 eV, the loss function essentially describes plasmon excitations which arise from intra- and interband transitions. All measurements are performed at room temperature. In contrast to optical spectroscopy which probes dipole allowed transitions at zero momentum transfer, EELS provides access to the momentum dependence (q dependence) of the dielectric function. Consequently, non-vertical transitions can also be excited and selection rules as well as dispersion relations of collective excitations can be probed. At higher energies, the loss function describes transitions from core or shallow core levels into unoccupied states derived from orbitals of the same atom. These core excitations are governed by the dipole selection rule. A more detailed description of the operation and principles behind EELS experiments can be found in [55] and references therein.

For our EELS measurements, thin films of peapods and reference SWCNTs with an effective thickness of about 100 nm were prepared by dropping an acetone suspension of the materials onto KBr single crystals. After dissolving KBr in distilled water, the films were transferred to a standard 200 mesh platinum electron microscopy grid and heated to 620 K for several hours in ultrahigh vacuum to remove organic contaminations in the films. Subsequently, the films were transferred into the measurement chamber (base pressure 10^{-10} mbar) of a purpose-built EELS spectrometer [55]. Then, EELS studies of these samples have been carried out in transmission in this high-resolution spectrometer, which combines both, good energy and momentum resolution. Unlike many other electron spectroscopies, this method is volume-sensitive since high energy electrons of 170 keV can penetrate through free-standing samples with an effective thickness of about 1000 Å. For the data shown here, an energy and momentum resolution of 180 meV and 0.03 Å^{-1} (valence band excitations and electron diffraction) and of 300 meV and 0.1 Å^{-1} (core excitations) were chosen.

The alkali metal intercalation (n-type doping) was carried out *in situ* in an ultrahigh vacuum chamber by evaporation of alkali metals from commercial SAES Getter sources. During evaporation, the film was kept at 400 K, and further annealed for 20 min at the same temperature to improve intercalant homogeneity and to remove possible excessive alkali metals from the film surface. This process was repeated several times until maximum

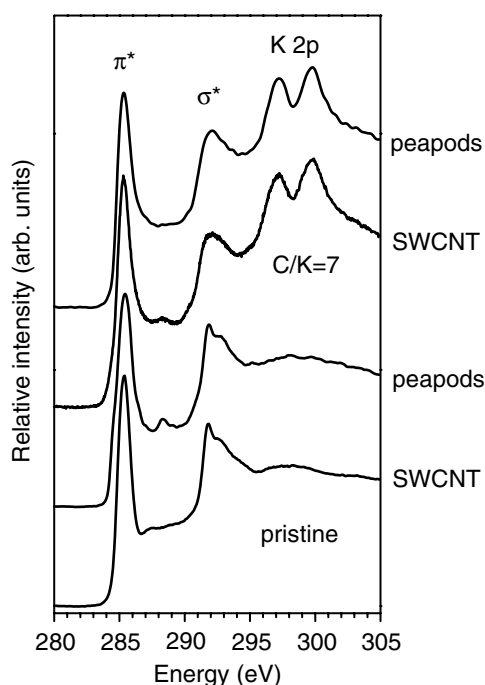


Figure 1. Core-level excitations of the pristine and fully doped SWCNTs and peapods [51].

intercalation was reached as revealed by a saturation in all characteristic changes discussed below. The p-type (FeCl_3) intercalation was carried out by the two-zone vapour method. The SWCNTs and FeCl_3 were stored in a quartz tube, then evacuated and sealed at a pressure of 10^{-7} mbar. The SWCNTs on TEM grids were heated up to 300°C , and FeCl_3 was heated to a lower temperature from 150 to 280°C to control the different intercalation levels. A 2 h post-annealing treatment at 150°C was applied to improve the sample homogeneity of the FeCl_3 intercalated SWCNTs. When the quartz tube is opened in argon gas, intercalated SWCNTs are transferred to the EELS chamber by the fast entry lock.

3. Results and discussion

3.1. Doping level and charge transfer from core-level excitations

Information on the electronic structure of intercalated SWCNTs and peapods can be extracted from the analysis of the core-level excitations from the C 1s level. The measured core edge structure in EELS spectra corresponds directly to electronic C 1s transitions into unoccupied states with C 2p-related π^* and σ^* character. For the SWCNTs (shown in figure 1) the former is characterized by a nearly symmetric peak centred at around 285.4 eV , while the latter start at around 292 eV . These peaks give a measure of the carbon-derived matrix element weighted density of states, a detailed analysis is complicated by the fact that both are strongly excitonic in nature [36, 37]. The same effect holds for the peapods [51]. In addition, the corresponding response from C_{60} is also present as can be seen e.g. by the small peak between π^* and σ^* in the spectrum of the pristine peapods.

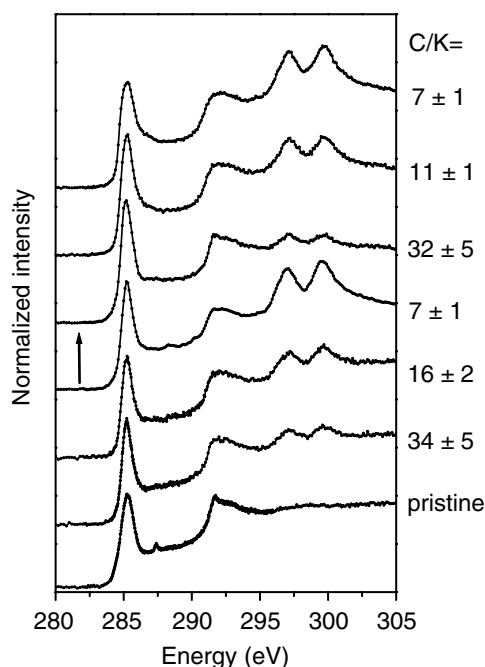


Figure 2. *In situ* potassium intercalation and de-intercalation of SWCNTs as indicated by the C/K ratio. The arrow indicates the de-intercalation step at 625 K for 50 h [19].

In order to quantify the degree of intercalation in the nanotube samples, the C 1s and K 2p core-level excitation spectra of both fully intercalated SWCNTs and peapods were recorded. The relative intensity of the K 2p/C 1s core-level excitation signals, shown in figure 1, give a measure of the C/K ratio and the corresponding degree of intercalation. For calibration, the intensity ratio of the two well-known phases K_6C_{60} and the stage I GIC KC_8 have been used [36]. A global stoichiometry of $C/K \approx 7$ for the SWCNT bundles intercalated to saturation and $C/K \approx 7$ for the fully intercalated peapods have been observed. These values are essentially the same as that of the stage I GIC KC_8 as well as consistent with Cs intercalated SWCNTs [56]. Using this calibration the intercalation process of the SWCNTs (peapods) was studied *in situ*. Hence, a subsequent intercalation, de-intercalation and re-intercalation process could be performed as depicted in figure 2.

De-intercalation was done by heating the sample under UHV conditions for 50 h at 625 K. The end-point of the de-intercalation process under these conditions is a SWCNT bundle with a ratio of $C/K = 32$ [19]. These results are consistent with the qualitative observation of de-intercalation reported in transport measurements [32]. The same samples can then be fully re-intercalated back to the $C/K = 7$ level, giving core level excitation spectra essentially identical to the first time of saturation doping [19].

In order to extract more information about the electronic structure in the conduction band, it will be useful to compare the C 1s spectra of pristine and fully intercalated SWCNTs for different alkali metal dopants. The spectral response of the potassium intercalated SWCNTs was found to be virtually identical in the energy range between 280 and 295 eV to those of sodium, rubidium or caesium intercalated SWCNTs [37]. Hence, it can be regarded as a

representative example. Compared to the pristine material, increasing alkali metal intercalation causes the σ^* states to become washed out. However, the two excitonic transitions (into π^* and σ^* states) in the pristine peapods and SWCNTs are only weakly influenced by the alkaline metal intercalation. Their line shape and positions remain unchanged after doping fully. It can be clearly seen that the spectral shape above the onset of excitation is identical for all doped SWCNTs (peapods) exhibiting only a single narrow peak at 285.4 eV, very similar to GIC KC_{24} [57], which means the states above the Fermi level remain rather unperturbed by the introduction of the intercalant. However, in all stage I alkali-metal GIC, the C 1s spectrum shows a double-peaked structure. This was ascribed to a hybridization of the π^* and metal states above the Fermi level [57], which could cause a splitting of the C π^* graphite bands. Since, due to filling, the peapods have a higher amount of carbon atoms, the maximal $\text{C}/\text{K} = 7$ also shows that the C_{60} peas are affected by the intercalation process. Hence, the saturation of doping is only determined by the charge storage capacity of the carbon compounds.

In order to determine the charge transfer and the shift of the Fermi level the position and area of the π^* resonance were investigated. Although there is a shift of the Fermi level to the conduction band in the intercalated compounds, the strong excitonic effect in this resonance renders it invisible in the C 1s core-level excitation spectrum. In a rigid band model, the amount of charge transfer from the alkali metal ions to the SWCNT (peapod) conduction band can be estimated from an analysis of the spectral weight of the π^* feature.

For all fully intercalated SWCNTs a decrease of that feature by about 10% as compared to pristine nanotubes is observed. This decrease is in good agreement with a complete charge transfer from the outer alkali s electrons to the nanotube DOS assuming a C/A (A: alkali metal) ratio of about 7, as derived in the fully intercalated K-compounds. In contrast, for the intercalated peapods, no reduction of the spectral weight is observed. This can be explained by the fact that for the K-doped peapods, due to the contribution of the C_{60} peas, this simple analysis can no longer be carried out [51].

To further analyse the electronic structure from C 1s EELS and clarify the role of the local bonding environment and charge transfer, it is useful to extract the signal of the doped C_{60} peas from that of the peapods. From the jump edge in core-level excitation spectrum and from the C_{60} shape resonances, the filling factor can be estimated on a bulk scale and the matrix element weighted conduction band spectrum of the C_{60} peas can be extracted, respectively [53, 54]. After normalization at 305 eV, the peapod spectrum had to be scaled by about 1.3 before subtracting the SWCNT reference spectrum to obtain the response of the C_{60} peas. As mentioned above, this corresponds to a filling factor of about 92% for SWCNTs with a mean diameter of 1.4 ± 0.1 nm [53, 54]. The spectrum of the extracted C_{60} peas using the above-mentioned scaling factor for both, the pristine and intercalated peapods is depicted in figure 3. For comparison, reference spectra of C_{60} , K_3C_{60} and K_6C_{60} are also shown [58]. In the spectrum of the doped C_{60} species, the filling of the lowest unoccupied molecular orbital (LUMO) with doping results in the disappearance of the corresponding peak. Compared to the FIC and the C_{60} peas the spectrum of the doped C_{60} peas is more complicated. This is a first hint that the charge transfer in this doped hybrid system shows a complex behaviour in agreement with previous results [48, 49]. Nevertheless, some general trends can be extracted from the response of the doped C_{60} peas. The spectrum of the K 2p doublet reveals that the doping level is similar to that in K_6C_{60} rather than K_3C_{60} . The overall shape of the response

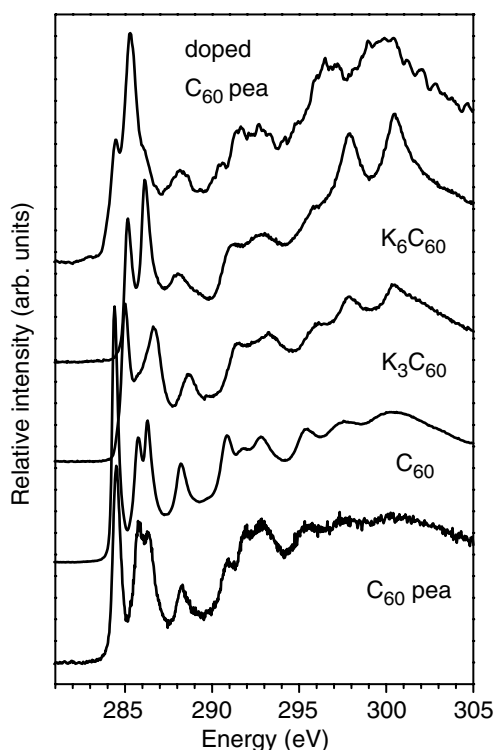


Figure 3. Core-level excitations of the extracted doped peas (top) in comparison with those of K_6C_{60} , K_3C_{60} , C_{60} in solid and the extracted C_{60} peas [51].

is modified compared to K_6C_{60} which is consistent with the observed formation of a one-dimensional charged C_{60} polymer [48].

It is now interesting to compare n-type and p-type doping. As a typical example of p-type doping, $FeCl_3$ intercalation was chosen. Again an analysis of the C 1s core edge yields information about the charge transfer, now from the valence band of the SWCNTs to the $FeCl_3$ molecules as depicted in figure 4.

Similar to $FeCl_3$ -doped graphite [55, 59], in the $FeCl_3$ intercalated SWCNT compounds an additional shoulder is observed at the low energy edge of the π^* resonance. Although one has to take into account strong excitonic effects, this additional spectral weight can be attributed to transitions into former valence band states which have been depopulated by the intercalation induced charge transfer. In detail, figure 4 clearly shows that a peak of similar shape as that of the pristine SWCNTs is observed at 285.5 eV, accompanied by the new charge transfer induced peak (CT-peak) between 283.7 and 284.5 eV. There is a small shift of the π^* peak to higher energy in the intercalated material, which is most likely due to an increase of the carbon 1s binding energy caused by the reduced net charge on the carbon atoms. This net charge can be extracted from the difference in spectral weight of the pristine and the doped SWCNTs. In analogy to $FeCl_3$ intercalated graphite [55, 59], the onset of the additional CT-peak is a measure of how much the Fermi level has been lowered upon intercalation. The resulting shift of the Fermi level is about 0.6–0.7 eV. In addition, the amount of charge transfer can be derived from the area ratio of the CT-peak in comparison to the total spectral weight of the π^* states in the pristine SWCNTs. A charge transfer of about $0.03 e^-$ per C atom is observed. Assuming a rigid band shift of the Fermi level this charge transfer corresponds to

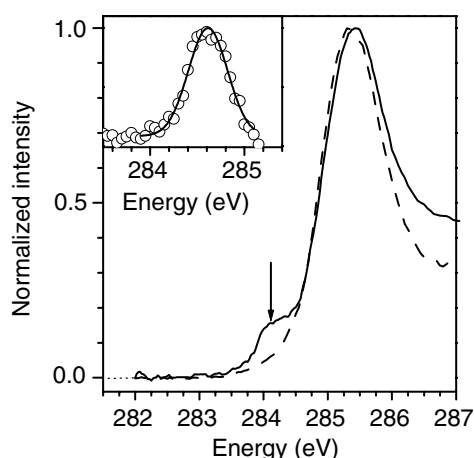


Figure 4. C 1s core-level excitations of pristine (dashed line) and FeCl₃-doped SWCNTs (solid line). The arrow indicates the additional doping induced spectral weight. The inset shows the difference between the spectral weight of doped and pristine nanotubes after normalizing the two spectra to the π^* states.

the shift of the Fermi level about 0.6 eV, in good agreement with the direct observation of the Fermi energy shift from the onset of the CT-peak. Hence, also for p-type doping a rigid band shift and an ionic charge transfer between the SWCNTs and the FeCl₃ molecules is observed.

It is now interesting to compare the maximum doping levels between the p-type and the n-type intercalated SWCNTs. In comparison to the alkali-metal intercalated SWCNTs, the maximum doping level for FeCl₃ intercalation is much lower. One reasonable explanation is the bigger size of (FeCl₃)₂ molecules. The intercalated (FeCl₃)₂²⁻ ions are platelets with a lateral ionic radius of about 6.1 Å and a vertical ionic radius about 1.5 Å. Hence, the lateral extension is about three times bigger than for potassium ions and the corresponding maximum doping of a SWCNT bundle with 1.4 nm mean diameter of the individual SWCNT will be about 0.6 of the corresponding potassium intercalated SWCNT bundle. This is fully consistent with the results derived from the C 1s absorption edge. Whereas, potassium intercalation leads to a 10% decrease of the π^* resonance, FeCl₃ doping results in an additional CT-peak which is about 6% of the π^* resonance. In addition, the slightly lower maximum doping can be explained by the fact that, due to the big size of the FeCl₃ ions, bundles containing a lot of SWCNTs with diameters below about 1.2 nm cannot be intercalated. This is in complete agreement with Raman measurements of FeCl₃ intercalated HiPCO SWCNTs with a mean diameter of 1.07 nm and a broad diameter distribution. It was found that p-type doping for SWCNTs with a diameter below about 1.2 nm is hard to realize by FeCl₃ intercalation [43, 44].

3.2. Structural analysis from electron diffraction

Next, we carried out a structural analysis using electron diffraction in the EELS spectrometer by setting the energy-loss to zero. Similar results were obtained by x-ray diffraction studies [34, 60, 61]. For the pristine peapods, compared with the corresponding spectrum of the empty SWCNT reference sample (insets of figure 5), the most obvious result is that additional diffraction peaks appear. The most pronounced additional Bragg peak is at about 0.63 Å⁻¹,

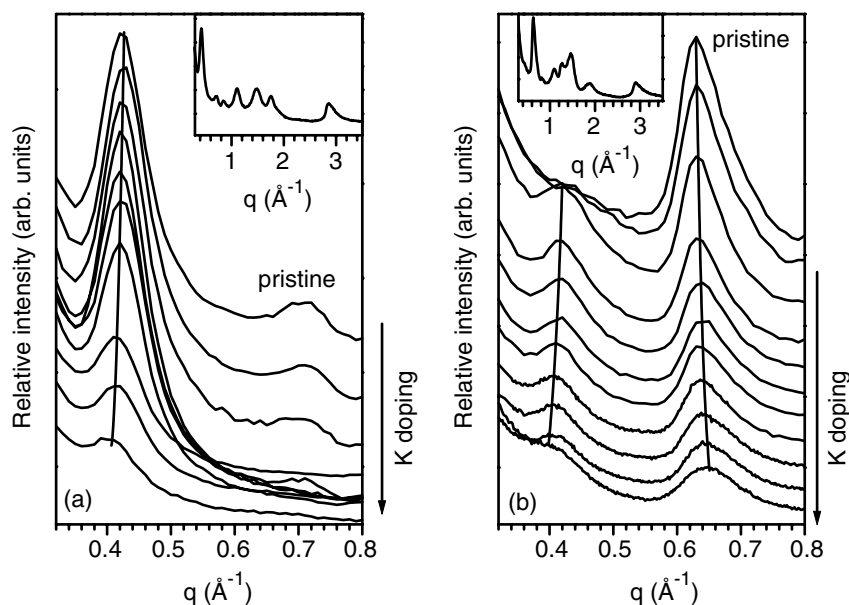


Figure 5. The evolution of the diffraction pattern of SWCNTs (a) and peapods (b) with increasing K concentration. The lines depict the evolution of the first bundle peak at about $0.42 \text{ \AA}^{-1}$ and of the first C_{60} Bragg reflection at about $0.63 \text{ \AA}^{-1}$. The insets show the typical electron diffraction pattern of pristine SWCNTs and peapods in an extended region [37, 51].

which derived from the diffraction of the C_{60} in a one-dimensional arrangement within SWCNTs. The corresponding next-nearest-neighbour distance of two encapsulated C_{60} molecules is about 0.99 nm . In addition, the first bundle peak at about $0.42 \text{ \AA}^{-1}$ is remarkably depressed as compared with the SWCNTs as a consequence of the change of the structure factor in the peapods due to the encapsulation of C_{60} [61]. This behaviour is also evidence for the encapsulation of the C_{60} molecules inside the nanotubes.

As depicted in figure 5, the effect of potassium intercalation is also reflected in changes of the diffraction pattern. Here we focus on the lower q region in the range between 0.3 and $0.9 \text{ \AA}^{-1}$ where the diffraction from both peas and pods are strongly pronounced. With increasing potassium content, the first bundle diffraction peak shifts to higher q and the intensity decreases. From the pronounced downshift, the expansion of the inter-nanotube spacing concomitant with intercalation in between the SWCNTs in the bundles can be derived. In the present samples, the downshift of that diffraction peak for the fully potassium intercalated material is about $0.02 \text{ \AA}^{-1}$. This corresponds to an increase of the intertube distance from about 1.7 nm to 1.82 nm . In addition, for the peapods, the diffraction peak which corresponds to the nearest-neighbour distance between two encapsulated C_{60} molecules shifts to higher q and its intensity decreases. It is obvious that there are no diffraction features in the region around $q = 0.65 \text{ \AA}^{-1}$ for the doped SWCNTs, which confirms that the above-mentioned diffraction pattern in the range of 0.6 to $0.7 \text{ \AA}^{-1}$ is only from the C_{60} peas. The upshift of the peak corresponding to the separation between the C_{60} peas stands for a decrease of their intermolecular distance from 0.99 to 0.96 nm . In pressure polymerized C_{60} the intermolecular distance is about 0.92 nm [62]. In the latter case the polymerization is established via a two-plus-two cycloaddition process. In single bonded polymers the

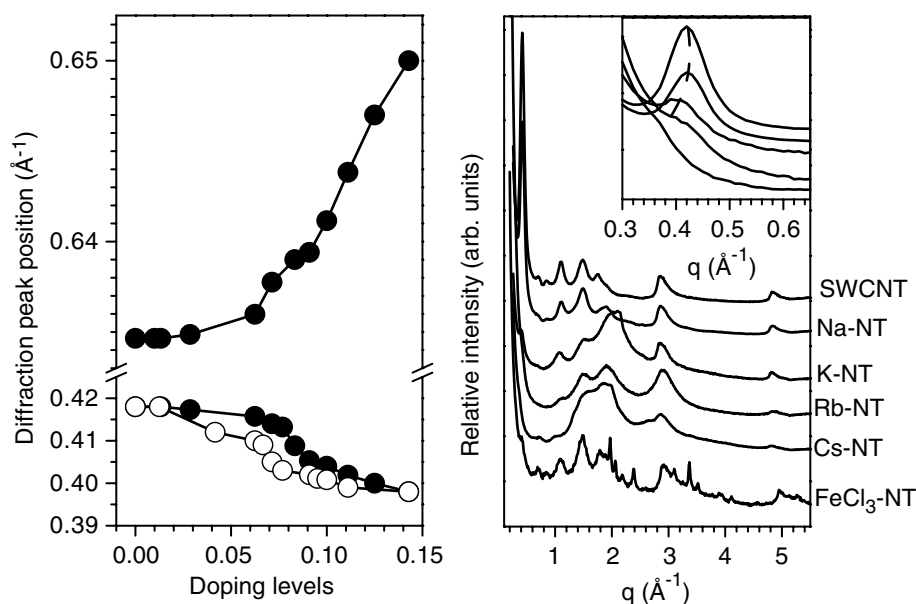


Figure 6. Left panel: peak position of the first C_{60} peak and of the first bundle peak as a function of the intercalation level. Also shown is the doping dependence of the first bundle peak in potassium intercalated SWCNTs (open circles) [51]. Right panel: electron diffraction pattern of pristine SWCNTs and fully Na, K, Rb, Cs and $FeCl_3$ intercalated SWCNTs. The inset shows the first bundle peak for the alkali intercalated samples, the dashed line indicates the downshift of the bundle peak with increasing size of the counter ions.

polymer bonds are weaker, which is consistent with the bigger C_{60} separation and supports for previous reports of a doping induced single bonded polymerization of C_{60} molecules inside SWCNTs [48]. However, as can be seen in the left panel of figure 6, the upshift of the peak corresponding to the intermolecular C_{60} separation is monotonic and no spontaneous polymerization is observed. Further work on oriented samples is needed to gain more insight into the details of this reaction within the peapods. Regarding the amount of expansion of the SWCNT lattice upon intercalation it is also useful to compare the electron diffraction of the first bundle peak from the reference SWCNTs using different intercalants. The results are depicted in the right panel of figure 6 for SWCNTs with 1.37 nm mean diameter and Na, K, Rb, Cs and $FeCl_3$ intercalation. The decrease in intensity of this first bundle peak with intercalation mostly results from the insertion of intercalants into the bundle which cause more disorder and thus a decrease of the respective Bragg peak intensity.

The bigger the size of the intercalant, the lower the intensity in the Bragg peak. Furthermore, the position of the first Bragg peak shifts to lower q with increasing alkali ion radius. In the inset of the right panel of figure 6, the diffraction pattern of the first bundle peak of the fully intercalated SWCNT films is plotted in an enlarged range for the different intercalants. The intertube distance for rubidium and caesium intercalation increases by 1.7 and 2.7 Å, respectively, which is consistent with the larger ionic radii of rubidium and caesium of 1.48 and 1.69 Å respectively, as compared to the ionic radius of 1.38 Å of potassium. For $FeCl_3$ intercalation, a lot of disorder is introduced into the SWCNT lattice. Hence, a detailed analysis of the size of the lattice expansion was not possible. For sodium intercalation, the

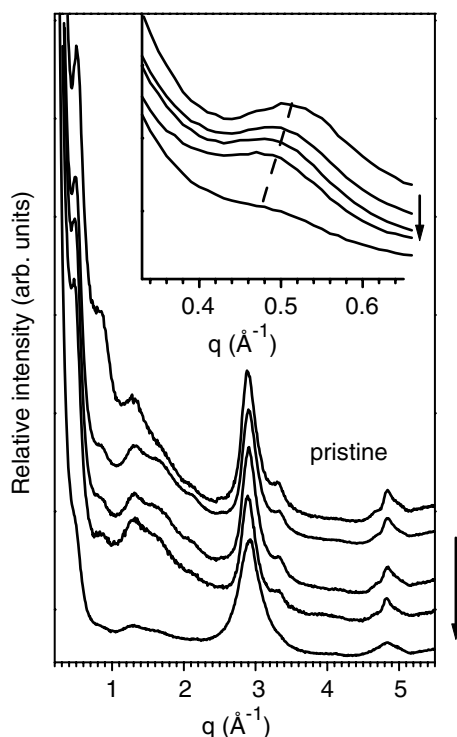


Figure 7. The electron diffraction pattern of SWCNTs with a mean diameter of 1.07 nm with different sodium intercalation levels indicated by the arrows. The inset shows the enlarged bundle peak shift. The dashed line indicates the downshift of the bundle peak with increasing sodium concentration.

position change of the first bundle peak is very weak as compared to pristine SWCNTs. This can be ascribed to the smaller diameter of sodium ions and to the relatively large space within SWCNT bundles in the present sample with a mean diameter of about 1.4 nm, where the intertube space is big enough to incorporate sodium ions with a radius of about 0.95 Å without any significant expansion in the nanotube bundles.

As a test, SWCNT films with a smaller diameter (about 1.07 nm) were intercalated with sodium and showed a lattice expansion as seen in figure 7. The downshift of the first Bragg peak is from about 0.52 to 0.48 Å⁻¹ which corresponds to the increase of the intertube distance from about 1.42 to 1.51 nm.

Under the above-mentioned assumption that the intercalation occurs in between the tubes a simple model, which was also successful to explain X-ray diffraction data [34], can be applied to check the structural configuration of the intercalation compounds. Although the exact positions of alkali metal ions are unknown, the minimum energy configuration of the intercalation compound will depend on the intercalation level. As shown in figure 8, a potassium intercalated bundle of (10,10) nanotubes (mean diameter about 1.4 nm) can at low intercalation levels incorporate the alkalis at the centre of the interstitial voids of the nanotube bundle lattice. In this case no lattice expansion is needed as observed for potassium intercalation. At saturation doping, three potassium per cavity at the extremities of the triangular cavities are needed to achieve a C/K ratio of about 7 for this tube diameter. This can be easily calculated for the example of the (10,10) nanotube which has 20 carbon

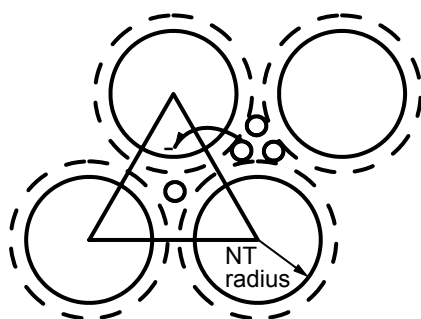


Figure 8. Sketch of a simple model for a bundle of (10,10) nanotubes intercalated by potassium for low and high intercalation levels. The dashed line is the nanotube radius plus the van der Waals distance.

atoms at the circumference and a length of the unit cell along the SWCNT axis of $2.49 \text{ \AA}$. Following the arguments of [34] and thus assuming a separation of the potassium ions along the nanotube axis of at least two times the radius of ions ($2.72 \text{ \AA}$), one needs about three potassium ions per unit cell of a (10,10) tube to achieve $20\text{C}/3\text{K} \sim 7$. The corresponding expansion of the bundle lattice is about $1.4 \text{ \AA}$. For a real macroscopic sample with about the same mean diameter and a Gaussian diameter distribution of $1.37 \pm 0.08 \text{ nm}$ the observed lattice expansion is only about $1.2 \text{ \AA}$ at full intercalation. This discrepancy can be explained by taking into account the finite size of the bundles of SWCNTs in the bulk samples. Experimentally, typical SWCNT bundles contain 30–100 SWCNT [60]. The potassium ions can be also absorbed at the surface of bundle. In this case they have a lower coordination number of SWCNTs yielding a higher C/K ratio at the surface of the bundle. For a simple estimation of the size of this surface related effect we take a parallelogram of 7×7 (10,10) tubes. In this case about 50% of the SWCNTs are at the surface of the bundle. For this configuration at the surface the coordination number of the potassium sites is reduced from three in the bulk to one in four cases and to two in 20 cases, respectively. This would lead to a much higher C/K ratio of about 3.3 at the surface assuming the same intercalation level as in the bulk. Under the assumption that the transferred electrons from the K ions are equally distributed within a SWCNT bundle this allows a much lower potassium coordination in the core of the bundle to achieve the experimentally found average $\text{C/K} = 7$. A lower limit for this potassium coordination in the bulk would be about two. This can explain that the lattice expansion of the intercalated SWCNTs is reduced as compared to the estimations from an infinite size bundle and that the lattice expansion for the intercalated peapods which have about 20% higher potassium content is about the same. Finally, we note that disorder and individual tubes which cannot be simply extracted from the electron diffraction pattern might also yield a higher carbon to potassium ratio.

3.3. Valence band excitations

We now turn our attention to the valence band excitations of the intercalated SWCNT (peapod) compounds. As a first example, the low energy loss function of SWCNTs was analysed for different potassium intercalation levels.

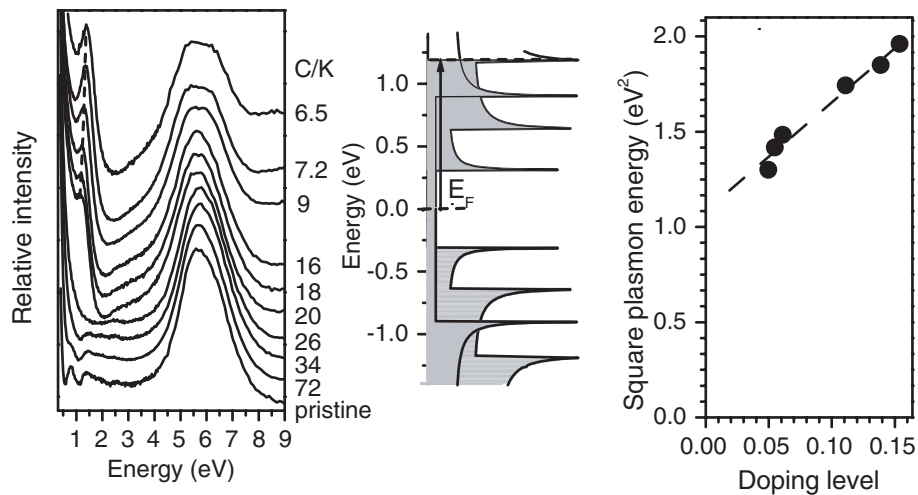


Figure 9. Left panel: the loss function of pristine SWCNTs and potassium-intercalated SWCNTs with different intercalation levels at $q = 0.1 \text{ \AA}^{-1}$, the potassium concentration increases from bottom to top as marked on the right side. The dashed line indicates the shift of the position of the charge carrier plasmons with increasing potassium concentration. Central panel: sketch of the Fermi level shift due to potassium intercalation. Right panel: quantitative relation between the square of the energy position of the charge carrier plasmon and the doping level [37].

The results are depicted in the left panel of figure 9 in the energy range between 0.2 and 9 eV at $q = 0.1 \text{ \AA}^{-1}$ after subtracting the quasi-elastic scattering. The wide peak at around 6 eV is the π plasmon related to a collective excitation of all π electrons. The three loss function peaks in the pristine peapods below 3.0 eV stem from the optically allowed interband transitions from the nanotubes [13]. The evolution of the loss function shows an intensity decrease of the lowest interband transitions with increasing potassium concentration. It can be clearly seen that the change in intensity of these interband transition peaks in EELS depends sensitively on the amount of the intercalant. With increasing potassium concentration, the three interband transitions finally disappear in good agreement with optical observations [33]. This can be straightforwardly interpreted via a charge transfer within the framework of a rigid-band model. In the case of alkali intercalation the conduction bands are populated with electrons. Consequently, some previously allowed optical transitions are suppressed as their final states become occupied. Gradual filling of the empty states within the density of states first quenches the lowest energy transitions, while the higher energy transitions are not affected initially. For higher intercalation levels, electronic final states of the second transition of semiconducting SWCNTs are filled such that the transition at the second lowest energy vanishes, as illustrated in the central panel of figure 9. The intercalation for this level is roughly achieved for a $C/K \approx 26$. Up to this intercalation level, the shape of the loss function at higher energies remains unchanged in comparison with that of pristine nanotubes.

With further increase of the potassium content an additional peak is observed in the loss function in the energy range between 1 and 2 eV. Its energy position shifts to higher values with increasing intercalation. Therefore, an origin of this peak due to interband transitions can be ruled out because its energy position then would be roughly independent

of the intercalation level. The new feature, in contrast, can be associated with the collective excitation of the introduced conduction electrons, the so-called charge carrier plasmon [36]. As can be seen in figure 9, it reaches about 1.4 eV at maximal doping. The upshift of this plasmon with increasing intercalation level is consistent with the increase of the density of charge carriers. In the right panel of figure 9, we show the dependence of the square of the charge carrier plasmon energy on the doping level (electrons per carbon atom as estimated from the intercalation level). Within the simplest approximation, the charge carrier plasmon energy, E_p , has a square root dependence upon the charge carrier density, n . From the right panel of figure 9, it is obvious that there is such a linear dependence of E_p^2 on the K concentration. It is possible to model the observed plasmon positions using the relation $E_p^2 = \hbar^2 n e^2 / (m^* \epsilon_\infty \epsilon_0)$ (m^* = charge carrier effective mass, ϵ_∞ = background dielectric constant). From optical reflectance measurements [63], the charge carrier plasmon (E_p) of the pristine SWCNTs is only about 200 meV. Therefore, its contribution to the charge carrier plasmon can be neglected. Since the charge carrier density n is proportional to the intercalation level, the right panel of figure 9 indicates that the product $m^* \epsilon_\infty$ in the denominator is not constant as a function of intercalation.

At high doping levels, the π plasmon becomes broader and broader with increasing intercalation, while its energy position shifts only very little to lower energies. This is in contrast to GIC KC_8 where a downshift of the π plasmon from about 7 to 6.3 eV is observed [57, 64, 65]. It should be mentioned that the small downshift in the case of SWCNTs is diameter dependent. The smaller the diameter of the SWCNTs, the larger the downshift of the π plasmon upon alkali metal intercalation. But it is always very small compared to the downshift in intercalated graphite KC_8 which shows that, in general, the electronic levels of SWCNTs are weakly affected by the intercalation process.

In order to obtain more detailed information about the charge carrier plasmon, the measured loss function was analysed using an effective Drude–Lorentz model of the dielectric response which was successfully applied to describe graphite or SWCNT intercalated compounds [30, 36, 37]. For a detailed analysis of this charge carrier plasmon subsequent fitting steps described elsewhere in detail were applied [37]. In this model the response from the π and $\pi + \sigma$ plasmons are contributing to an effective screening expressed by an effective background dielectric function ϵ_∞ . The results from the fit are depicted in figure 10.

For all potassium intercalated SWCNTs, the corresponding fit parameters for the charge carrier plasmon (unscreened plasmon energy $E_{p,0}$, the plasmon width Γ , and ϵ_∞) are presented in table 1 together with the calculated effective mass m^* and the evaluated DC limit of the optical conductivity σ_0 . For comparison, the data for GIC KC_8 and KC_{24} are also shown.

It turns out that the dielectric background ϵ_∞ is about 6.1 and almost independent of the intercalation level. This can be attributed to the fact that intercalation does not result in a significant rearrangement of the majority of the π and $\pi + \sigma$ electronic states. Thus, considering $\epsilon_\infty = 6.1$ and a change in the charge carrier density which is proportional to the intercalation level one arrives at an effective mass of the charge carriers, m^* , in the range of 0.37–0.82 times that of the free electron mass, m_0 . However, m^* is increasing upon increasing intercalation. Here a (10,10) nanotube is used to calculate the volume of the unit cell for determination of the electron density. The obtained optical effective mass for GIC KC_8 in the present experiment is consistent with the effective mass from the optical measurement [38, 66] but it is slightly lower compared with the value from de Hass–van

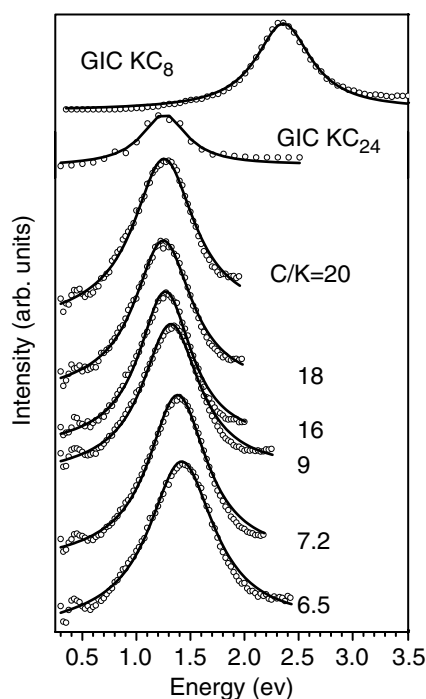


Figure 10. Loss function of potassium-intercalated SWCNTs in the range of the charge carrier plasmon after removing the quasi-elastic background (open circles) in comparison to the results from the Drude–Lorentz model (solid line). The potassium stoichiometry is indicated by the numbers. For comparison, the data and fitting results of GIC KC_8 and GIC KC_{24} are also shown [37].

Table 1. Parameters for the charge carrier plasmon in eV from the simulation of the loss function of GIC KC_8 , KC_{24} , and the K intercalated SWCNTs with stoichiometry as indicated [37].

	Charge carrier				
	$E_{p,0}$	Γ_0	ϵ_∞	m^*/m_0	σ_0 (S cm^{-1})
GIC KC_8	5.8	0.2	6.7	0.36	22 625
GIC KC_{24}	3.48	0.5	6.4	0.33	3277
C/K = 20	3.43	0.68	6	0.37	2330
C/K = 18	3.44	0.64	6.1	0.41	2450
C/K = 16	3.47	0.6	6.1	0.45	2730
C/K = 9	3.63	0.64	6.1	0.71	2780
C/K = 7.2	3.78	0.66	6.1	0.81	2900
C/K = 6.5	3.87	0.7	6.1	0.82	2940

Alphen experiments [67]. For the intercalated SWCNTs, the increase of the effective mass with intercalation might be related to the upshift of the Fermi level to an energy region where the conduction bands become flatter.

We now turn to the analysis of the optical properties of other alkali metal intercalated SWCNT and potassium intercalated peapods at saturation doping. As can be seen from the

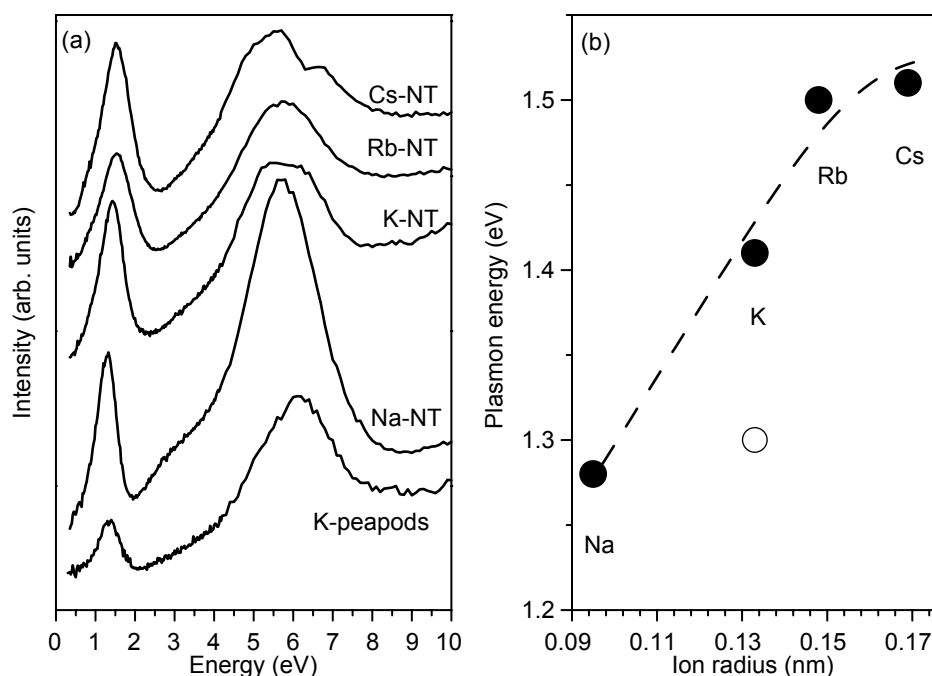


Figure 11. (a) The loss function of fully potassium intercalated peapods and of fully sodium, potassium, rubidium, and caesium-intercalated SWCNTs in the energy range between 0 to 10 eV after background subtraction. (b) The dependence of the charge carrier plasmon energy on the ion radius of different alkali-metal intercalated SWCNTs (full circles) and potassium intercalated peapods (open circle).

loss function shown in figure 11(a) the appearance of a charge carrier plasmon is common to all alkali-metal intercalants.

As depicted in figure 11(b) the charge carrier plasmon shifts to higher energies going from Na to Cs intercalation of SWCNTs. This is in contrast to GIC where for the alkali metals (Na, K, Rb, and Cs) the charge carrier plasmon is found in all cases at about 2.4 eV [65]. Interestingly, although the potassium content is about 20% higher, the position of the plasmon energy for the potassium intercalated peapods is lowered to about 1.3 eV as compared to the potassium intercalated SWCNTs. There is again no clear shift of the position of π plasmon near 6 eV for different alkali-metal intercalated samples. Such a behaviour is consistent with GIC with different intercalants [57]. However, as mentioned earlier, there is an obvious downshift of the π plasmon in GIC as compared to pristine graphite [57, 64, 65] which is not observed in the case of SWCNTs. The energy position of the π plasmon in the fully doped peapods is higher than that of SWCNTs, but it is lower than that in GIC KC_{80} .

To shed more light on this behaviour the loss function was again modelled as described above. Results of the fitting are shown in figure 12, and the parameters are included in table 2. For the doped peapods, the contribution from doped peas was also considered in the fit. Since we observed a fully occupied LUMO for our doped C_{60} peas we have included one additional transition of K_6C_{60} , which has a fully occupied LUMO in our Drude–Lorentz model. The intensity and width of the HOMO–LUMO transition of K_6C_{60} at 1.2 eV were taken from

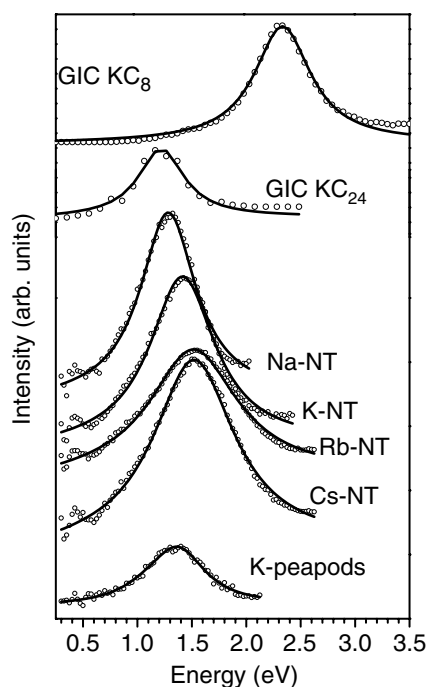


Figure 12. Analysis of the loss function of Na, K, Rb and Cs intercalated SWCNTs and potassium intercalated peapods as compared with GIC KC_8 and GIC KC_{24} . The solid lines are fitted curves, and the open circles represent experimental data.

Table 2. Parameters for the charge carrier plasmon in eV from the simulation of the loss function of GIC KC_8 , KC_{24} and of fully Na-, Rb-, K- and Cs-intercalated SWCNTs as well as K-intercalated peapods [37, 51].

	Charge carrier		ϵ_∞	m^*/m_0	σ_0 (S cm^{-1})
	$E_{p,0}$	Γ_0			
GIC KC_8	5.8	0.2	6.7	0.36	22 625
GIC KC_{24}	3.48	0.5	6.4	0.33	3277
K-peapods	4	0.5	8.4	0.33	3500
Cs-NT	3.55	0.9	4	0.83	1890
Rb-NT	3.8	0.98	4.7	0.74	1980
K-NT	3.9	0.7	6.1	0.82	2940
Na-NT	3.4	0.6	5.45	1.11	2470

previous experiments [68] considering the scaling factor in the peapods. All other C_{60} related transitions contribute to the dielectric background [51].

Upon increasing ion radius, the dielectric background tends to smaller values. This might be related to the larger distance between the tubes as a result of intercalation (see the discussion above). However, it is worth noting that alkali metal cause electronic excitations (e.g. excitations from K 3p into K 3d electronic levels) also contributing to the dielectric

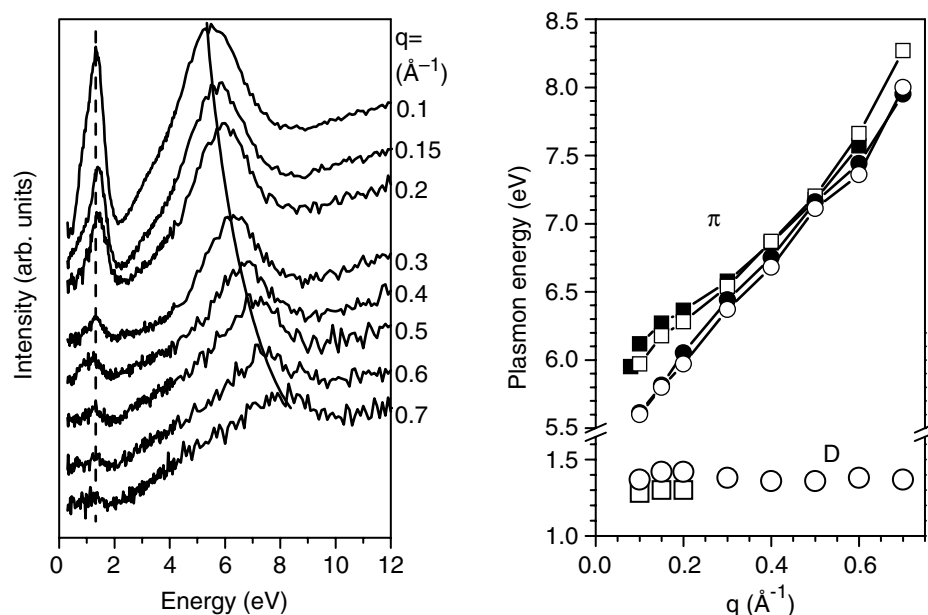


Figure 13. Left panel: loss function of fully potassium doped SWCNTs as a function of momentum transfer. The dashed (solid) line indicates the charge carrier (π) plasmon dispersion. Right panel: the charge carrier and π plasmon dispersion of fully doped peapods (open squares) and SWCNTs (open circles) compared with the pristine ones (black squares and black circles).

background, i.e. the screening of the charge carrier plasmon. Their contribution is not directly related to the ion radius as it sensitively depends upon the energy position and the spectral weight of the corresponding excitation. The unscreened plasma energy, $E_{p,0}$ is about 3.4–3.8 eV almost independent of the alkali metals which suggests that the bundle lattice expansion only little affects the plasma energy. As can be also seen from table 2, the effective mass of the charge carriers is about 0.74–1.11 times that of the free electron mass for the fully intercalated SWCNTs. The scatter between the different intercalants might be related to the uncertainties concerning the exact intercalation level which is assumed to be the same for saturated intercalation independent of the intercalant.

The dc limit of the optical conductivity of the doped peapods is very similar to that of the doped SWCNTs but it is much different from the GIC KC_8 . One reason is that the K doping causes the same structural disorder within the nanotube bundle for both peapods and SWCNTs, which is consistent with the above-mentioned electron diffraction results. Within the accuracy of this analysis the extracted dc conductivity of about $3000\text{--}3500 \text{ S cm}^{-1}$ in the fully intercalated peapods and SWCNT is the same. This is in good agreement with previous measurements of the resistance of an intercalated buckypaper [48].

Finally, we turn to the dispersion of the plasmons in the fully doped compounds. Since the measured dispersions are basically independent of the type of alkali metal, potassium intercalated SWCNTs and peapods were taken as typical examples. The results are shown in figure 13 for the loss function of fully potassium intercalated SWCNTs (left panel), and for the charge carrier and π plasmon dispersion of fully doped peapods and SWCNTs compared with the pristine ones (right panel).

Generally, in low-dimensional systems, the localization of the plasmon excitations depends on their polarization. This has been shown, for example, for trans-polyacetylene [69], where a dispersive plasmon is only visible in the one-dimensional direction. Thus, in combination with the well-known one-dimensionality of nanotubes the non-dispersive peaks in the loss function can be attributed to excitations between localized states which are polarized perpendicular to the nanotube axis and thus resemble molecular interband transitions such as those of C_{60} . In contrast, the π plasmon (at 5.2 eV for low momentum transfer), represents a plasma oscillation of delocalized states polarized along the nanotube axis [13]. As can be seen in the right panel of figure 13, upon intercalation the plasmon dispersion relations are rather similar for peapods and SWCNTs. The π plasmon disperses almost linearly to higher energies with increasing momentum and the dispersion is very similar to that found for the π plasmon in the pristine peapods. However, the π plasmon energy of the doped samples is slightly lower than that of the pristine ones. This again indicates that the electronic states of nanotubes are to a large extent only slightly affected by the intercalation process.

In contrast to the π plasmon, the charge carrier plasmon of the doped peapods does not show a dispersion, or only a very weak dispersion. It is also very similar to that of the doped SWCNTs [37]. Since the plasmon dispersion is proportional to the mean Fermi velocity, this indicates that the Fermi velocity of doped peapods and SWCNTs is rather small, a conclusion which is consistent with the arguments presented above that in fully intercalated compounds the Fermi level lies in a flat band region. Furthermore, with increasing momentum transfer the intensity of the charge carrier plasmon decreases very rapidly. For K-doped peapods, it almost disappears above $0.3 \text{ \AA}^{-1}$ which renders it difficult to follow its energy position at higher momentum. The drastic decrease in intensity can be ascribed to a damping of the plasmon as a result of a decay into interband excitations between valence and conduction bands in intercalated compounds (Landau damping) [65].

4. Conclusions

In summary, studies of the unoccupied electronic structure and of the optical properties of n-type (alkali-metal) and p-type (FeCl_3) intercalated SWCNTs and peapods using EELS in transmission were presented. The intercalation process modifies the bundle structure of SWCNTs (peapods). Compared with the spectra of the alkali-metal GIC, the core-level excitations of intercalated SWCNTs show that there is no hybridization between nanotube π^* states and metal valence states and that states above the nanotube Fermi level remain rather unperturbed by the intercalant. Furthermore, the intercalation systematically changes the optical response of the SWCNTs (peapods). Measurements of the dependence on doping show an intensity variation of the optical excitations due to the shift in the position of the Fermi level. This indicates the possibility of tuning the Fermi level into the conduction bands upon different electron donor intercalation. Upon intercalation, a charge carrier plasmon appears in the loss function. Its plasmon energy increases with the intercalation level and with the ionic radius of the alkali metal. The low energy loss function can be described within a Drude–Lorentz model. Within this model, the optical dc conductivity of sodium, potassium, rubidium and caesium intercalated SWCNTs, as well as potassium intercalated peapods could be determined and they give similar values for maximum intercalation. The results have also been used to derive the dielectric background and the effective (optical) charge carrier mass

of the intercalated SWCNTs which is found to be about two or three times bigger than in the corresponding GIC. Finally, the p-type doped SWCNTs (using FeCl_3) show that the Fermi level shifts into the valence band as reflected by the additional pre-peak in the C 1s core-level excitations. The maximum doping for FeCl_3 intercalation is found to be roughly 0.6 times that of the alkali-metal intercalated SWCNTs.

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