Novel properties of 0.4 nm single-walled carbon nanotubes templated in the channels of AlPO$_4$-5 single crystals

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Abstract. We review our experimental and theoretical studies on the ultra-small single-walled carbon nanotubes (SWNTs) fabricated in the 1 nm channels of AlPO$_4$-5 (AFI) zeolite single crystals. The structure of the SWNT was characterized by transmission electron microscopy (TEM), diffuse x-ray diffraction, and micro-Raman measurements, all consistently indicating a diameter of 0.4 nm, at or close to the theoretical limit. The large curvature in the 0.4 nm SWNTs makes the nanotubes marginally stable. On the one hand, the free-standing 0.4 nm SWNTs can be thermally destroyed at a much lower temperature than larger sized SWNTs but, on the other hand, it introduces a variety of interesting material characteristics such as the large split of the G-like Raman modes, softening of the radial breathing modes, closing of the semiconducting gap so that the (5, 0) nanotubes are metallic, and the enhancement of the electron–phonon coupling that makes these ultra-small nanotubes superconducting at a relatively high temperature (15 K). Band structure and dielectric function of the 0.4 nm SWNTs were calculated using the local-density-functional approach. The calculated dielectric functions yield predictions in very good agreement with the experimentally measured absorption spectra. The absorption bands can be identified as dipole transitions between states in the vicinity of the van Hove singularities. Further confirmation of these dipole-allowed transitions was obtained by the resonant Raman excitation spectrum. Electric transport measurements were conducted on the SWNT@AFI crystals. As the zeolite matrix is insulating, electric conduction can be ascribed to the nanotubes. It was shown that the conductivity of the 0.4 nm SWNTs is governed by a 1D electron hopping process at temperatures above 20 K. The measured magnetic and...
transport properties revealed that at temperatures below 20 K, these ultra-small SWNTs exhibit superconducting behaviour with a mean-field superconducting transition temperature of 15 K. The superconducting characteristics display smooth temperature variations owing to 1D fluctuation. The observed anisotropic Meissner effect, the superconducting gap and fluctuation supercurrent were consistently explained on the basis of the Ginzburg–Landau formalism. By means of lithium doping, the electronic structure of the ultra-small SWNTs can be modified. Results of a first-principles calculation as well as experimental observation show that the SWNT@AFI system can adsorb lithium atoms up to a density as high as 10 wt%.

1. Introduction

Since their discovery in 1991 [1], carbon nanotubes have been intensively investigated because of their remarkable electronic and mechanical properties. A multi-walled nanotube can be regarded as graphite sheets wrapped into a coaxial seamless cylinder. In 1993, Iijima’s group and Bethune’s group found that the use of transition-metal catalysts could lead to the formation of single-walled carbon nanotubes (SWNTs) [2, 3]. The diameter of each freestanding SWNT ranges from 0.7 nm to a few tens of nanometres. While theoretical calculations have predicted the stability of SWNT with a diameter as small as 0.4 nm [4, 5], the existence of free-standing SWNTs with a diameter smaller than that of C₆₀ fullerene (0.7 nm) was in doubt for some time [6].
because of the extreme curvature and reactivity of these structures. Smaller carbon nanotubes can exist, however, in a spatially confined environment. Carbon nanotubes with diameters of as small as 0.5 nm [7] and 0.4 nm [8] were subsequently observed in the centre of multi-walled carbon nanotubes. It is still not clear, however, that these small-diameter nanotubes can be formed in free space.

We have fabricated 0.4 nm SWNTs in 0.73 nm-sized channels of AlPO₄-5 (AFI) single crystals [9, 10]. These 0.4 nm SWNTs have the same diameter as the smallest possible fullerene C₂₀ [11], and they are stable inside the AFI channels, but probably only marginally stable in free space. These mono-sized, well-aligned ultra-small SWNTs provide a platform in which the experimental and theoretical studies can be carried out on this near one-dimensional (1D) material system.

The electronic properties of a SWNT are determined by its geometric structure. Within the band-folding scheme, it is predicted that only the zero-helicity armchair tubes are metallic, the others being small-gap semiconductors or insulators depending on their radius and chirality [12]–[14]. In very small SWNTs, however, the presence of $\sigma^{*-}\pi^{*}$ hybridization introduced by the strong curvature effect leads to deviations from the band-folding theory [12]. The increased curvature also enhances electron–phonon coupling and makes superconductivity much more likely [15]. Experimentally, superconductivity has been observed in ropes of SWNTs (1.4 nm diameter) at temperature below 0.55 K [16], and in 0.4 nm SWNTs with a mean-field superconducting temperature as high as 15 K [17].

In this paper, we review the fabrication, characterization and the novel properties of the 0.4 nm SWNTs. In what follows, we present the fabrication details in section 2, followed by a description of structural characterizations in section 3. Direct evidence by transmission electron microscopy (TEM) as well as indirect evidences by diffuse x-ray scattering and micro-Raman measurements of the nanotube breathing mode consistently indicated that the SWNTs have a diameter of 0.4 nm, at or close to the theoretical limit. Three possible structures for the 0.4 nm SWNTs can be identified: the zigzag $(5, 0)$, the armchair $(3, 3)$ and the chiral $(4, 2)$. Because the SWNTs are isolated in the ordered channels of AFI, they constitute an almost ideal 1D system. Results of the phonon density-of-state (PDOS) calculation and Raman spectra are shown in section 4. It is shown that the curvature effect not only leads to a large split of the G-like Raman modes, but also softens the radial breathing modes (RBM). Thermal stability of the 0.4 nm SWNTs is also discussed. In section 5, we report the properties related to the electronic structures of the 0.4 nm SWNTs. Calculations based on the local-density-functional approach indicate that while the $(5, 0)$ and the $(3, 3)$ nanotubes are metallic, the $(4, 2)$ nanotubes are semiconducting with a small indirect band gap. The calculated dielectric functions yield prediction in good agreement with the experimentally measured absorption spectrum. When the electric field ($E$) of light is polarized parallel to the $c$-axis, the spectra display a sharp peak at 1.37 eV, with two broad bands at higher frequencies. These absorption bands can be related to dipole transitions between electronic states in the vicinity of the van Hove singularities. For the $E_{\perp c}$ configuration, the tube is nearly transparent. Optical dipole selection rules are discussed. The intensity of the Raman-active breathing modes is shown to depend sensitively on the energy of the laser line used for excitation. The $(5, 0)$ and $(4, 2)$ nanotubes were found to be responsible for the observed resonance peak in the excitation laser frequency region. Electric transport characteristics are presented in section 6. Due to defects and imperfection in the nanotubes, the electronic conductivity is dominated by 1D electron hopping at temperatures above 20 K. The measured magnetic and transport properties revealed that at temperatures below 20 K, the 0.4 nm

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carbon nanotubes exhibit superconducting behaviour with a mean-field transition temperature of 15 K. In particular, we observed the anisotropic Meissner effect, with a superconducting gap and fluctuation supercurrent. The measured superconducting characteristics display smooth temperature variations owing to 1D fluctuation. Statistical mechanical calculations based on the Ginzburg–Landau formalism yielded predictions showing that the experimental observations can be consistently explained under a unified framework. In the last section, we report the modification of electronic structure of the 0.4 nm SWNTs by means of electron doping. Results of a first-principles calculation, as well as experimental observation, show that Li can be adsorbed into the SWNT@AFI system, with a density as high as 10 wt%. Electronic charge transfer from Li atoms to the nanotubes can lead to variation in the electronic density near the Fermi level. Results of \textit{ab initio} calculations are shown to be well approximated by the rigid-band picture.

2. Sample fabrication

AFI is a type of nano-porous aluminophosphate crystallites. Its framework consists of strictly alternating tetrahedrons of \((\text{AlO}_4)^-\) and \((\text{PO}_4)^+\) which form the hexagonal \(P6_{\text{cc}}\) structure with open one-dimensional channels along the \((001)\) direction. The inner diameter of the channel is 0.73 nm, and the distance between two neighbouring parallel channels is 1.37 nm. Figure 1(a) schematically shows the framework structure of the AFI crystal viewed along the \([001]\) direction. The AFI single crystals were grown by means of a hydrothermal technique [18]. The reactants were 85% \(\text{H}_3\text{PO}_4\), aluminium isopropoxide, and hydrofluoric acid. The aluminium isopropoxide was first hydrolyzed in water, and then \(\text{H}_3\text{PO}_4\), tripropylamine (\((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{N}\), hereafter named as TPA), and HF acid were slowly added into the aluminium isopropoxide solution under vigorous stirring. After keeping this mixed gel in a Teflon-lined autoclave at 170 °C for 10–24 h, single crystals with a beautiful hexagonal shape were obtained. A scanning-electron-microscope (SEM) image of the AFI single crystals is shown in figure 1(b). The as-grown AFI single crystals have a typical dimension of 500 \(\mu\text{m} \times 100 \mu\text{m} \times 100 \mu\text{m}\). A pure AFI crystal is optically transparent from the ultraviolet to near-infrared wavelength region, and it is a good insulator. Hence, it is easy to study the optical and electrical properties of nano-materials accommodated in the channels.

SWNTs are produced inside the AFI channels by pyrolyzing TPA molecules which are incorporated in the channels as templates during the AFI crystal growth [9, 10, 19]. When the TPA@AFI crystal was gradually heated in a vacuum of \(10^{-3}\) Torr at temperature up to 400 °C, the crystal turned its colour from transparent into homogeneous black. The H–C bonds of the TPA molecules broke at this temperature. Hydrogen molecules were pumped out while carbon atoms remained in the channels. When treated at higher temperature, however, the crystal behaved as a good polarizer with high absorption for the light polarized parallel to the \(c\)-axis of the crystal, and high transmission for the light polarized perpendicular to the \(c\)-axis. This anisotropic optical property implies that an ordered carbon species with a large aspect ratio was formed along the channel. When treated at temperatures higher than 850 °C, the crystal became dark black homogeneously, losing its optical polarization behaviour. In figure 2, we show the degree of polarization (DOP) measured for a TPA@AFI crystal pyrolyzed at different temperatures. It is seen that the DOP value increases very quickly at the temperature range of 430–470 °C, indicating that a rapid structural phase transition, from an amorphous form of carbon to a highly structured form of carbon, occurred in this temperature region. There is a preponderance of evidence, as we will establish later, that these carbon structures are SWNTs of
Figure 1. (a) Framework structure of the AFI single crystal viewed along the (001) direction; (b) SEM image of the AFI single crystals.

0.4 nm diameter. It is worth pointing out that the decomposition temperature (\(~430^\circ\text{C}\)) of the TPA molecules in the AFI channels is much lower than the normal decomposition temperature (700–800°C) of the molecules in free space. The exact reason is not very clear yet. The strong confinement of the AFI channels as well as the catalyst effect of the zeolite framework might play an important role in lowering the decomposition temperature.

3. Structural characterization

In order to provide direct evidence of the existence SWNTs using high-resolution TEM, we first ground the SWNT-containing AFI crystals into powder and then extracted the SWNTs by dissolving the SWNT@AFI crystals in HCl (30%) acid. The SWNT-containing solution was subsequently enriched and dispersed on a carbon lacey film for TEM investigation. Figure 3(a) shows a typical TEM image of the specimens (JEOL2010 electron microscope, operating at 200 kV), in which narrow and long paired dark fringes of SWNTs are observed. In order to determine the diameter of the SWNTs, TEM image simulations have been carried out [20, 21]. This is because, by HRTEM, an isolated SWNT is generally imaged as paired fringes whose separation distance is varied and often different from the diameter defined for the SWNT even at

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Figure 2. Plot of the DOP as a function of pyrolysis temperature. The DOP is defined as $\text{DOP} = |I_\perp - I_\parallel|/|I_\perp + I_\parallel|$, where $I_\parallel (I_\perp)$ represents the intensity of the transmission light polarized parallel (perpendicular) to the $c$-axis of the AFI crystal.

In this study, the diameter of SWNTs was determined by using {002}-lattice plane spacing of graphite stripe in the same image as the internal reference, and by measuring the separation between the dark paired fringes of SWNT images. This can minimize the error of the measurement arising from the TEM magnification. We have carried out image simulations for SWNTs with different diameters and found that the image of a SWNT with a diameter of 0.4 nm matched well that obtained by TEM. Diffuse x-ray diffraction measurements consistently showed that the SWNTs have a diameter of 0.4 nm [22]. It is worth pointing out that Qin et al [23] disputed the presence of 0.4 nm SWNTs. They used an ideal model that assumed a 0.4 nm SWNT lying flat on an amorphous carbon film, and concluded that a 0.4 nm sized SWNT cannot be imaged by HRTEM. However, Qin’s assumption that all nanotubes lie flat on the amorphous carbon film does not cope with the real experimental situation. Because of the existence of small patches of carbon fragments, there are always some tilt angles between nanotubes and the amorphous carbon films. In this case, because of the defocusing conditions, the 0.4 nm SWNTs can be clearly imaged, as shown in the simulated images in figure 3(a). Our image simulations of the SWNTs superposed on a carbon film are based on the artificial unit cell illustrated in figure 3(b). The incline angle $\theta$ is the critical parameter for image contrast of the SWNTs lying flat on the carbon thin film. For $\theta = 0$, no contrast from SWNTs is visible under any defocus condition, as expected. The SWNT contrast is totally overwhelmed by the typical contrast of the amorphous carbon (see figures 3(c) and (d)). However, by increasing $\theta$, the SWNT contrast (paired dark fringes) appears gradually (with a fixed defocus of $-60 \text{ nm}$), as illustrated in figure 3(e). Clearly, a larger incline angle results in a better nanotube contrast. We also find that defocusing TEM affects the contrast of the inclined SWNTs. Figure 3(f) shows the variation of the tube contrast versus TEM defocus. We observed that a better contrast of the
Figure 3. (a) TEM image of the 0.4 nm SWNTs. The paired dark fringes generated from the SWNT structure are indicated by the arrows. (b) The artificial unit cell for the image simulation of SWNTs/carbon film specimens. (c) Simulated image of amorphous carbon film without SWNT (thickness = 5.1 nm). (d) Simulated image of the 0.4 nm SWNT lying on the carbon film with an inclining angle $\theta = 0$. The SWNT was invisible. (e) Simulated images of the 0.4 nm SWNT inclining with different angles on the thin carbon film (5.1 nm thick) with a fixed defocus of $-60$ nm. (f) Simulated images of the 0.4 nm SWNT with a fixed incline angle of $60^\circ$ and different defocus conditions on a thicker carbon film (8 nm thick).

SWNT with a tilting angle of $60^\circ$ can be achieved at the defocus condition of $-80$ nm. This value is slightly larger than that of the Scherzer defocus ($-60$ nm) [20]. These ultra-small SWNTs are very stable when confined in the AFI channels. They are, however, not as stable as larger diameter SWNTs after being extracted from the channels, especially when they are exposed under the electron beam in TEM. During TEM observation, the image of SWNTs faded away in a few seconds, while that of graphite persisted. We believe that the SWNTs were gradually cracked after extraction from the AFI channels, and transformed into graphitic fragments in free space. The thermal stability of these extracted 0.4 nm SWNTs will be discussed in more detail in the next section.

4. Raman spectra

4.1. General spectra and PDOS

The Raman spectra were measured using a Renishaw 3000 micro-Raman system. A 50× microscope objective was used to focus the laser beam and to collect the scattered light. The laser
Figure 4. Raman spectrum (the curve on the top) and the calculated PDOS for the (5, 0), (3, 3) and (4, 2) nanotubes, respectively. The inset shows the 2D graphite phonon dispersion relation [68, 69].

spot has a diameter of 2 µm. A representative Raman spectrum of the SWNT@AFI is shown in figure 4 (the top curve). Even though the diameter distribution is very narrow, the Raman spectrum of the 0.4 nm SWNTs turned out to have a complex profile. It should be pointed out that there also exist Raman signals for the AFI framework at frequencies of 1100 and 450 cm$^{-1}$, resulting from the P–O and P–O–Al vibrations. Because of the resonant behaviour, however, the intensity of the Raman signal from the SWNTs is at least 20 times stronger than that of AFI. Thus the effect of the AFI framework is negligible in the Raman spectrum of nanotubes.

To understand how phonon modes of the SWNTs are related to the Raman spectra, we calculated the PDOS of the 0.4 nm SWNTs using a force constant model [14]. The calculated PDOS are shown by the bottom three curves in figure 4 for the (5, 0), (3, 3) and (4, 2), respectively. As seen in the figure, most of the features in the Raman spectrum can be assigned to various structures in the PDOS of the (5, 0), (3, 3) and (4, 2) nanotubes [25, 35], except for the region from 800 to 1200 cm$^{-1}$. The mismatch might be due to the fact that the phonon modes around this region are not Raman active. In general, the spectrum can be divided into three features in the region ranging up to 1800 cm$^{-1}$.

(i) RBM in the low-frequency side. There are three significant peaks at 515, 548, 584 cm$^{-1}$, as well as a small shoulder at 485 cm$^{-1}$. As most of the tubes observed from the TEM image have a diameter of 0.4 nm, it is reasonable to attribute the significant three peaks to the 0.4 nm-sized (5, 0), (3, 3) and (4, 2) tubes, respectively [24, 25]. Energetically, besides the 0.4 nm SWNTs, 0.5 nm-sized (6, 0) tubes may also exist inside the 0.73 nm channels. The growth process of SWNTs in the channels should be dominated by kinetics. Given the confined environment, it is reasonable to expect that the 0.4 nm tubes such as the (5, 0), (3, 3) and (4, 2) tubes should have a higher probability of existing in the AFI channels than...
the 0.5 nm tubes. Nevertheless, we could not exclude the possibility of (6, 0) tubes in the channels, which would relate to the small shoulder at 485 cm\(^{-1}\) in the RMB spectra, but the amount of (6, 0) tubes might be much smaller than that of the other three tubes.

(ii) The disorder-induced D band in the frequency region of 1000–1500 cm\(^{-1}\). Theoretical calculation showed that the Raman-active modes have no intensity in this frequency region for large-diameter nanotubes [26]. Hence the Raman signals observed in this frequency region might come from the strong curvature effect in the ultra-small nanotubes, or due to some imperfect disordered carbon structures. In fact, broad Raman peaks around 1350 cm\(^{-1}\) were observed in disordered carbon nanoclusters, and their intensities were sensitive to the symmetry-lowering effect [27]–[30].

(iii) Finally, the graphite-like G band near 1600 cm\(^{-1}\). There are three peaks at 1619, 1603 and 1586 cm\(^{-1}\), respectively. The tangential G-band is common to all chiralities of SWNTs and is related to a flat region in the highest LO 2D graphite phonon branch (see the inset in figure 4). For a general chiral tube, the G band consists of modes of three symmetries: \(A_1\), \(E_1\) and \(E_2\) [31]. Each of them is further split into two lines denoted by \(G^+\) and \(G^-\) because of the curvature effect [32, 33]. The upper frequency \(\omega_{G^+}\) located near 1600 cm\(^{-1}\) is associated with carbon atom displacement along the tube axis, which shows very small diameter dependence. The lower frequency \(\omega_{G^-}\) is associated with carbon atom oscillation in the circumferential direction, which strongly depends on the tube diameter [33]. For the tubes with diameter larger than 0.9 nm, the separation between \(\omega_{G^+}\) and \(\omega_{G^-}\) can be fitted well with an experiential equation \(\omega_{G^+} - \omega_{G^-} = C/d^2\), where the constant \(C\) equals 47.7 cm\(^{-1}\) nm\(^2\) for semiconducting SWNTs and 79.5 cm\(^{-1}\) nm\(^2\) for metallic ones [34]. For the 0.4 nm SWNTs, the splitting can be large which leads to a small \(\omega_{G^-}\). For example, \(\omega_{G^-} \sim 1300\) cm\(^{-1}\) can be assigned to the (4, 2) semiconducting tube, and \(\omega_{G^-} \sim 1100\) cm\(^{-1}\) can be assigned to the metallic (5, 0) and (3, 3) tubes. These two modes are marked by * and ⋄, respectively, in the Raman spectrum in figure 4. They are crowded together with the broad features in the D-band region.

4.2. Perfect alignment of the 0.4 nm SWNTs confirmed by Raman spectra

As the length-to-diameter ratio of a SWNT is very large, the polarization effect of its dielectric function is obvious [36, 37]. Assuming that only the light polarized along the tubes’ axes can be absorbed by the nanotubes, i.e. the polarizability factor in the tube direction is \(\alpha_{zz} = 1\), and all other elements are zero [38], then for perfectly aligned SWNTs the intensity of resonant Raman signals are given by \(I_{R-VV} \propto \cos^4 \theta\) in the VV configuration (polarizations of laser light and the Raman scattering light are parallel) and by \(I_{R-VH} \propto \cos^2 \theta \sin^2 \theta\) in the VH configuration (polarizations of laser light and Raman scattering light are perpendicular), where \(\theta\) is the polarization angle (see the inset of figure 5(a)). (In the case of \(\theta = 0\), V polarization is along the \(Z\) axis, and H polarization is along the \(X\) or \(Y\)-axis.) Thus, by examining the \(\theta\)-dependence of the resonance Raman intensities of the nanotubes, we can see how the SWNTs are aligned in the AFI channels.

Figure 5 shows the polarized Raman spectra in the RBM region (figure 5(a)) and in the G-like region (figure 5(b)) for polarization angles from 0° to 90° after suppressing the broad luminescent background. The polarization configuration is shown in the inset of figure 5(a). Both the VV (upper curves) and the VH (lower curves) configurations are shown in each figure. It is obvious in the figures that the intensities of all Raman modes decrease dramatically with
Figure 5. Polarized Raman spectra measured in VV and VH configurations for (a) the RBM bands and (b) the G-like bands. Polarization configuration is shown in the inset of (a). The inset in (b) shows the normalized Raman intensities plotted as a function of polarization angle both for RBM and G-like modes in the two configurations.

The increase of polarization angle from $\theta = 0^\circ$ to $90^\circ$ in the VV configuration. In the VH configuration, the intensities of these Raman modes increase with increase of the polarization angle until $\theta = 45^\circ$, then decrease symmetrically to $90^\circ$. The $\theta$-dependence of the integrated Raman intensities of the RBM modes (triangles) as well as the G-like modes (squares) are plotted.
in the inset of figure 5(b). The open symbols correspond to the VV configuration, and the solid symbols correspond to the VH configuration (the Raman intensities are normalized). They are well fitted by two lines with the functions of $\cos^4\theta$ and $\cos^2\theta\sin^2\theta$, consistent with the fact that the carbon nanotubes inside the channels of AFI crystals are perfectly aligned.

4.3. Curvature effect on the RBM vibration

In order to study the curvature effect on the RBM vibrations in the ultra-small tubes, we dissolved the AFI framework using HCl acid (37.5 wt%), then extracted nanotubes by adding the dichloroethane organic solvent. The nanotube-contained dichloroethane phase was then dropped onto a fresh gold substrate. After evaporating the organic solvent, we got free-standing SWNTs on the substrate. Figure 6 shows the Raman spectra measured for the free-standing nanotubes. Because the nanotube is sparsely distributed on the substrate, the Raman signal is relatively weak although data have accumulated for a long time. From figure 6, we can safely identify that there are three peaks centred at 490, 510, 540 cm$^{-1}$, respectively, which are slightly shifted towards the lower frequencies in comparison with that confined inside the AFI channels. In the regime of elastic approximation, the frequency of the RBM, $\omega_{\text{RBM}}$, scales inversely proportional to the tube diameter $d$, $[39, 40]$, which explained experimental results pretty well for large-diameter SWNTs. The good description using the simple elastic approximation is due to sp$^2$ hybridization in the flat circumference of large tubes. However, using this reciprocal relation, the calculated RBM frequency for the 0.4 nm SWNTs, $\omega = 620$ cm$^{-1}$, is apparently higher than the average RBM frequency shown in figures 4–6, implying that the elastic approximation is no longer a good approximation for the 0.4 nm SWNT. In such small nanotubes, the curvature effect introduces a remarkable rehybridization of $\sigma^*$ and $\pi^*$ bands, which not only changes the electronic structures of the tubes $[12]$ but also softens the radial breathing vibrations $[24]$. We calculated the RBM frequencies for the (5, 0), (3, 3) and (4, 2) tubes with the frozen phonon approach based on the first principles ab initio approximation. Before the calculation, the geometry of the nanotubes

Figure 6. Raman spectra of the free-standing 0.4 nm SWNTs in the frequency region of around RBM. Inset: the relation between the vibration frequency change and the displacement of the carbon atoms, calculated using a frozen method for the RBM vibrations.
is optimized by relaxation; therefore the most stable lattice constant can be obtained. The frozen phonon method assumes that one knows the eigenvector of the phonon mode and the change of the total energy is calculated as a function of distortion according to this phonon mode eigenvector. For the case of the RBM mode, the eigenmode corresponds to an expansion of the tube radius. The tube radius is changed by a few per cent, and the total energy is calculated for each configuration deviated from the equilibrium position. In order to eliminate the inharmonic terms, we take the average value of the increased energy in positive and negative displacements. From a quadratic fit, the harmonic constant $k$ is obtained by $k = 2 \Delta E / \Delta r^2$, where $\Delta r$ is the displacement and $\Delta E$ is the energy change corresponding to the displacement. In turn, using $\omega = (k/m)^{1/2}$ ($m$ is the mass of the unit cell), we can obtain the RBM frequencies [24]. For fully relaxed (5, 0), (3, 3) and (4, 2) tubes, the calculated frequencies are 527, 541 and 531 cm$^{-1}$, respectively. The actual relaxed tube radii are slightly larger than those resulting from an ideal rolling of the graphite sheet. In comparison with the tube diameters without energy relaxation, the dilations of the tube diameters are 2.44, 1.97, 2.05% for the relaxed (5, 0), (3, 3) and (4, 2) tubes, respectively. We note that the tube with the largest chiral angle (armchair: 30°) has the smallest percentage dilation (1.97), while the tube with the smallest chiral angle (zigzag: 0°) has the largest dilation (2.44), and the percentage dilation is larger for a tube with smaller diameter. This indicates that the curvature effect is more significant for the smaller tube, as expected, and has the most pronounced effects in the zigzag (5, 0) tube, but has less effect in the chiral (4, 2) tube and armchair (3, 3) tube. Besides the dilation in the diameters, the calculated RBM frequencies show obvious softening when compared to the values given by reciprocal relations. The softening of the RBM frequency is the largest in the zigzag (5, 0) tube, and smallest in the armchair tube (3, 3). Comparing with the calculated values, the observed RBM peaks match the theoretical calculations to well within 6%.

4.4. Thermal stability of the 0.4 nm SWNTs

As mentioned above, the 0.4 nm SWNTs are stable inside the AFI channels. They are, however, not very stable after being extracted from the channels. The stability of an isolated SWNT is determined mainly by the competition between the strain energy introduced by rolling up a planar graphene strip to form the tube and the decrease in edge energy resulting from elimination of the dangling bonds along the edges of the strip. The strain energy is inversely proportional to the square of the radius, while the edge energy is inversely proportional to the radius of the nanotube [41]–[44]. Hence, as $r$ decreases the strain energy for a SWNT increases more rapidly than the edge energy of the corresponding planar graphene strip, which makes small-radius SWNTs unstable. First principles calculations [44] as well as molecular dynamics simulations [42] showed that the smallest energetically stable SWNTs have a diameter of about 0.4 nm. Our 0.4 nm SWNTs produced in the AFI channels are close to the theoretical lower limit. It is of interest to examine the stability of the 0.4 nm SWNTs when they are extracted from the AFI channels in a free-standing state.

Figure 7 shows the Raman spectra of the 0.4 nm SWNTs in the free-standing state (after removing the zeolite framework) measured at temperatures of 300–873 K in a vacuum of $10^{-3}$ Torr. At room temperature (300 K), the general feature of the Raman spectrum is similar to that of nanotubes confined inside the AFI channels, but with a few notable differences: (a) the G-like bands as well as the RBM bands are slightly shifted to the lower-frequency side, and (b) the relative intensity of the disorder-induced D line is increased. The signal of the RBM bands
Figure 7. Raman spectra of the free-standing 0.4 nm SWNTs measured at different temperatures in vacuum. The spectra in the G-like frequency region are expanded in the inset.

weakens with the increase of temperature, and finally becomes undetectable when the sample is heated at temperature above 580 K. On the other hand, with increasing temperature, the G-like bands gradually shift to lower frequency and finally become featureless at temperatures above 580 K. At higher temperature, the G-like bands change into a typical symmetrical G-line of graphite (see the inset). These results indicate that most of the 0.4 nm SWNTs start to be cracked into graphitic structure at 580 K. In figure 8, we show the Raman spectra measured by keeping the temperature at 600 °C for different heating time. As seen from the figure, with increasing the heating time, the Raman spectra become weaker and broader. After being heated for 30 min, the SWNT sample was completely changed into amorphous carbon with a mixture of graphite, characterized by the broad Raman bands centred around 1300 and 1580 cm⁻¹. It is noted that the thermal decomposition temperature (∼600 °C) of the 0.4 nm SWNT is much lower than that of large-diameter carbon nanotubes that are reported to be thermally stable up to the graphite instability temperature [45]. The decomposition temperature observed here is even lower than that predicted for 0.33 nm SWNTs using tight-binding molecular dynamics simulations [46].

5. Electronic properties

5.1. Band structure calculation

The electronic structures of a SWNT can be obtained from the graphite band structure simply within the band-folding approach [14]. It works well for large-diameter carbon nanotubes.
Figure 8. Raman spectra of the free-standing 0.4 nm SWNTs heated in vacuum at 600°C for 1, 10, 20 and 30 min, respectively.

However, the carbon–carbon bond is severely bent and stretched when the diameter becomes small, leading to the hybridization of the $\sigma^*$ and $\pi^*$ bands [12]. To obtain accurate results of the electronic properties of the 0.4 nm SWNTs, ab initio calculations within the framework of local density approximation (LDA) were carried out [47, 48]. The calculated band structure is shown in figure 9. For the (5, 0) tube, the large curvature effect pushes a $\pi^*$ band labelled as $\alpha$ down and across to the Fermi level, making the (5, 0) tube metallic. The same $\pi^*$ band is originally located at about 3.0 eV above the Fermi level at Gamma point in the simple tight binding calculation. The (3, 3) tube is metallic, as required by the symmetry and predicted by the band-folding approach, but the band crossing marked by $\Delta$ shifts to a smaller wavevector. The (4, 2) tube is semiconducting as expected, but with a much smaller indirect band gap (0.2 eV), instead of a 2 eV direct gap predicted by the band-folding approach. Recently, Cabria et al [49] also calculated band structures for various narrow SWNTs with diameters in the range 0.34–0.5 nm using the LDA approach.

Optical dipole transitions can occur between these van Hove singularities with specific selection rules. To investigate dipole-allowed optical transitions, we calculated the imaginary part of the dielectric function $\varepsilon_2$ [47]. The results calculated for the (5, 0), (4, 2) and (3, 3) nanotubes are shown in figure 10 for the case of light polarized parallel (figure 10(a)) and perpendicular (figure 10(b)) to the nanotube axis. The dielectric tensor components are significantly larger in the parallel configuration than that in the perpendicular one. There is a conspicuous peak at 1.1 eV and a weaker one near 2.3 eV for the (5, 0) tube, and a peak at 2.8 eV for the (3, 3) tube. For the (4, 2) tube, there is a strong peak at about 1.9 eV, with a long tail and some small peaks at 2.9 and 3.6 eV. These peaks in the dielectric function spectra result from the dipole-
allowed transitions from the $\pi$ states to the $\pi^*$ states. Although there are many possible pairs for bonding and antibonding $\pi$ states, the selection rules limit the dipole-allowed pairs to only a few. Detailed discussions on the dielectric function and the optical absorption spectra calculated using an \textit{ab initio} approach for the 0.4 nm SWNTs have also been reported recently by Machon \textit{et al} [50] and Yang \textit{et al} [51].

5.2. Polarized absorption spectra

We measured the absorption spectra as a function of the polarization angle. In order to easily handle the small crystal for optical measurements, the SWNT@AFI crystal was horizontally fixed using epoxy resin inside a small hole drilled on a machinable ceramic plate. After the
Figure 11. Polarized absorption spectra of the SWNT@AFI single crystal measured at different polarization angles. The topmost and bottommost curves are for the $E \parallel c$ and the $E \perp c$ polarization configurations. Inset: normalized absorbance of the absorption peaks A, B and C, plotted as a function of the polarization angle.

resin became hardened, the sample was polished mechanically and then using Ar ion milling to a thickness of about 10 µm. Transmission spectra were measured at room temperature, using a tungsten–halogen incandescent lamp as a light source. The incident polarized light was focused onto the sample by a reflecting microscope objective, and the transmission light was collected by another reflecting objective coupled with an optical fibre and dispersed by a 275 mm single-grating monochromator. Figure 11 shows a series of optical absorption spectra (plotted in optical density, OD) of the SWNT@AFI crystal for different polarization configurations. The top curve labelled 0° corresponds to the configuration $E \parallel c$. In this spectrum, we see a sharp peak A at 1.37 eV with a shoulder at 1.19 eV, and two broad bands B and C centred at 2.1 and 3.1 eV, respectively. The intensities of these absorption bands gradually decrease with increasing polarization angle (the increment is 10° in figure 11). In the configuration of $E \perp c$, the absorption bands eventually vanish and the nanotube is nearly transparent in the whole measured energy region, as indicated by the rather flat curve labelled 90°. The inset of figure 11 shows the normalized absorbance ($A = 1 - \exp(-\text{OD})$) plotted as a function of polarization angle $\theta$. The squares, circles and triangles are for the absorption bands A, B and C, respectively; all of them can be well fitted by using a $\cos^2 \theta$ line shape (solid curve). This is an indication that only the light polarized along the tube direction could be absorbed by the nanotube. Comparing the calculated results with the measured absorption spectra, we can clearly identify the A band with the strong peak at 1.1 eV for the $(5, 0)$ tube, and the C band with the peak at 2.8 eV for the $(3, 3)$ tube in the $\varepsilon_2$ spectra. The broad band marked as B in the absorption spectrum is assigned to the convolution of the peak of the $(4, 2)$ tube and the second peak of the $(5, 0)$ tube. The optical absorption of the three tubes is strongly selective by their different chirality, although their diameters are almost the same. The symmetries of the $(5, 0)$, $(3, 3)$ and $(4, 2)$ tubes correspond to the group of D$_{5d}$, D$_{3d}$ and C$_{28}$, respectively. Their allowed dipole transitions in the $E \parallel c$ polarization are $A_{1g} \rightarrow A_{2u}$, $A_{2g} \rightarrow A_{1u}$, $E_{1g} \rightarrow E_{1u}$, and $E_{2g} \rightarrow E_{2u}$ for the D$_{5d}$ symmetry, $A_{1g} \rightarrow A_{2u}$, $A_{2g} \rightarrow A_{1u}$, and $E_g \rightarrow E_u$ for the D$_{3d}$ symmetry, and $A_g \rightarrow A_u$, $B_g \rightarrow B_u$, and
Table 1. Allowed dipole transitions of the (5, 0), (3, 3) and (4, 2) tubes corresponding to the absorption bands labelled A, B and C in figure 9.

| Tube | Group | A (1.37 eV) | B (2.1 eV) | C (3.1 eV) |
|------|-------|-------------|-------------|-------------|
| (5, 0) | D_{5d} | E_{1g} → E_{1u} | E_{2g} → E_{2u} | |
| (3, 3) | D_{3d} | | | E_{g} → E_{u} |
| (4, 2) | C_{28} | E_{10g} → E_{10u} | | |

$E_{jg} \rightarrow E_{ju}$, ($j = 1, 2, \ldots, 13$) for the C_{28} symmetry, respectively [48]. We can then assign absorption peaks to dipole-allowed transitions of the three types of nanotube in reference to the dielectric function calculation as summarized in table 1.

5.3. Resonant Raman scattering

Although the 0.4 nm SWNTs are mono-dispersed in size, the absorption bands shown in figure 11 are relatively broad. The broadness of the absorption bands can result from overlapping of different dipole-allowed transitions, as well as from the edge effect resulting from the pieces of short nanotubes in the channels. Using resonant Raman scattering technique, we should be able to see more precise electronic structures as the Raman intensity is very sensitively enhanced when the photon energy of the excitation laser line is close to the allowed dipole transition energy. Recently, Hulman et al. [25] studied the resonant behaviour of the Raman scattering by exciting 0.4 nm SWNT@AFI single crystals using laser light with wavelength ranging from 454 to 771 nm. The profile of the integrated intensity of the RBM lines is visualized as a function of photon energy of the excitation laser lines in figure 12(a). Integration was performed in the spectral range between 450 and 650 cm\(^{-1}\), after background subtraction, and the results were corrected for the sensitivity of the Raman system in addition to the laser power normalization. Two dominating peaks are clearly seen at ~2.0 and ~2.4 eV. The Raman signal is obviously resonance enhanced for the two particular energies. For comparison, we plotted the $\epsilon_2$ dielectric function spectra (figure 12(b)) and the absorption spectrum (figure 12(c)) again in the same figure. It is clearly seen that the resonant energies match the electronic transitions between two van Hove singularities in the electronic density of states of the (5, 0) and (4, 2) tubes very well.

6. Transport properties

6.1. One-dimensional electron hopping at temperatures above 20 K

As discussed in the previous section, the electronic DOS of the SWNTs is characterized by the many van Hove singularities typical for 1D systems. This 1D behaviour might also be reflected in electric transport. Due to the fact that even weak Coulomb interaction can cause strong perturbations in a 1D system, bundles of SWNTs may exhibit Luttinger-liquid behaviour [52]. In a 1D conductor, however, defects and imperfections exist in series with the more perfect parts of the conductor, making it difficult to study the intrinsic conductance for a small-sized SWNT.

To measure the electric transport for the 0.4 nm SWNT@AFI crystal, the sample was fixed by epoxy inside a small hole drilled on a machinable ceramic. Both sides of the sample were then
polished until the hexagonal ends of the crystal were exposed. Electrical contacts were made by evaporating a thin layer of gold on the two ends of the SWNT@AFI crystal. The conductance of the nanotubes was measured in a two-probe configuration at temperatures ranging from 300 to 0.3 K. Figure 13 shows the current–voltage curves of a SWNT@AFI crystal measured at different temperatures using the two-probe configuration shown in the inset. The backbone of the AFI crystal is highly insulating, thus the current contribution from the AFI crystal is negligibly small. At high temperatures, the current is linearly proportional to the applied voltage and there is a good symmetry between positive and negative bias voltages, indicating good ohmic contact of the electrodes. The room temperature conductivity is of the order of $10^{-1} \Omega^{-1} \text{cm}^{-1}$, lower than the conductivity reported for the metallic single-wall carbon nanotubes of larger diameters [53]–[55]. The conductance decreases monotonically with the decrease of temperature, though the 0.4 nm (3, 3) and (5, 0) tubes are metallic. The non-metallic temperature dependence of the conductivity is strongly suggestive of electron localization. This is due to the fact that each SWNT is most likely to have defects along its length, leading to localized electronic states. In that case, the only conduction channel is by hopping of localized electrons from one site to another. Hopping is a combination of two processes: thermal activation and tunnelling [56]. Therefore the hopping conductance is the product of the two factors: $\exp(-\Delta E/K_BT)\exp(-2\alpha r)$, where $\Delta E$ is the energy difference between the initial and the final localized states, $k_B$ is the Boltzmann constant,
Figure 13. Current–voltage curves measured at different temperatures. Inset: the two-probe measurement configuration.

Figure 14. The conductance near zero bias voltage plotted as a function of $T^{-1/(1+d)}$ with the dimensionality of $d = 1, 2$ and 3, respectively. The solid dots are experimental results, the lines are calculations.

$\alpha$ is the inverse of the tunnelling length, and $r$ the distance between the two localized positions. By using the critical path method [56], the hopping conductance at zero electric field can be deduced as $\sigma = \sigma_0 \exp[-(T_0/T)^{1/(d+1)}]$, with $k_B T_0 = \alpha/4 \rho_0$, $\rho_0$ being the (constant) density of states near the Fermi level, and $d$ the dimensionality [16]. For a 1D system, $d = 1$, thus $\ln(\sigma_{1D})$ should be inversely proportional to $T^{1/2}$. In figure 14, the logarithm scale of the conductance of the 0.4 nm SWNTs is plotted as a function of $(T_0/T)^{1/(d+1)}$ with $d = 1, 2$, and 3, respectively. It is seen that the measured results are in good agreement with the $\ln \sigma \sim (T_0/T)^{1/2}$ behaviour, giving support to the 1D hopping mechanism.
6.2. Fluctuation superconductivity at low temperatures

When the transport measurements were pushed to lower temperatures, it was observed that the linear $I-V$ relationship seen at higher temperatures gave way to a nonlinear behaviour below 20 K. While initially suspect, the electrical transport behaviour depicted in figure 15 proved to be one of the most robust. Samples put on a shelf for some time and then re-measured, and different samples fabricated in different batches, all yielded similar behaviour. Clearly, charge carriers disappeared at low bias voltages. For every temperature below 15 K, there exists a clear voltage threshold above which the charge carriers appear again. The value of the threshold, which may be estimated by extrapolating from the asymptote back to the horizontal axis, increases with decreasing temperature. That characteristic voltage scaled linearly with the length of the zeolite crystal. In other words, when the sample thickness was halved, the $I-V$ curves would remain the same if the horizontal voltage scale shown in figure 15 was also halved. Also, at high applied voltage, just before the sample was burned, the slope of the $I-V$ relationship was seen to decrease.

The temperature variation of the threshold voltage is summarized in figure 16 by solid circles. The value is normalized by the one measured at 0.33 K. In the light of experimental data on the Meissner effect, obtained later chronologically, this gap-opening is interpreted to be indicative of a transition from a normal conducting phase to a superconducting phase, accompanied by the opening of the superconducting gap. Because of the imperfection in the nanotubes (as seen in the 1D hopping conduction), a series of superconducting pieces are separated by potential barriers. Thus, the $I-V$ curves measure only the normal current, as the potential barriers would destroy the phase coherence required for the observation of the supercurrent. Thus the threshold in each of the $I-V$ curves is a measure of the superconducting gap, in the manner of the Giaever tunnelling experiments [57).

To confirm the superconducting behaviour at temperatures below 20 K, we measured magnetic properties for the SWNT@AFI crystals as a function of temperature and magnetic field. Two samples were measured. Sample A, used for background deduction, consists of columnar zeolite crystallites with empty channels, about 300 $\mu$m long and 100 $\mu$m in diameter. Sample B is composed of similar crystallites but with nanotubes formed inside their channels. For both samples, the $c$-axes of the crystallites were aligned by hand to form a parallel array.
Figure 16. Temperature dependence of the threshold voltage normalized to its value at 0.33 K for experimental data (solid circles) and theoretical prediction (open circles) [17].

and fixed. It is estimated that there is a maximum error of ±10° in the alignment. All samples were dried and weighed. The magnetization was measured as a function of temperature while warming from 1.8 to 50 K. At each temperature, the magnetization was measured after the temperature was stabilized for 60 s. The measured magnetization is anisotropic with respect to the field orientation. After a simple deduction of the pure zeolite crystallite contribution and normalizing to the nanotube volume, the temperature dependence of the SWNTs’ magnetic susceptibility is shown in figure 17 by the solid circles, for five values of applied magnetic field perpendicular to the c-axes. A strongly temperature-dependent diamagnetism is seen below 10 K, in magnetic field ≤0.2 T. The magnitude of the susceptibility decreases monotonically with increasing field and becomes very small at 5 T. The result is in quantitative agreement with the Meissner effect of 1D fluctuation superconductivity [17]. The most intriguing feature is that the magnetic susceptibility for field applied parallel to the c-axis is only one tenth of that shown in figure 17, which is within the error caused by the crystallites’ misalignment and consistent with the observation that there is no Meissner effect under a parallel field for 1D systems. Thus the nanotube susceptibility is strongly anisotropic. The Meissner effect associated with 1D superconductivity differs substantially from the conventional behaviour of an abrupt susceptibility jump at superconducting-transition temperature $T_c$. Here, the dominance of 1D fluctuations means that the critical phenomenon around $T_c$ is replaced by smooth temperature and magnetic-field variations.

The anisotropy in the measured magnetic signal ruled out point magnetic impurities as the source of the signal, since point impurities should yield isotropic signal. Due to the small quantity of the sample, however, a relatively large magnetic field has to be applied in order to obtain reasonably accurate magnetization measurements. Thus the smooth temperature variation could be due to either the applied field or to more intrinsic causes, such as fluctuations. In order to understand the magnetic results, statistical mechanic calculations were carried out by using the Ginzburg–Landau formalism [17, 18]. The calculated results are shown by open circles in figures 16–18. Due to the clear importance of fluctuations, especially the phase fluctuations, to the Meissner effect, the functional integral approach was adopted. Four fitting parameters were involved. The solid circles in figure 17 show that with reasonable parameter values, e.g. a mean...
Figure 17. Normalized magnetic susceptibility of the SWNT@AFI crystals plotted as a function of temperature for five values of the magnetic field. The data are displaced vertically for clarity. Values shown are for theory (open circles) [17] and experiment (solid circles). $\chi_0$ denotes the value of the susceptibility at 1.6 K and magnetic field of 0.2 T.

field $T_c = 15$ K, an energy scale of 6 meV and an effective electron mass of 0.36 times the bare electron mass, one can indeed obtain a qualitative fit to the experimental temperature and magnetic field variations of the diamagnetic susceptibility. The effective mass of the electron is fairly close to the value estimated from LDA calculations for the $(5, 0)$ nanotubes, but differs significantly from the $(3, 3)$ nanotubes.

The success of the fitting exercise for the magnetic data shows that the (phase) fluctuations do indeed play an important role. In particular, the Meissner effect became obvious only at temperatures much lower than $T_c$. However, much more important was the consistency between the magnetic and transport data. Since the magnetic data also required a $T_c = 15$ K, this means that the ‘gap’ seen in the transport data could indeed be superconducting in origin. A simple Monte Carlo calculation of the expectation value for the absolute value of the complex order parameter, with all the parameters fixed by the magnetic data, showed the temperature dependence of the transport gap to be indeed consistent with the observed Meissner effect. This is shown in figure 16. In particular, the temperature dependence of the gap shows a very good 1D behaviour, in which fluctuation effects smoothed away the abrupt transition, although the mean field $T_c = 15$ K can still be clearly identified.

In order to further verify the consistency of the physical picture that superconductivity exists in segments along the nanotubes, it is necessary to observe the supercurrent within each of the segments. Here it is necessary to fabricate very thin samples so as to ensure that there are no imperfections (potential barriers) within the length of the SWNTs. A rough estimate of the sample thickness required is provided by the measured voltage threshold at low temperatures (about 4 V) and the relevant sample thickness (100 µm). Since a transition temperature $T_c$ of 15 K
Figure 18. The normalized conductivity plotted as a function of temperature for the SWNT@AFI sample with thickness of about 50 nm. Experimental values (solid circles) and theoretical predictions for the fluctuation supercurrent (open circles) are shown.

would imply a superconducting gap of \( \sim 4 \text{ meV} \), there should be \( \sim 1000 \) potential barriers over 100 \( \mu \text{m} \). That means an average superconducting segment of \( \sim 100 \) nanometres. Experimentally, a sample thickness of 50 nm is achieved by argon ion milling both sides of the sample. After etching (with HCl) and cleaning (with distilled water) of the foil, Pt electrodes were made on both sides of the foil by FIB deposition. The size and location of the Pt electrodes were precisely controlled by FIB, ensuring good contact between the electrodes and the ends of SWNTs [17]. In figure 18, the measured conductance \( \sigma \) (measured at 1 V, or an electric field \( \approx 2 \times 10^5 \text{ V cm}^{-1} \)) is normalized by the conductance at 0.455 K, and is plotted as a function of temperature. The observed temperature dependence is opposite to the thick sample. Moreover, the conductance of the sample exhibits a diverging behaviour, very different from the usual metallic behaviour of saturation at low temperatures. Such behaviour is characteristic of a fluctuation supercurrent in 1D, shown to be consistent with both the magnetic Meissner effect as well as the appearance of the gap [17] through Monte Carlo calculations where the parameters are again fixed by the fitting to the Meissner effect.

7. Modulation of electronic states by metal doping

Modification of physical properties of carbon nanotubes by means of doping is of considerable interest [58, 59]. By adding electrons into the electronic states, the Fermi level can be tuned to coincide with a van Hove singularity, leading to enhancement of conductivity or even superconductivity. Some calculations for intercalation of alkali metal in small nanotubes have been carried out. Miyamoto et al [60] have shown that a chain of K atoms exhibits an exothermic interaction with (7, 0) and (8, 0) tubes. The potassium metal, however, is not suitable for intercalation into the 0.4 nm SWNTs because of the small tube diameter [61]. In the family of alkali metals, lithium is the obvious candidate which is thermodynamically and kinetically favourable for such a small SWNT [62]. There are three possible locations for intercalation of lithium atoms in the SWNT@AFI crystal: inside the nanotube, the interstitial space between...
the tube and the inner wall of the AFI channel, and inside the small six-ring AFI channels [48]. Interestingly, we found that lithium atoms can be intercalated inside the nanotube to line up as a single-atom chain [62], as long as the mouth of the tubes is not capped. The lithium atoms donate their valence electrons to the tube, which leads to modulation of electronic DOS structure of the nanotubes. Calculations based on the first principles approach showed that the DOS at

Figure 19. The DOS at the Fermi level as a function of lithium concentration calculated for (a) the (5, 0) tube, (b) the (3, 3) tube and (c) the (4, 2) tube, respectively.
Fermi level can be modulated upon lithium doping, and is chirality dependent [62]. We show the corresponding DOS at $E_f$ as a function of Li concentration (Li/C ratio) in figures 19(a)–(c) for the (5, 0), (3, 3) and (4, 2), respectively. The solid curve is determined from the DOS of pristine tubes, assuming a rigid-band picture and complete charge transfer. The squares in the figures mark the calculated DOS for Li intercalated tubes with various concentrations of Li at $E_f$. We see that the rigid-band picture gives a very good description of the physics near the Fermi level. For pristine (5, 0), the DOS at $E_f$ is fairly high (0.33 states/eV/carbon-atom) since the Fermi level is just below a van Hove singularity. When Li is added, the DOS at $E_f$ rises rapidly and attains a maximum at a Li/C ratio of about 0.02 (figure 19(a)). At that concentration, the additional electrons fill up to the peak of the van Hove singularity. Further increase in Li concentration will decrease the DOS at $E_f$ to a nearly constant value of about 0.025 states/eV/carbon-atom. Upon a further increase in Li concentration, the DOS at $E_f$ rises again when there are enough additional electrons to occupy another van Hove singularity. Such abrupt changes of DOS upon doping are due to the quasi-one-dimensional character of the tube. For the (3, 3) tube, the DOS at $E_f$ is small at low Li concentration up to about 0.05, and it is nearly constant up to that concentration since the two bands crossing the Fermi level have fairly linear dispersion near $E_f$. Upon further addition of Li, the DOS jumps to a very high value when a van Hove singularity is being filled at a concentration of about 0.06 Li per carbon atom (figure 19(b)). The corresponding DOS at $E_f$ is nearly 1.0 states/eV/carbon-atom, which is a significant increase compared with 0.06 states/eV/carbon-atom for the pristine (3, 3). Upon doping with Li atoms, the semiconducting (4, 2) tube becomes metallic [62]. The DOS of the (4, 2) tube increases from zero to a finite value at very small Li concentration, and then settles to about 0.03 states/eV/carbon-atom for a certain range of Li concentration. The DOS at $E_f$ can reach a high value when the concentration is about 0.037 Li per carbon atom (figure 19(c)).

Experimentally, we doped lithium atoms into the SWNT@AFI system by means of vapour phase adsorption. The SWNT@AFI crystals are sealed together with pre-distilled lithium metal into a Pyrex glass tube under vacuum of $10^{-6}$ mbar, and then heated at 220°C for 5 h. The SWNT@AFI crystal with a saturate doping of lithium looks deep black with no polarization behaviour. The experiments find that the tubes have strong affinity for Li, as predicted by theory. Because of active chemical reaction, the lithium doped sample can be destroyed immediately if the sample is exposed to air. Thus, the sample must be kept in the glass tube in vacuum. The charge transfer from doped lithium atom to the nanotubes can be evidenced by means of Raman scattering. Upon electron doping, the tangential graphite-like modes will be broadened and shifted to lower frequencies because of interactions between continuum electronic states and the discrete phonon states [58, 63, 64]. In order to perform Raman measurements, a rectangular Pyrex tube with a $2 \times 5$ mm$^2$ cross section was used. The affect of lithium doping on the feature of the Raman spectra in the RBM region and in middle frequency region (1300–1500 cm$^{-1}$) have been discussed in a previous paper [65]. In figure 20, we only plot the Raman spectra of the G-like modes as a function of the lithium doping level. Spectrum 0 in the figure is for the pristine SWNT@AFI crystal. Lithium concentration gradually increases from spectrum 0 to spectrum 10. In general, the Raman intensity of the G-like modes decreases with the increase of the lithium concentration. Meanwhile, at low frequency a new asymmetrical broad band gradually appears and, finally, the Raman spectrum is dominated by the asymmetrical band, as shown by spectrum 10 in figure 20. We fit the line shape of different doping levels using three Lorentzians for the three high-frequency peaks and one Breit–Wigner–Fano (BWF) line shape for the peak near 1558 cm$^{-1}$. The BWF line shape is given
Figure 20. Raman spectra (solid dots) in the frequency region of the G-like modes. Spectrum 0 is for pristine nanotubes. From spectrum 1 to 10, the lithium density increases in the same order. The spectra are fitted using two Lorentzian line shapes (solid curves) and a BWF component (dotted curve). The coupling constant \( \frac{1}{q} \) is labelled on the left shoulder of each BWF curve.

by \( I(\omega) = I_0 \frac{[1+(\omega - \omega_{BWF})/q \Gamma]^2}{[1+(\omega - \omega_{BWF})/\Gamma]^2} \), where \( I_0, \omega_{BWF} \) and \( \Gamma \) are, respectively, the intensity, renormalized frequency and broadening parameter [66]. The asymmetric line shape is governed by the \(-1/q\) value which characterizes the interaction between the discrete phonon state and electronic continuum. We traced the line shapes of these G-like bands as a function of the doping level. For the Lorentzians, the behaviour can be described mainly by intensity competition with fixed line width and centre frequency. For the BWF component near 1558 cm\(^{-1}\), the variation is characterized by gradual changes of the line shape and downshifts in frequency, and finally dominates the spectra. The peak at 1558 cm\(^{-1}\) turns out to be the discrete phonon state coupled with the electronic continuum, which indicates the charge transfer from lithium atom to the SWNTs. The frequency of the BWF line shape is remarkably close to that observed in nanotubes with diameters of 1–2 nm [58, 63]. The region near 1550 cm\(^{-1}\) exhibits to be a general BWF region where coupling occurs between a discrete phonon mode and an electronic continuum. The \(-1/q\) value of the BWF component increases from 0.03 to 0.50, leading to a downshift of the BWF peak from 1558 to 1537 cm\(^{-1}\) and significant broadening in line shape. The \(-1/q\) value is
larger than that reported for alkali metal doped SWNT bundles [58], but a factor of \(\sim 2\) smaller than that observed in the first stage alkali metal graphite intercalated compounds (MC\(_8\), where M is K, Cs, and Rb). The value of the \(-1/q\) is known to be proportional to the DOS at the Fermi level [67]. However, the relation between the \(-1/q\) value and the electronic DOS at the Fermi level does not seem to be straightforward, as we did not see the change in the \(-1/q\) value as that expected from the \textit{ab initio} DOS calculation (figure 19) but, rather, a monotonic increase with increasing doping level. It should be pointed out that the value of \(-1/q\) obtained from the BWF line shape is just an average number of all three possible structures of the \((5, 0)\), \((3, 3)\) and \((4, 2)\) tubes. It is not possible to assign the individual contributions of these tubes to the BWF line shape in figure 20.

8. Concluding remarks

In this paper we have detailed the fabrication, characterization, and the various theoretical and experimental studies of the 0.4 nm carbon nanotubes templated in the channels of AFI zeolite crystals. Future research is expected to focus on the selective growth of a specific chirality of the 0.4 nm SWNT with better crystal quality, so that we would be able to have even better control over the optical, transport, mechanical and thermal properties. Better understanding of the physics at the atomic level, and the exploitation of the unique properties of these ultra-small carbon nanotubes in various applications, are the other challenges that we are currently undertaking. Advances in these endeavours will be reported elsewhere.

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References

[1] Iijima S 1991 Nature \textbf{354} 56
[2] Iijima S and Ichibashi T 1993 Nature \textbf{363} 603
[3] Bethune D S, Kiang C H, de Vries M S, Gorman G, Savoy R, Vazquez J and Beyens R 1993 Nature \textbf{363} 605
[4] Sawada S and Hamada N 1992 \textit{Solid State Commun.} \textbf{83} 917
[5] Cabria I, Mintmire J W and White C T 2003 \textit{Int. J. Quantum Chem.} \textbf{91} 51
[6] Ajayan P M and Iijima S 1992 Nature \textbf{358} 23
[7] Sun L F, Xie S S, Liu W, Zhou W Y, Liu Z Q, Tang D S, Wang G and Qiang X L 2000 Nature \textbf{403} 384
[8] Qin L C, Zhao X L, Hirahara K, Miyamoto Y, Ando Y and Iijima S 2000 Nature \textbf{408} 50
[9] Tang Z K, Sun H D, Wang J, Chen J and Li G 1998 \textit{Appl. Phys. Lett.} \textbf{73} 2287
[10] Wang N, Tang Z K, Li G D and Chen J S 2000 Nature \textbf{408} 50
[11] Prinzbach H, Weller A, Landenberger P, Wahl F, Worth J, Scott L, Gelmont M, Olevano D and Issendorff B V 2000 Nature \textbf{407} 60
[12] Blase X, Benedict L X, Shirley E L and Louie S G 1994 \textit{Phys. Rev. Lett.} \textbf{72} 1878
[13] Dresselhaus M S, Dresselhaus G and Eklund P C 1996 \textit{Science of Fullerenes and Carbon Nanotubes} (San Diego, CA: Academic)

\textit{New Journal of Physics} \textbf{5} (2003) 146.1–146.29 (http://www.njp.org/)
[14] Saito R, Dresselhaus G and Dresselhaus M S 1998 *Physical Properties of Carbon Nanotubes* (London: Imperial College Press)

[15] Benedikt L X, Crespi V H, Louie S G and Cohen M L 1995 *Phys. Rev.* B **52** 14935

[16] Kociak M, Kasumov A Y, Gueron S, Reulet B, Khodos I I, Gorbatov Y B, Volkov V T, Vaccarini L and Bouchiat H 2001 *Phys. Rev. Lett.* **86** 2416

[17] Tang Z K, Zhang L Y, Wang N, Zhang X X, Wen G H, Li G D, Wang J N, Chan C T and Sheng P 2001 *Science* **292** 2462

[18] Qiu S and Pang W 1989 *Zeolites* **9** 440

[19] Sun H D, Tang Z K, Chen J and Li G D 1999 *Appl. Phys.* A **69** 381

[20] Kociak M, Kasumov A Y, Gueron S, Reulet B, Khodos I I, Gorbatov Y B, Volkov V T, Vaccarini L and Bouchiat H 2001 *Phys. Rev. Lett.* **86** 2416

[21] Tang Z K, Zhang L Y, Wang N, Zhang X X, Wen G H, Li G D, Wang J N, Chan C T and Sheng P 2001 *Science* **292** 2462

[22] Qin L, Zhao X, Hirahara K, Ando Y and Iijima S 2001 *Chem. Phys. Lett.* **349** 389

[23] Qin L, Zhao X, Hirahara K, Ando Y and Iijima S 2001 *Chem. Phys. Lett.* **349** 389

[24] Li I L, Li G D, Liu H J, Chan C T and Tang Z K 2001 *Appl. Phys. Lett.* **82** 1467

[25] Hulman M, Kuzmany H, Dubay O, Kresse G, Li I L and Tang Z K 2003 *J. Chem. Phys.* **119** 3384

[26] Saito R, Takeya T, Kuzmany H, Dubay O, Kresse G, Li I L and Tang Z K 2003 *J. Chem. Phys.* **119** 3384

[27] Baca W S, De Heer W A, Ugarte D and Châtelain A 1993 *Chem. Phys. Lett.* **211** 346

[28] Holden J M, Ping Z, Bi X X, Eklund P C, Bandow S J, Jishi R A, Daschowdhury K, Dresselhaus G and Dresselhaus M S 1994 *Chem. Phys. Lett.* **220** 186

[29] Knight D S and White W B 1989 *J. Mater. Res.* **4** 385

[30] Jorio A, Dresselhaus G, Dresselhaus M S, Souza M, Dantas M S S, Pimenta M A, Rao A M, Saito R, Liu C and Cheng H M 2000 *Phys. Rev. Lett.* **85** 2617

[31] Jorio A, Dresselhaus G, Dresselhaus M S, Souza M, Dantas M S S, Pimenta M A, Rao A M, Saito R, Liu C and Cheng H M 2000 *Phys. Rev. Lett.* **85** 2617

[32] Duesberg G S, Loa I, Burghard M, Syassen K and Roth S 2000 *Phys. Rev. Lett.* **85** 5436

[33] Dresselhaus M, Dresselhaus G, Jorio A, Filho A S and Saito R 2002 *Carbon* **40** 2043

[34] Jorio A, Filho A G S, Dresselhaus G, Dresselhaus M S, Swan A K, Niu M S, Goldberg B B, Pimenta M A, Hafner J H and Lieber C M 2002 *Phys. Rev. B* **65** 155412

[35] Jorio A et al 2002 *Chem. Phys. Lett.* **351** 27

[36] Ajiki H and Ando T 1994 *Physica B* **201** 349

[37] Tasaki S, Maekawa K and Yamabe T 1998 *Phys. Rev. B* **57** 9301

[38] Gommans H H, Alldredge J W, Tashiro H, Park J, Magnuson J and Rinzler A G 2000 *J. Appl. Phys.* **88** 2509

[39] Jorio A, Saito R, Hafner J H, Lieber C M, Hunter M, McClure T, Dresselhaus G and Dresselhaus M S 2001 *Phys. Rev. Lett.* **86** 1118

[40] Kurti J, Kresse G and Kuzmany H 1998 *Phys. Rev. B* **58** R8869

[41] Robertson D H, Brenner D W and Mintmire J W 1992 *Phys. Rev. B* **45** 12592

[42] Adams G B, Sankey O F, Page J B, O’Keefe M and Drabold D A 1992 *Science* **256** 1792

[43] Sawada S and Hamada N 1992 *Solid State Commun.* **83** 917

[44] Carrial I, Mintmire J W and White C T 2003 *Int. J. Quantum Chem.* **91** 51

[45] Rao A M 2001 *Mater. Res. Soc. Symp. Proc.* **633** F14.8.1

[46] Peng L M, Zhang Z L, Xue Z Q, Wu Q D, Gu Z N and Pettifor D G 2000 *Phys. Rev. Lett.* **85** 3249

[47] Liu H J and Chan C T 2002 *Phys. Rev. B* **66** 115416

[48] Li Z M, Tang Z K, Liu H J, Wang N, Chan C T, Saito R, Okada S, Li G D, Chen J S and Nagasawa N 2001 *Phys. Rev. Lett.* **87** 127401

[49] Cabria I, Mintmire J W and White C T 2003 *Phys. Rev. B* **67** 121406

[50] Machon M, Reich S, Thomsen C, Sanchez-Portal D and Ordejon P 2002 *Phys. Rev. B* **66** 155410

[51] Yang X P, Weng H M and Dong J 2003 *Eur. Phys. J. B* **32** 345

[52] Bockrath M, Cobden D H, Lu J, Rinzler A G, Smalley R E, Balents L and McEuen P L 1999 *Nature* **397** 598

*New Journal of Physics* 5 (2003) 146.1–146.29 (http://www.njp.org/)
[53] Ebbesen T W, Lezec H J, Hiura H, Bennet J W, Ghaemi H F and Thio T 1996 Nature 382 54
[54] Thess A et al 1996 Science 273 483
[55] Kasumov A Y, Khodos I I, Ajayan P M and Colliex C 1996 Europhys. Lett. 34 429
[56] Sheng P 1995 Introduction to Wave Scattering, Localization, and Mesoscopic Phenomena (New York: Academic) pp 293–8
[57] Giaever I 1960 Phys. Rev. Lett. 5 147
[58] Rao A M, Eklund P C, Bandow S, Thess A and Smalley R E 1997 Nature 388 257
[59] Lee R S, Kim H J, Fischer J E, Thess A and Smalley R E 1997 Nature 388 255
[60] Miyamoto Y, Rubio A, Blase X, Cohen M and Louie S G 1995 Solid State Commun. 74 299
[61] Yang J, Liu H J and Chan C T 2001 Phys. Rev. B 64 085420
[62] Liu H J and Chan C T 2003 Solid State Commun. 125 77
[63] Claye A, Rahman S, Fisher J E, Sirenko A, Sumanasekera G U and Eklund P C 2001 Chem. Phys. Lett. 333 16
[64] Bendiab N, Anglaret E, Bantignies J L, Zahab A, Sauvajol J L, Petit P, Mathis C and Lefrant S 2001 Phys. Rev. B 64 245424
[65] Ye J T, Li Z M, Tang Z K and Saito R 2001 Phys. Rev. B 67 113404
[66] Brown S D M, Jorio A, Corio P, Dresselhaus M S, Dresselhaus G, Saito R and Kneipp K 2001 Phys. Rev. B 63 155414
[67] Eklund P C and Subbaswamy K R 1979 Phys. Rev. B 20 5157
[68] Aizawa T, Souda R, Otani S, Ishizawa Y and Oshima C 1990 Phys. Rev. B 42 11469
[69] Siebentritt S, Pues R, Rieder K H and Shikin A M 1997 Phys. Rev. B 55 7927