

Metallic Polymers of C₆₀ Inside Single-Walled Carbon Nanotubes

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(Received 4 May 2001; published 4 December 2001)

Doping induced polymerization of C₆₀ inside single-walled carbon nanotubes is reported using Raman spectroscopy and resistivity measurements as a probe. The resistivity changes from semiconducting for the undoped system to metallic for the doped system. For full intercalation, we observe a chemical reaction inside the nanotubes which leads to a one-dimensional polymeric C₆₀⁻⁶ chain which has metallic character. The resonance and the oscillations of the radial breathing mode are lost suggesting an up-shift of the Fermi level to beyond the third Van Hove singularity in the semiconducting tubes. The linewidth of the radial breathing mode now represents directly the Gaussian distribution of tube diameters.

DOI: 10.1103/PhysRevLett.87.267401

PACS numbers: 78.30.-j, 63.20.Dj, 78.66.Qn, 78.67.Ch

New forms of carbon such as fullerenes and single-walled carbon nanotubes (SWCNT) have considerably attracted the interest of scientists for many years [1]. Among other properties, doping has been studied extensively for fullerenes and to a lesser degree also for SWCNT. Doped fullerenes can have semiconducting, metallic, and even superconducting properties with T_c up to 117 K [2]. A distinct separation between the individual phases of the fullerene salts was observed and, under certain conditions pristine as well as doped fullerenes can exhibit polymeric structures [3].

Recently SWCNT filled with C₆₀ molecules, so-called peapods, were observed using high-resolution transmission electron microscopy [4] and have been produced in high yield by simultaneously heating opened SWCNT and C₆₀ in a sealed quartz tube [5]. Filling of nanotubes with other fullerenes or with inorganic material [6] has been demonstrated as well, which promotes the impression that SWCNT are ready to accept various types of molecules and thus provide a nanocavity for new materials.

In this Letter, we demonstrate for the first time that fullerene molecules undergo a chemical reaction in this cavity to form covalently bonded and charged linear chains which do not exist outside the nanoreactor. The bonding is induced by doping the peapod system with potassium. The resulting linear chains exhibit fingerprints of a metallic polymeric state. Such fingerprints are the observation of a metallic temperature dependence for the resistivity, Fano interferences for at least two of the Raman lines, and characteristic new lines at about 370 and 620 cm⁻¹. Electronic states of the tubes are demonstrated to be filled up to the third Van Hove singularity (VHS) but part of the transferred electrons are accommodated at the fullerene cage and eventually drive the chemical reaction. As a consequence of the filling of the tube states, the photoselective resonance scattering of light is quenched and the quantum oscillations of the cross section for the radial breathing mode (RBM) are lost. The linewidth of the Raman

response now replicates directly the distribution of tube diameters.

Raman spectroscopy has been demonstrated to be a key technique to study structural changes and doping in C₆₀ as well as in SWCNT. In the case of C₆₀, two modes of symmetry A_g and eight modes of symmetry H_g are Raman active. Most prominent is the pentagonal pinch mode $A_g(2)$, located at 1469 cm⁻¹ at room temperature. This mode exhibits a well-established quasilinear softening of about 6.5 cm⁻¹ per extra electron transferred to the cage. Similarly, covalent bonding in polymers or dimers shifts the $A_g(2)$ mode by about 3 cm⁻¹ per extra bond. For the SWCNT two groups of lines are relevant. Between 1500 and 1600 cm⁻¹, several strong lines appear which are globally assigned as graphitic species since they can be derived from the G line observed at 1580 cm⁻¹ in pyrolytic graphite. Around 200 cm⁻¹ the RBM of the tubes responds strongly to the Raman excitation. This mode scales as C/d , where d is the diameter of the tubes and $C = 234$ cm⁻¹ nm is a constant determined recently from an *ab initio* calculation [7]. The Raman response for this mode is subjected to a photoselective resonance scattering when the spectra are excited with different lasers [8–11]. This resonance was recently demonstrated to be responsible for the fine structure in the RBM pattern and for an oscillating behavior of the spectral moments [12]. Much less is known about the Raman response of alkali metal doped SWCNTs. Only very recently some details were reported [13–15] indicating first an up-shift and eventually a down-shift and a Fano line shape for the G line in the heavily doped state [13].

The nanotubes were prepared by laser desorption and were purified and filled as described previously [5]. The resulting mats of bundled tubes (peapods) were vacuum annealed at 800 K to get rid of any nonencapsulated C₆₀ molecules. Measurements of the filling ratio using bulk sensitive electron energy loss spectroscopy (EELS) revealed a C₆₀ occupancy of about 60% [16]. This is

consistent with an almost complete filling since only tubes with diameters larger than 1.3 nm can accept C_{60} as recently predicted theoretically [17]. The intercalation was performed in a purpose built cryostat by exposing the tube material to potassium vapor in front of the spectrometer at a sample temperature of 450 K. In order to provide optimum conditions for comparison the doping process, the recording of the Raman spectra and the four point resistivity measurements were carried out simultaneously and *in situ* for empty and C_{60} filled samples from the same batch. Raman spectra were recorded for laser lines extending from 1.6 to 3 eV and between 20 and 450 K using a Dilor *xy* triple spectrometer calibrated for intensities.

The Raman pattern of the radial part and of the tangential part of the peapod spectrum are depicted in Fig. 1. The G mode from the tubes is strongest for the blue-green excitation. It becomes rather weak and Fano distorted for red laser excitation [see Fig. 3 (below), spectrum (a)], very similar to the response from pristine tubes. The response from C_{60} is also resonant for excitation in this spectral range. The strongest line of the fullerene comes from the $A_g(2)$ mode and is observed at 1466 cm^{-1} with an intensity 20 times lower than the one for the G line. A satellite line is observed at 1474 cm^{-1} which dominates for red laser excitation. The features at about 1320 and 1430 cm^{-1} correspond to the D line of the tubes and the $H_g(7)$ mode of the peas, respectively. As shown in the left panel of Fig. 1, the relative intensities between the response from the tubes and from C_{60} are almost the same in the radial part of the spectrum. Very similar to the free molecule, the $H_g(1)$, $H_g(2)$, and $A_g(1)$ lines are seen at 270 , 430 , and 495 cm^{-1} , respectively.

The resistance was studied as a function of temperature at various doping levels. It reached a saturation value after several hours doping which was considered as the fully doped state of the peapod system. Figure 2 displays the resistance versus inverse temperature between 500 and 77 K.

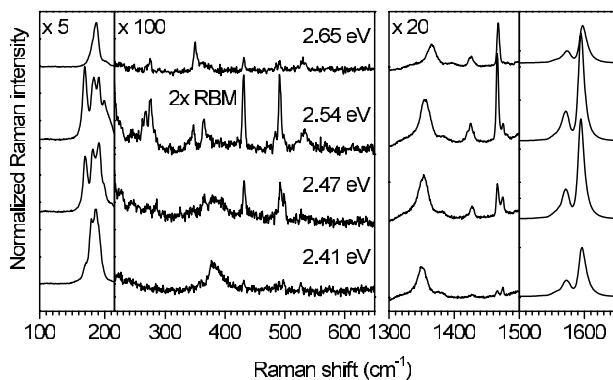


FIG. 1. Radial and tangential part of the Raman spectrum at $T = 20$ K for peapod material as excited with four different lasers indicated by the photon energies. The scaling factor is relative to the G line of the SWNT. The lines between 360 and 390 cm^{-1} originate from the RBM overtone.

Whereas the temperature dependence for the pristine reference sample was metallic, the peapods exhibited clearly a semiconducting behavior. In the fully doped state the overall system became metallic again, particularly between RT and 130 K. At low temperatures the overall decrease in resistance was about a factor of 100 as compared to the pristine state. The conductivity increase in the peapod salt is about 3 times larger than for saturation doping of the reference sample. The value for the latter is in good agreement with previously reported results [18].

During the initial process of doping, the overall Raman response decreased gradually but the resonance cross section of the metallic tubes was dramatically reduced. This can be seen from the bleaching of the low frequency part of the G mode if the spectra were excited with a red laser as shown in Fig. 3. The response from the C_{60} cages exhibited almost no change at this stage of doping (inset of Fig. 3). In contrast, for heavy doping also the overall resonance enhancement is almost lost [spectrum (c) in the Fig. 3]. The response of the main maximum is up-shifted by 7 to 1605 cm^{-1} and all components are broadened.

To demonstrate the doping of the C_{60} cages inside the tubes, it needs to record the spectra at low temperatures. Results for several lasers and for the spectral region of the radial breathing and of the tangential modes are depicted in Figs. 4(a) and 4(b), respectively. The RBM [Fig. 4(a)] is not oscillating anymore and reduced in intensity by about a factor of 100. For the blue-green laser excitation, its peak intensity is now almost equal to the intensity of the $H_g(1)$ mode of C_{60} . The shape of the line is almost Gaussian with a maximum at 185 cm^{-1} and a FWHM of about 20 cm^{-1} , corresponding to $1.37 \pm 0.08\text{ nm}$ for the diameter distribution. This is almost identical to the results obtained from the Raman analysis of the undoped material. The loss of any fine structure in the response is consistent with a line

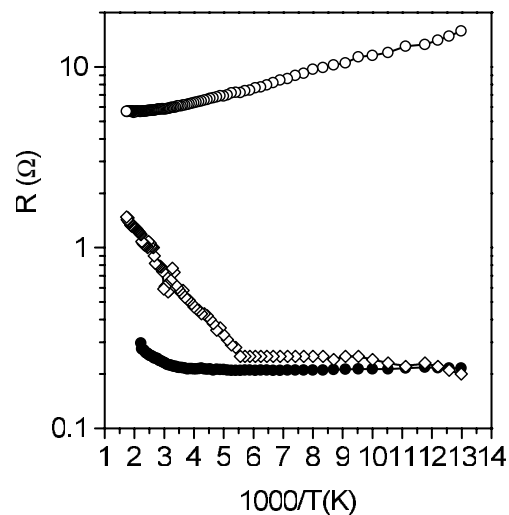


FIG. 2. Sample resistance versus inverse temperature for nanotube films in different states: pristine nanotube material (\diamond), pristine peapods (\circ), and heavily potassium doped peapods (\bullet).

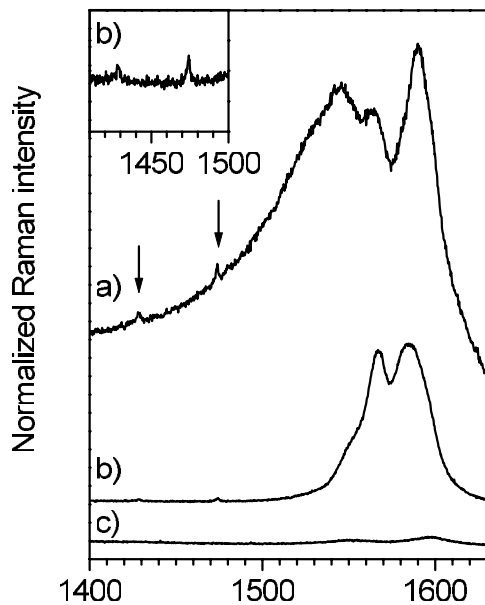


FIG. 3. Tangential part of the Raman spectrum for peapod material as excited with a red laser (1.84 eV) at $T = 77$ K. The arrows indicate the response from C_{60} . Spectra (a), (b), and (c) were obtained for the pristine peapod material, the weakly intercalated material, and for the heavily doped system, respectively. The inset shows a blowup of the C_{60} modes for the weakly intercalated compound.

broadening of the individual contributions which may well originate from a coupling of the RBM to free carriers. The response from the $H_g(1)$ mode exhibits a clear Fano resonance for blue laser excitation with a coupling constant of $1/q = -0.33$. The Fano character of the line is not only evident from its asymmetric shape but even more importantly from the depression of the background on the high frequency side of the peak.

The tangential part of the Raman spectra as depicted in Fig. 4(b) yields additional information. The G line also

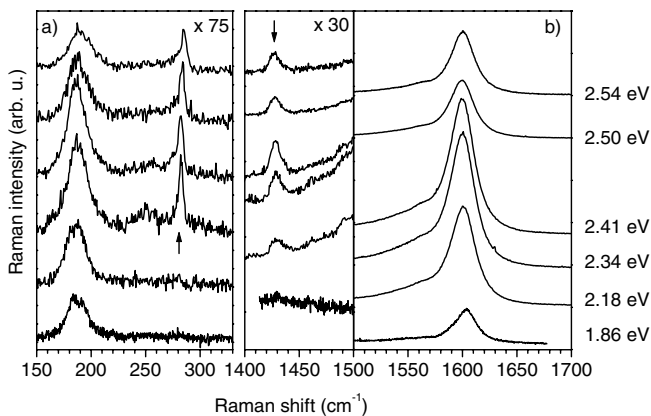


FIG. 4. Raman response of the radial modes (a) and the tangential modes (b) of the heavily doped peapod material at 20 K. Energies of the lasers used for excitation are as indicated in eV. The arrows indicate the response of the $H_g(1)$ and $A_g(2)$ lines from the C_{60} .

exhibits a Fano resonance underlining the metallic character of the doped peapods. The Fano line with a coupling constant as high as $1/q = -0.1$ is recorded only for a rather narrow window of about 100 meV around 2.50 eV. In addition, a new line occurs at 1428 cm^{-1} which is not detected in the pristine or doped tube material without encapsulated C_{60} . Following the above-mentioned charge-frequency relation, this line is safely assigned to a C_{60}^{-6} cage and indicates a substantial charge transfer to the encapsulated fullerenes.

Finally, inspecting the extended radial part of the spectra from the heavily doped peapods additional features can be detected (Fig. 5). The response is compared to the one from the polymeric phase of $o\text{-RbC}_{60}$ and to Rb_6C_{60} . Besides the well-known lines from the RBM and from the $H_g(1)$ and $A_g(1)$ modes of C_{60} , two new strong lines appear at about 370 and 620 cm^{-1} . These lines are not observed in Rb_6C_{60} but correspond well to the polymerization induced line seen, e.g., in $o\text{-RbC}_{60}$ and thus indicate that a chemical reaction to a polymeric chain had occurred inside the tubes. Moreover, as Rb_6C_{60} is an insulator $H_g(1)$ does not exhibit a Fano line shape in contrast to the same mode from C_{60} inside the tubes.

The experiments clearly show that doping the peapod material starts with a charge transfer from the K atoms to the nanotubes. Only for the heavily doped state the peas are included in the doping process and eventually a chemical reaction is induced. The bleaching of the resonance excitation for the metallic tubes in the early stages of doping can be understood from a filling of the electronic states beyond the first VHS. If all states up to this level are occupied, no resonance excitation will be possible. Then, in these tubes the Fermi level is shifted up as high as 0.9 eV. At the same stage of doping, the Fermi level in semiconducting tubes is shifted only to about 0.35 eV if the

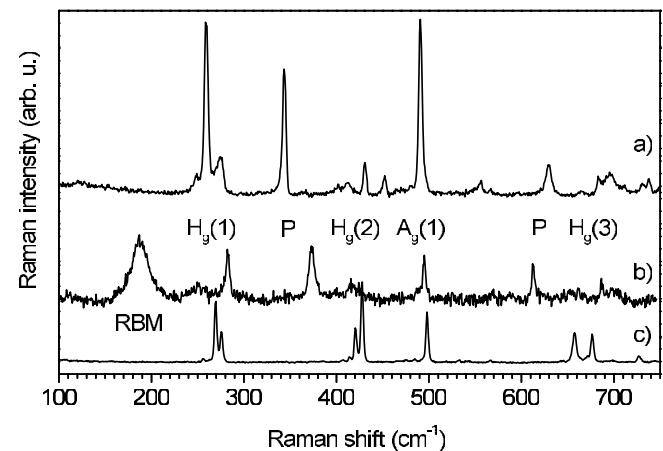


FIG. 5. Raman response from the heavily doped peapod material for the extended radial mode spectral range (recorded at 20 K) (b), as compared to the room temperature response from orthorhombic RbC_{60} polymer (a) and Rb_6C_{60} (c). P assigns typical polymer modes. Excitation energy was 2.41 eV.

states are also filled up only to beyond the first VHS. The electronic transitions responsible for the resonance in the semiconducting tubes are not touched by this process. The required leveling of the Fermi level must be established by contact potentials between the tubes. This interpretation anticipates similar electron affinity for all tubes which is a reasonable assumption when we consider only the overall behavior. For a value of $\gamma_0 \approx 2.9$ eV, the width of the conduction band is 8.7 eV. For infinitely high VHS about $0.06 e^-/C$ or KC_{18} is required to fill the states. For a finite width of the VHS, the concentration can be considerably smaller.

In the heavily doped material, the resonance is strongly reduced even for the semiconducting tubes. This means the states are filled to about 1.2 eV which is the position of the third VHS in the semiconducting tubes. Assuming a complete charge transfer, the tight binding model shows that about 2 times more electrons are needed to fill it. This means about $0.11 e^-/C$ or KC_9 even without the doping of the C_{60} cage. This value is very close to the maximum doping level of KC_8 obtained for intercalated graphite and with the highest C to K ratios of about 7 for heavily intercalated nanotubes as observed from EELS measurements [19]. It also correlates well to a previously reported vanishing of the lower optical transitions with doping [20].

Regarding the charge transfer to the encapsulated C_{60} , the line position of the $A_g(2)$ mode at 1428 cm^{-1} is lower than for K_6C_{60} (1432 cm^{-1}). This reduction in frequency is consistent with the additional covalent bonds in the charged polymer. The polymerization of C_{60}^{-6} is further supported by a recent semiempirical calculation, which demonstrated that the most stable one-dimensional polymer of C_{60} is a single bonded $(C_{60}^{-6})_n$ chain [21]. The observation of the Fano resonance for the $H_g(1)$ mode is a strong indication for the coupling of the C_{60} polymer phonons to an electron continuum. Therefore the orbitals of the polymeric C_{60}^{-6} peas must be close to the Fermi level and contribute to the metallic state which nicely proves a prediction from a recent theoretical paper of Okada *et al.* [17].

In summary, from a study of the intercalation properties of C_{60} peapods we found evidence for a chemical reaction inside the nanotubes which leads to a unique structural feature in the form of a polymeric metallic chain. Charge transfer is competitive between the SWCNT pods and the C_{60} chains for the heavily doped state where the charge on the chain is about $-6/C_{60}$. In contrast to the C_{60}^{-6}

ions in K_6C_{60} , the C_{60} peas in the chain have metallic character. For the SWCNT pods the resonance and the oscillation of the RBM is completely lost, and the width of the lines now represents directly the Gaussian distribution of the tube diameters. The observed reaction inside the tube and the competitive charge transfer between tubes and fullerene cages bear ample concepts for new materials and are challenging subjects for further studies and theoretical analyses.

This work was supported by the FWF in Austria, Projects No. P14386 and No. P14146, and by Projects No. HPRN-CT-1999-00011 and No. IST-1999-10593 of the EU. T.P. acknowledges the ÖAW for an APART grant. H.K. acknowledges a Grant-in-Aid for Scientific Research (A), 13304026 by the Ministry of Education of Japan. Y.A. acknowledges a grant from JSPS-RFP. We also acknowledge M. Krause for the Raman spectrum of Rb_6C_{60} .

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