Transition from a Tomonaga-Luttinger Liquid to a Fermi Liquid in Potassium-Intercalated Bundles of Single-Wall Carbon Nanotubes

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We report on the first direct observation of a transition from a Tomonaga-Luttinger liquid to a Fermi-liquid behavior in potassium-intercalated mats of single-wall carbon nanotubes. Using high resolution photoemission spectroscopy, an analysis of the spectral shape near the Fermi level reveals a Tomonaga-Luttinger liquid power law scaling in the density of states for the pristine sample and for low dopant concentration. As soon as the doping is high enough to achieve a filling of the conduction bands of the semiconducting tubes, a distinct transition to metallic single-wall carbon nanotube bundles with the scaling behavior of a normal Fermi liquid occurs.

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The charge transport properties of carbon nanotubes have been investigated intensively over the last years since they represent an archetype of a one-dimensional (1D) system [1–3]. For metallic 1D systems, conventional Fermi-liquid (FL) theory fails due to strong correlation effects. Correlation effects are one of the central research areas in solid state physics and therefore 1D metals are a paradigm for solids, where a breakdown of the FL theory due to many-body problems is expected. Under certain conditions a one-dimensional metal forms a Tomonaga-Luttinger liquid (TLL) which shows peculiar behavior such as spin charge separation and interaction dependent exponents in the density of states, correlation function, and momentum distribution of the electrons [1,2,4,5]. Results from transport measurements through junctions between metals and individual metallic carbon nanotubes as well as between carbon nanotubes have been extensively analyzed in the framework of a tunneling into or between TLL [6–8]. Recently, the electronic density of states (DOS) of the valence band electrons of mats of single-wall carbon nanotubes (SWCNT) was directly monitored by angle integrated high resolution photoemission experiments [9]. The spectral function and the temperature dependence of the intensity at the Fermi level exhibited a power law dependence with exponents of 0.46 and 0.48, respectively, which are identical within experimental error. This value yields a TLL parameter $g = 0.18$ which is in very good agreement with theoretical predictions [1,2] and consistent with transport experiments through carbon nanotubes between normal metals [8]. This photoemission study clearly evidenced that metallic SWCNT within a bundle of SWCNT can be described within TLL theory regarding their low energy properties without uncertainties regarding their contacting. However, there is still an open question regarding the amount of metallic SWCNT within a bundle of SWCNT. The interaction within a bundle could yield to the opening

of a small gap in all SWCNT [10]. Hence, all SWCNT would be narrow gap semiconductors which could not be described within TLL theory. On the other hand, tight binding calculations of bundles of metallic SWCNT pointed out that only for a (10,10) crystal a pronounced pseudogap of about 0.1 eV is observed, whereas in a disordered bundle of metallic SWCNT with different chirality, the interaction between neighboring SWCNT is weak and has a negligible effect on the DOS in the vicinity of the Fermi level [11].

In this Letter we first address the question if the power law behavior observed in the recent photoemission study [9] is related to the existence of the above mentioned pseudogap or to a TLL behavior. By means of doping, the Fermi level for the metallic tubes could be shifted away from the pseudogap region and still a power law behavior with the same α is observed. Second, it is interesting to study the case where the Fermi level is shifted into the states of the semiconducting tubes of the bundle. A strong reduction of α is observed due to the filling of a band from the semiconducting tubes with non-one-dimensional character. Finally, at the highest doping levels and probably due to the filling of nonlinear dispersing bands of the metallic tubes, a clear Fermi edge, typical of a normal FL behavior, is observed.

One very efficient possibility to change the electronic properties by doping with electrons or holes is intercalation, which has been studied extensively for compounds such as fullerene intercalation compounds (FICs) [12] and graphite intercalation compounds (GICs) [13]. For SWCNT intercalation compounds, in contrast to FICs and GICs, no distinct intercalation stages have been observed as yet. Alkali metal intercalation of mats of bundled SWCNT takes place inside the channels of the triangular bundle lattice [14,15] and leads to a shift of the Fermi energy, a loss of the optical transitions [16], and an increase of the conductivity by about a factor of 30

[14,17]. A complete charge transfer between the donors and the SWCNT was observed up to saturation doping, which was achieved at a carbon to alkali metal ratio of about seven [14,15]. However, much less has been reported on direct measurements of the low energy electronic properties as a function of doping. First results using photoemission revealed a Fermi edge at high doping [18]. Here, we report the first detailed study of the change in the low energy electronic properties in mats of SWCNT as a function of potassium intercalation using high resolution photoemission as a probe.

Mats of purified SWCNT, which consist of a mixture of roughly 2/3 of semiconducting and 1/3 metallic SWCNT, with a narrow diameter distribution which is peaked at 1.37 nm with a variance of about 0.05 nm [9] were produced by subsequent dropping of SWCNT suspended in acetone onto NaCl single crystals. The produced SWCNT film of about 500 nm thickness was floated off in distilled water and recaptured on sapphire plates. For the photoemission experiments the sample was mounted onto a copper sample holder and cleaned in a preparation chamber under ultrahigh vacuum conditions (base pressure 9×10^{-11} mbar) by electron beam heating to 800 K. Electrical contact of the SWCNT film was established by contacting the surface to the sample holder via a Ta foil. Then the sample was cooled down to $T = 35$ K and transferred under ultrahigh vacuum conditions to the measuring chamber and analyzed regarding the electronic properties using a hemispherical high resolution Scienta SES 200 analyzer. For the angle integrated valence band photoemission spectra using monochromatic HeIα (21.22 eV) excitation, the energy resolution was set to 10 meV. The core level x-ray photoemission spectroscopy was performed at 400 meV energy resolution using monochromatic AlKα excitation (14 86.6 eV). The Fermi energy and overall resolution was measured on freshly cleaned Ta. The intercalation was performed *in situ* after heating the sample to 450 K using commercial SAES potassium getter sources. After subsequent exposure to the dopant vapor an additional equilibration for about 30 min at 450 K was performed to increase the sample homogeneity.

The sample stoichiometry and purity was checked by core level photoemission spectroscopy. In the spectrum, no structures other than C and K could be observed. The binding energy of the C1s line is shifted by about 0.8 eV to higher values for the highest dopant concentration (here C/K = 15). This can be explained by an upshift of the Fermi level into the conduction band in good agreement with results from electron energy loss and Raman spectroscopy [15,19], and similar to the corresponding GICs [20]. The doping level was determined by the ratio of the C1s/K2p intensities taking into account the different photoionization cross sections.

We now turn to the detailed analysis of the high resolution valence band photoemission experiments at

$T = 35$ K. The results are depicted in Fig. 1. Compared to graphite, only close to the Fermi level distinct differences are observed in the photoemission response of the SWCNT mats [9,21]. For the pristine SWCNT, the photoemission peaks corresponding to the first and second Van Hove singularity (VHs) of the semiconducting SWCNT (S_1/S_2) and that of the first VHs of the metallic SWCNT (M_1) are observed — in very good agreement with previous results [9]— at binding energies of 0.44, 0.76, and 1.06 eV, respectively. In the simplest picture the valence band VHs S_1 and the conduction band VHs S_1^* would be symmetric around the Fermi level of the SWCNT bundle yielding a S_1^* position of 0.44 eV above the Fermi level. However, it is well known from scanning tunneling spectroscopy [22] of individual nanotubes that the VHs peaks of semiconducting SWCNT can be shifted away up to 0.1 eV with respect to the Fermi level due to charge carrier injection from the substrate. A similar effect can be expected for our photoemission experiments due to a redistribution of the charges within a bundle consisting of a mixture of semiconducting and metallic SWCNT by contact potentials. This allows us to safely estimate the position of the conduction band S_1^* being at least 0.3 eV above the Fermi level of the SWCNT bundle. With increasing doping, the peaks corresponding to the SWCNT VHs (S_1/S_2, and M_1) shift to higher binding energy due to a filling of the conduction band of the SWCNT with K 4s electrons (see dashed lines in Fig. 1). At low doping ($< 0.0066 e^-$/C, C/K = 150), the conduction band of the metallic SWCNT within the SWCNT bundles is subsequently doped. Interestingly, the conduction band of the semiconducting SWCNT (S_1^* VHs) is not
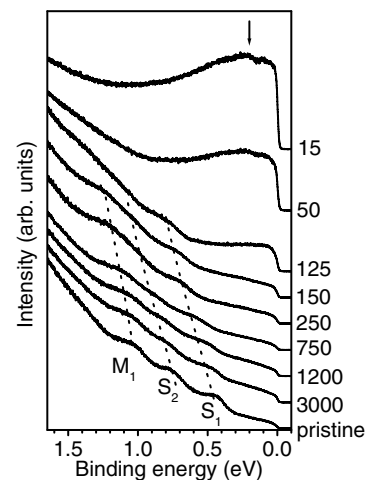

FIG. 1. Doping dependence of the valence band photoemission spectra in the vicinity of the Fermi edge for high doping levels. The numbers correspond to the C/K ratio derived from core level photoemission. The dotted lines are guidelines for the evolution of the S_1, S_2 and M_1 peaks with increasing doping. The arrow highlights the satellite in the photoemission response at high doping levels.

filled for these doping levels, hence, they remain semi-conducting. In the photoemission response this leads to a parallel shift of the positions of the S_1 and S_2 peaks to a higher binding energy (up to 0.3 eV). For the corresponding metallic SWCNT within the bundle the shift of the M_1 peak is lower than for the semiconducting SWCNT [23]. At higher doping ($> 0.0008 e^-/C$, C/K = 125), the S_1 peak shifts upward beyond the original position of the S_2 peak and the corresponding S_1^* VHs is occupied. As can be seen in the figure for further increasing the doping level the peaks of the VHs are smeared out and finally disappear completely ($> 0.02 e^-/C$, C/K = 50). This can be explained by effects like an increasing number of scattering centers (K$^+$ counter ions) and by an increasing intertube interaction within the SWCNT bundle in the intercalation compound. The overall shape of the spectra of these highly doped samples are also very similar to the corresponding GICs [20]. The Fermi level shift can be extracted from the shift of the π band at 3 eV. For the sample with C/K = 15 we observe $\Delta E_F = 1$ eV, which is consistent with the 1.25 eV shift observed for the GICs KC$_8$ [20] and in good agreement with the above mentioned core level shifts. Notably, none of the doping levels exhibit peaks corresponding to the former unoccupied S_1^*, S_2^*, and M_1^* VHs. On the other hand, for all highly doped samples a satellite in the photoemission response occurs at about 200 meV, which is very close to the frequency of the G line of the doped SWCNT [19]. Hence, it is tempting to explain this as a redistribution of the spectral weight by electron-phonon coupling. This explanation is also supported by the close analogy of the line shape to the low temperature photoemission spectra of the metallic C$_{60}$ intercalation compound K$_3$C$_{60}$, which is dominated by strong satellites due to coupling to phonons and to the charge carrier plasmon [24]. This change in the line shape due to electron-phonon coupling also explains the absence of the above mentioned photoemission peaks related to the S_1^*, S_2^*, and M_1^* VHs.

We now turn to the analysis of the low energy electronic properties (below 0.3 eV binding energy). For a three-dimensional system one would expect a constant DOS and a typical Fermi edge. As can easily be seen in Fig. 2, this is only observed at very high doping levels. For the pristine SWCNT sample, on the other hand, there is a strong suppression in the DOS near the Fermi energy. This behavior can be fully explained within a TLL theory of one-dimensional metals. A key manifestation of the TLL state is the renormalization of the DOS ($n(E)$) near the Fermi edge, which shows a power law dependence $n(E) \propto E^\alpha$, where α depends on the size of the Coulomb interaction and can be expressed in terms of the Luttinger parameter g as $\alpha = (g - g^{-1} - 2)/8$ [1–3]. In the case of photoemission, α can be directly derived from a linear fit of the double-logarithmic representation of the response at low binding energy (see Fig. 3). For the pristine SWCNT (bottom curves in Figs. 1 and 3,), we observe a
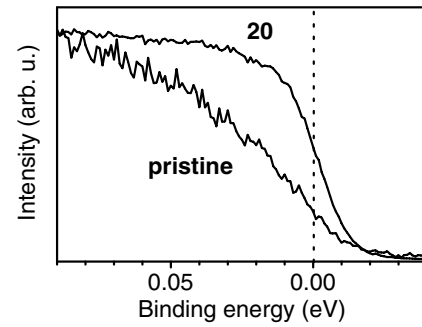

FIG. 2. Valence band photoemission spectra in the vicinity of the Fermi level (dotted line) for pristine (upscaled for clarity) and highly doped (C/K=20) SWCNT mats.

power law scaling $\alpha = 0.43$, $g = 0.18$, which is — within the experimental error — identical to the previously reported value ($\alpha = 0.46$–0.48) [9].

These results give rise to the important question as to what happens to the TLL as a function of doping and especially at what doping level the transition from a TLL ground state to a FL behavior occurs. Figure 3 shows typical examples for the TLL scaling for doping levels up to C/K = 125. The solid lines in the figure represent the linear fit for the determination of the scaling factor α. It can be easily seen that α depends on the doping level and vanishes at C/K = 125. The details in the doping dependence of α are depicted in Fig. 4. For doping levels $< 0.0003 e^-/C$ no change in the TLL parameter is observed within experimental error. As mentioned above, up to this doping level the shift of the S_1 peak to a higher binding energy is 0.3 eV, which is small enough not to start any filling of the S_1^* level and only the metallic SWCNT within the bundle are doped. Hence, the metallic
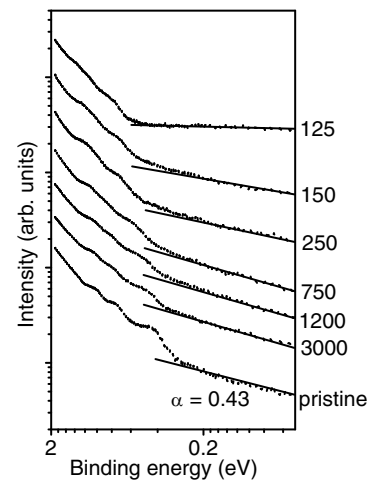

FIG. 3. Double-logarithmic representation of the photoemission spectra for the analysis of the power law scaling within TLL theory close to the chemical potential. α results from a linear fit between 0.05 and 0.2 eV (solid lines in the figure) and is also shown for the pristine case.
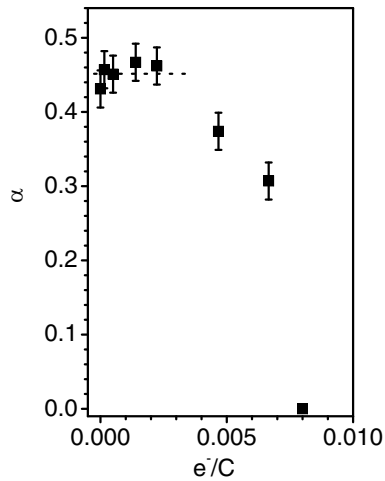
FIG. 4. Power law scaling factor α as a function of different doping levels (e^-/C).

SWCNT remain TLL upon filling of the conduction band and a corresponding Fermi level shift up to 0.3 eV. This also means that the long range Coulomb interaction is essentially unaffected by the potential of the counter ions. This is in good agreement with predictions showing that for a TLL the power law scaling parameter α is not affected until the first VHs M_1^* is reached and additional conduction channels are possible [3].

For the intermediate doping levels ($0.0003 < 0.0008e^-/C$) one starts to dope the semiconducting SWCNT. This can be substantiated by two facts. First, the additional shift of the S_1 peak over this doping range is only 0.07 eV, namely, from 0.3 to 0.37 eV. Second, the photoemission spectral weight close to the Fermi level strongly increases (see also Fig. 1). Regarding the TLL scaling, α decreases to 0.35 ($0.0046e^-/C$), then yet further to 0.3 ($0.0066e^-/C$), and finally shows a rapid transition to zero at $0.008e^-/C$. At this doping level the Fermi level is within the S_1^* VHs for the majority of the semiconducting SWCNT. We can explain this observation as a transition from a sample with roughly 1/3 of metallic SWCNT with TLL behavior to a sample which consists of only metallic SWCNT and has the scaling behavior of a normal FL. At even higher doping levels a Fermi edge is observed. This can be explained by the fact that at this dopant concentration the Coulomb interaction between charge carriers is strongly screened by neighboring tubes, now being all metallic, and/or by the fact that in a sample of only metallic tubes the hopping matrix element between the tubes is strongly enhanced, thus yielding a more three-dimensional electronic structure [4].

In summary, we have studied the character of the electron liquid of bundles of SWCNT as a function of dopant concentration, i.e., as a function of the position of the Fermi level. As long as the Fermi level shift is small enough to only affect the states of the metallic tubes, a TLL behavior is observed, indicating a weak interaction between the individual metallic tubes within a bundle. When the Fermi level is shifted into the states of the semiconducting tubes, the reduced power law behavior indicates a transition to a FL. This can be explained by a more three-dimensional band structure and/or screening effects, which lead to a normal FL behavior of the entire bundle. Thus, we have expounded for the first time a doping induced transition from a quasi-one-dimensional system with a TLL behavior to an intercalation compound with normal FL behavior.

[1] R. Egger et al., Phys. Rev. Lett. **79**, 5082 (1997).
[2] C. Kane et al., Phys. Rev. Lett. **79**, 5086 (1997).
[3] R. Egger, Phys. Rev. Lett. **83**, 5547 (1999).
[4] J. Voit, Rep. Prog. Phys. **58**, 977 (1995).
[5] M. Grioni and J. Voit, in *Electronic Spectroscopies Applied to Low-Dimensional Materials*, edited by H. P. Hughes and H. I. Starnberg (Kluwer Academic, Dordrecht, 2000), p. 209 281.
[6] M. Bockrath et al., Nature (London) **397**, 598 (1999).
[7] H. Postma et al., Phys. Rev. B **62**, R10653 (2000).
[8] A. Bachtold et al., Phys. Rev. Lett. **87**, 166801 (2001).
[9] H. Ishii et al., Nature (London) **426**, 540 (2003).
[10] M. Ouyang et al., Science **292**, 702 (2001).
[11] A. A. Maarouf, C. L. Kane, and E. J. Mele, Phys. Rev. B **61**, 11 156 (2000).
[12] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996).
[13] M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. **30**, 139 (1981).
[14] T. Pichler et al., Solid State Commun. **109**, 721 (1999).
[15] X. Liu et al., Phys. Rev. B **67**, 125403 (2003).
[16] S. Kazaoui et al., Phys. Rev. B **60**, 13 339 (1999).
[17] R. S. Lee et al., Nature (London) **388**, 255 (1997).
[18] S. Suzuki et al., Phys. Rev. B **67**, 115418 (2003).
[19] T. Pichler et al., Phys. Rev. Lett. **87**, 267401 (2001).
[20] P. Oelhafen et al., Phys. Rev. Lett. **44**, 197 (1980).
[21] S. Suzuki et al., Phys. Rev. B **63**, 245418 (2001).
[22] J. W. G. Wildör et al., Nature (London) **391**, 59 (1998).
[23] At very low doping levels, only the metallic tubes are doped. The position of the Fermi level of the semiconducting tubes in the gap is only determined by contact or impurity potentials and does not change upon doping in the same way as the Fermi level of the metallic tubes. This causes a different shift of S_1/S_2 compared to M_1.
[24] M. Knupfer et al., Phys. Rev. B **47**, 13 944 (1993).