Optical and dc conductivity study of potassium-doped single-walled carbon nanotube films

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We have performed dc transport and optical conductivity measurements on purified and potassium doped thick films of single walled carbon nanotubes. The pristine sample is characterized by a metallic (Drude) response of the optical properties despite the non-metallic behavior in the dc resistivity measurements. Even though the spectral weight of the metallic component in the electrodynamic response increases with doping, in agreement with the trend of the dc transport properties, there is a quantitative mismatch between the optical $[\sigma_1(\omega \rightarrow 0)]$ and dc transport. Comparing the dc and optical conductivity measurements we conclude that potassium doping influences differently the non-metallic tube-tube contact regions and the intrinsic on-tube transport.

The electronic properties of a one-dimensional (1D) conductor have generated a lot of interest both experimentally and theoretically. The reason for this excitement lies in the very rich phase diagram of a 1D conductor (expressed in terms of the *g*-ology framework) and the prediction that in a 1D system Coulomb interactions should lead to a strongly correlated electron gas called Luttinger Liquid (LL), instead of the usual quasi-particle (or Fermi liquid) picture.[1–3] For instance, recent transport and optical measurements on the quasi-one-dimensional organic Bechgaard salts give evidence for typical fingerprints of the LL state.[2–4]

The synthesis of single walled carbon nanotubes[5,6] (SWNT) opened a new field of investigation for a 1D system. Carbon nanotubes (CN) are cylinders of a few μm length and of a diameter in the nm range, obtained by wrapping up a single graphene layer, the starting ingredient. There are many possibilities to roll-up a graphene layer into a cylinder, and the CN are classified according to the helical symmetry around the axis of the cylinder. The different classes of nanotubes are indicated by the lattice vectors *(n,m)* in the graphene layer to make the tube. Depending on the choice of *(n,m)*, the tube is either a metal, a narrow gap semiconductor or an insulator.[7,8] Although *(n,m)* cannot be controlled during the synthesis, scanning tunnel microscopy (STM) studies show that 30–40 % of the SWNT are metallic.[9]

The LL behavior was also identified in these metallic SWNT's.[10] However, the manifestation of the (exotic) metallic behavior in SWNT is controversial since twists of the nanotube or interaction with the substrate, over which CNs are deposited, can strongly perturb the CN electronic structure. It is believed that in mats of SWNT (called bucky paper) the metallic nature of the nanotubes manifests much easier. This is because of the absence of the substrate, even though the tube-tube contact resistances can still be present and undermine the dc transport.[11,12] Nonetheless, it has been demonstrated that the carrier density in SWNT can be changed by doping as in the case of graphite.[13] In order to have a clear picture of the effect of the charge transfer upon

doping on the transport properties, it is necessary to understand the interplay between different sources of transport: namely, the transport primarily induced by on-tube doping or governed by the doping of the tube-tube contacts. In this respect, we have performed dc transport measurements and optical experiments on pristine and potassium doped bucky paper samples. The measurements are not devoted to decide whether the SWNT behaves like a LL, but rather as a first step in order to obtain information on the intrinsic conductivity of these novel materials.

We have used several samples from several batches: our own production with the arc discharge method and our own purification, and samples bought from Carbolex and Rice University and repurified. The data of the pristine sample were comparable for all three batches if they were well purified. The pristine bucky paper was purified by the usual acid treatment and heat treated in vacuum at 1200 °C. The diameter of the SWNT in the ropes is around 1.4 nm. The volume fraction of the metallic catalytic particles is less than 1%. Potassium doping was performed in an oxygen-free, sealed atmosphere at 300 °C, for 48 h. The potassium doped samples are air sensitive. For this reason sealed cells that keep the samples in a safe atmosphere have been used both for dc and optical measurements. Four probe resistivity measurements were performed both during and after the doping in the sealed sample holder. For the optical investigation a specially designed cell with a wedged diamond window, that permits infrared reflectivity measurements, was used. Diamond is in fact transparent in a broad spectral range, from the ultraviolet to the far infrared (FIR) (extending also to microwave frequencies) except for a multi-phonon absorption band between 1500 and 4000 cm^{-1}. Moreover the wedged diamond window significantly reduces the amplitude of the interference fringes which are present especially in the FIR for windows with parallel faces. After the measurements, the sample has been removed from the diamond cell and a reference (aluminum mirror) has been measured in the same configuration. The reflectivity $R(\omega)$ was measured as a function of temperature over a broad spectral range from 30 up to 3×10^4 cm^{-1}, using three different spectrometers with overlapping frequency ranges (see Ref. 3 for more technical
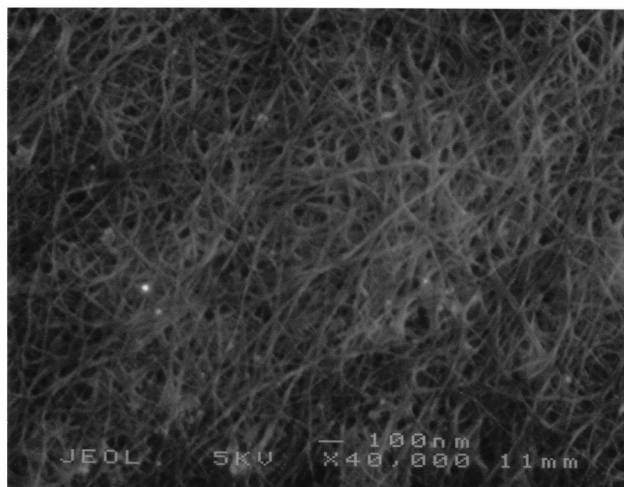
FIG. 1. Scanning electron microscopy (SEM) image of the pristine SWNT thick film used in dc transport and optical conductivity measurements.

details). The optical conductivity was obtained from Kramers-Kronig (KK) transformations of the measured reflectivity. Standard extrapolations [i.e., $R(\omega) \sim \omega^{-2}$ for $\omega > 3 \times 10^4$ cm^{-1} and $R(\omega) \sim \omega^{-4}$ for $\omega > 5 \times 10^5$ cm^{-1}] were used above our highest frequency limit, while below the lowest measured frequency we performed the Hagen-Rubens (HR) extrapolation.[3]

Figure 1 shows the scanning electron microscopy (SEM) image of the pristine sample. The sample consists of high density of SWNT ropes of different diameters with very low density of impurities. Due to the preparation method of the bucky paper by depositing it on a filtration membrane, the bucky paper quality is quite reproducible. The density is around 40 mg/cm^3 range (the theoretical density of the rope is 1.3 g/cm^3). This can vary slightly from batch to batch, and consequently the bucky paper resistivity too. However, the dc and optical conductivity were measured on the same bucky paper. Figure 2 shows a typical dc resistivity versus temperature curve for a stripe of the pristine and potassium doped sample. In the pristine sample the resistivity displays a shallow minimum at 360 K and below this temperature it shows a nonmetallic temperature dependence, in qualitative
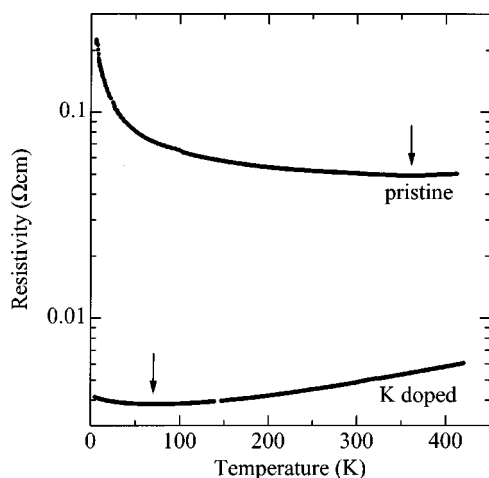

FIG. 2. dc resistivity versus temperature of a pristine and a potassium doped SWNT sample. The arrows indicate the shallow minimum at 360 and 70 K for the pristine and doped sample, respectively.
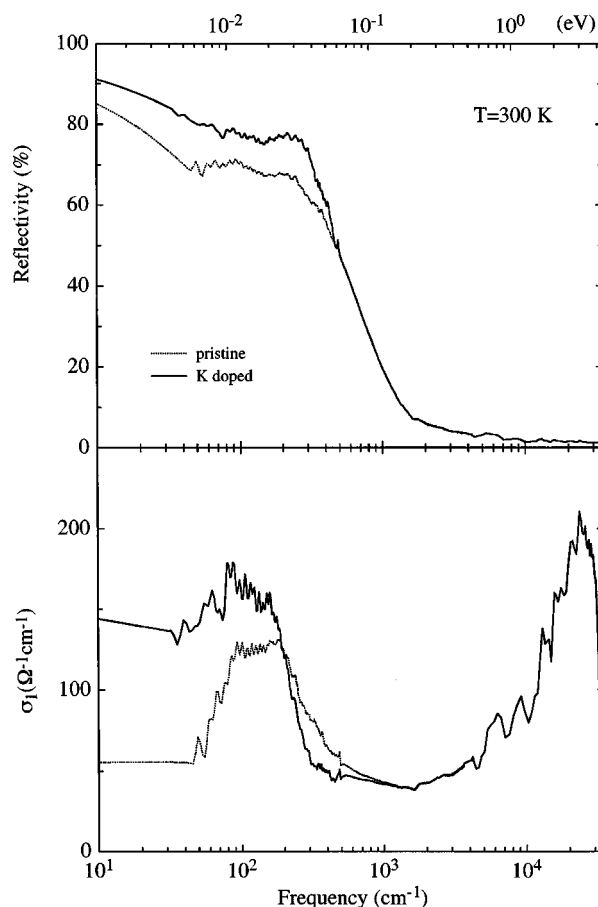

FIG. 3. Optical reflectivity (a) and optical conductivity (b) as a function of wave number (photon energy) for pristine and potassium doped SWNT sample.

agreement with previous investigations.[11–13] In the potassium doped sample the resistivity has decreased by a factor of 10 at 300 K and it shows a positive metalliclike slope down to 70 K, where a shallow minimum is evident before the slight increase of $\rho(T)$ below 50 K. $\rho(T)$ in the doped sample demonstrates the enhanced metallicity, at least down to 70 K, of SWNT upon doping, in accord with the electron-spin-resonance results[14] and resistivity[13] of potassium intercalated SWNT. By comparing resistivity measurements,[13] we can say that the relative change of the resistivity between the pristine and K-doped sample interpolates well between the changes of the pristine and fully saturated samples (that is KC8) cited in the literature.

Figure 3 displays the reflectivity spectra $R(\omega)$ and the corresponding real part $\sigma_1(\omega)$ of the optical conductivity for the pristine and the potassium-doped SWNT samples at $T = 300$ K. In all measured samples we did not find any temperature dependence in the optical spectra. We also note that the bucky paper thickness of about 20 μm was large enough so that our samples were not transparent in the investigated frequency range. In fact, the samples were mounted either on a Cu or on a glass plate and no contribution from or interference effects due to the bucky paper substrate were found. For both samples the reflectivity increases for decreasing frequency from the visible down to the FIR range showing the typical optical fingerprint for the metallic behavior, with a plasma edge at about 2000 cm^{-1}. A broad bump at about 200 cm^{-1} is also evident for both samples. However, for the

doped sample an increase of reflectivity in the mid and far infrared region (at frequencies lower than 400 cm^{-1}) is evident with the appearance of a stronger free charge carrier contribution at very low frequencies. There is a significant difference between the samples in the σ_{dc} values used for the HR extrapolations of $R(\omega)$ for $\omega \to 0$. In fact, our spectra are consistent with a HR law with $\sigma_{dc} = 60 \ (\Omega \ \text{cm})^{-1}$ for the undoped sample and $170 \ (\Omega \ \text{cm})^{-1}$ for the doped one, indicating also from the optical point of view an increased metallicity of the sample upon doping. While this is in accord with the trend of the transport measurements (Fig. 2), there is a quantitative disagreement (see below).

The real part of the optical conductivity is characterized by a broad absorption centered at about 150–200 cm^{-1} and by a peak at higher frequency that corresponds to an electronic interband transition. The intensity of this latter absorption is little affected by the extrapolation used for frequencies higher than the measured ones. Going from the pristine to the doped sample one can observe that at frequencies lower than 200 cm^{-1} the intensity of the optical conductivity is significantly increased and the broad FIR peak weakly shifts towards lower frequency. Our data are in agreement with the spectra measured by Ugawa *et al.*[15] and Kuzmany *et al.*[16] on an undoped SWNT bucky paper. The former data show a plasma edge at about 2500 cm^{-1} in the reflectivity spectra and a peak at about 120 cm^{-1} in the optical conductivity, in good accord with our results. Moreover, Ugawa *et al.* did not find any temperature dependence.[15] It is worthwhile to compare the present optical results with our investigation of mechanically aligned multi-walled CN.[17] Qualitatively, the spectra in both investigations are quite similar. Anyway, the multi-walled CN film has an apparent insulating-like behavior [i.e., $\sigma_1(\omega) \to 0$, for $\omega \to 0$], characterized by an absorption of about 50–70 cm^{-1}.[17] Because of the morphology of the multi-walled CN film we interpreted the spectra in terms of the Maxwell-Garnett (MG) approach which allows us to extract the intrinsic metallic contribution in the transport properties.[17] The MG approach is here not suitable since the SWNT specimen seems to be already in the so-called percolation limit, and furthermore the bucky paper does not allow any distinction between different (polarization or tube axis) directions. Therefore, our analysis and discussion of the optical data assumes that the specimens may be considered as homogeneous (bulklike) samples.

Pichler *et al.*[18,19] have recently performed high-resolution electron-energy-loss spectroscopy measurements of SWNT and potassium intercalated bundles of SWNT's. For the intercalated SWNT the loss function was fitted within a simple Drude-Lorentz model[20] with a charge carrier plasmon and three oscillators. From the fit parameters of Ref. 18 it is possible to calculate the expected reflectivity spectra. The calculated $R(\omega)$ curves are very similar to our spectra, with the same metallic behavior and a plasma edge feature somehow shifted to higher frequency. Our data better compare with the reflectivity obtained from the parameters of the less doped sample (with a ratio of $C/K = 16 \pm 2$) than with the reflectivity calculated from the most doped one (with $C/K = 7 \pm 1$).[18] This is actually consistent with microprobe analysis. We also note that one could use the energy loss spectra in order to complete our optical spectra for $\omega > 4 \times 10^4$ cm^{-1}. However, since $R(\omega)$ is very small at such high frequencies, it turns out that the doping dependence of the optical conductivity at $\omega < 10^4$ cm^{-1}, which is the relevant spectral range for the present discussion, is not affected by different extrapolations in view of the KK transformations. In the common investigated spectral range (i.e., between 0.5 and 3 eV), our optical spectra on SWNT are characterized by similar electronic interband transitions (see for comparison Fig. 3 and its inset of Ref. 19). We did not find any doping dependence in this range. This is in contrast to the results of Ref. 18, where changes in the energy loss spectra (see, e.g., Fig. 3 of Ref. 18) occur between 1 and 2 eV. We might speculate that the low reflectivity in the visible spectral range (because of relevant surface scattering of our bucky paper specimen) do not allow for enough resolution. Nevertheless, the effective changes upon doping of $R(\omega)$ in that spectral range should be rather tiny (see also below), as it could be evinced by calculating the expected reflectivity starting from the energy loss spectra.[18]

Our spectra can be perfectly reproduced by a Drude-Lorentz model.[20] Besides a Drude term at zero frequency for the effective metallic component of $\sigma_1(\omega)$, we consider three Lorentz harmonic oscillators (HO's) at higher frequencies. The first oscillator describes the absorption at about 150–200 cm^{-1} while the other two oscillators are necessary to qualitatively reproduce the spectra at high frequency. The aim of the fit is to account for the spectral weight distribution in $\sigma_1(\omega)$ and not for a specific assignment of the electronic interband transitions (see Refs. 18 and 19 for a more ample discussion of this issue). Since the doping has remarkable effect on the spectrum at frequencies lower than 200 cm^{-1}, the parameters of the two phenomenological oscillators at higher frequencies remain unchanged for the two samples. We then focus our attention on the remaining two components of the spectra: the Drude and the FIR absorption (i.e., the first HOs in our fit). The Drude term is enhanced in the doped sample. The parameters characterizing the Drude term of the pristine sample are $\omega_{pD} = 593$ cm^{-1} for the plasma frequency and $\gamma_D = 115$ cm^{-1} for the scattering rate, while for the doped sample we find a bigger value for the plasma frequency $\omega_{pD} = 984$ cm^{-1} and the same one for the scattering rate γ_D. The increasing plasma frequency upon doping is a further indication of the enhanced metallic contribution in the doped SWNT. Within our fits, we can also observe that the spectral weight gained by the Drude term upon doping is actually lost by the broad FIR absorption. Such a redistribution of the spectral weight upon doping leads to an enhancement of $R(\omega)$ in the FIR instead of an enhancement of the plasma edge feature. This seems to be consistent with the results of Pichler *et al.*[18] It is obviously possible that such a doping-independent plasma edge is the consequence of changes in the screening of the plasma frequency by electronic interband transitions outside our measurable spectral range (i.e., for $\omega > 4 \times 10^4$ cm^{-1}). It is necessary to achieve higher intercalations in order to observe remarkable effects on the plasma edge.

The absolute value of the dc conductivity of the pristine sample is $20 \ (\Omega \ \text{cm})^{-1}$ at room temperature, lower than the value deduced from the optical conductivity. This is probably associated with the fact that in pristine samples the dc transport is limited by the tube-tube (rope-rope) contacts, instead of being a measurement of the intrinsic conductivity

of the metallic nanotubes. In the case of the K-doped sample the dc-conductivity value changes by more than a factor of 10 at room temperature. This is due to the dramatic changes of the tube-tube contact resistance upon doping. Once the passage from tube to tube has been improved, the percolating path through the sample picks up more from the intrinsic, high on-tube conductivity. Consequently, the resistivity minimum is due to the interplay of a metallic (on-tube) and activated conduction (hopping of the electrons between the tubes through regions where they touch each other) across the sample. Due to surface effects and disorder (e.g., amorphous carbon on the tubes), the transport looks like a thermally activated passage through a barrier. Doping with potassium makes these regions much more conducting, rendering the inter-tube transport easier. Thus the resistivity minimum shifts to lower temperatures. On the other hand, since the SWNT are randomly oriented, the optical conductivity is averaged for all directions and its value for the doped sample [more specifically the dc limit of $\sigma_1(\omega)$] is lower than the conductivity along the metallic tubes. Indeed, the average $\sigma_1(\omega \to 0)$ value only increases by a factor of 3 upon doping. Nevertheless, we shall note that the optical spectra, while qualitatively similar, were found to be quantitatively very much dependent from the sample preparation (like, e.g., the content of potassium or the distribution of tubes with well defined n and m). Indeed, the optical conductivity never displayed a simple Drude-like behavior and the FIR feature (i.e., the absorption around 200 cm^{-1}) was sometimes smeared out within the high frequency tail of the Drude component and only a detailed fit of σ_1 reveals the presence of this absorption.

One possibility would be to ascribe this FIR feature to a gap on metallic tubes due to tube-tube interaction in the bundle. In fact, the symmetry of the individual tube in the rope is broken which induces a hybridization of the two crossing bands at the Fermi level, opening a small gap. In a simple model the dc resistivity minimum is related to the excitation through this gap. If this is the case the shift of the resistivity minimum in the K-doped sample to low temperature would mean the closing of the gap. In the optical spectra such a gap looks like a pseudo-gap because of the effective metallic contribution. However, the peak in the optical conductivity hardly changes its position, making this possibility unlikely. One could also speculate that this FIR feature is an ensemble of gaps belonging to those CN with (n,m) combination for which a semiconducting or insulating state is predicted.[8,15] In this respect, it is worth noting again, that the total spectral weight of the Drude component and the FIR absorption is constant in both specimen. However, the relative ratio of the Drude spectral weight with respect to the total is 16% for the pristine and 48% for the doped SWNT. Such a shift of spectral weight upon doping in favor of the effective metallic component in $\sigma_1(\omega)$ would suggest that the doping enhances anyway the metallic channels and/or the relative amount of intrinsically metallic CN. It remains to be seen why these gaps appear in such a small frequency range only. Alternatively, the FIR absorption could be associated with the convolution of several infrared active phonon modes. For a generic nanotube the number of optically active phonon modes depends on the chirality, while their resonance frequencies depend on both chirality and diameter (this seems to be especially true for the modes at lower frequencies). All nanotubes, independent of chirality, have infrared active modes in the range between 100 and 200 cm^{-1}.[21] Consequently, the convolution of these phonon modes could originate from a distribution of nanotubes with different chirality and diameter, forming our SWNT bucky paper samples.

In conclusion, we have performed dc transport and optical conductivity measurements on purified pristine and potassium doped SWNT thick films, emphasizing particularly the effect of doping on transport. The pristine sample shows a Drude component in the optical conductivity despite the nonmetallic behavior in dc resistivity measurements. We attribute this disagreement to effects due to the nonmetallic tube-tube contacts. The latter principally affects the transport. It also turns out that the potassium doping much more strongly influences the tube-tube contact regions than the intrinsic on-tube transport, so that the average dc conductivity is higher than the $\omega \to 0$ optical contribution, averaged over all directions.

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