ELECTRON ADDITION AND EXCITATION SPECTRA OF INDIVIDUAL SINGLE-WALL CARBON NANOTUBES*

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We present mK-temperature non-linear current-voltage characteristics of an individual single-wall carbon nanotube as a function of magnetic field. The measurements show Coulomb blockade and resonant tunneling through single molecular levels. Correlations between the addition spectrum and the excitation spectrum are observed. The magnetic field dependence of the addition and excitation spectra is discussed.

PACS numbers: 73.61.Wp, 72.80.Rj

1. INTRODUCTION

Carbon nanotubes are conducting molecules with either semiconducting or metallic electronic properties.[1] The combination of their long length of several micrometers and small nanometer diameter make them ideal candidates for studying the effects of one-dimensional confinement of the electrons on their transport properties.

Previous studies of carbon nanotubes have shown that their low-temperature transport properties can be described by Coulomb blockade theory,[2–4] where the thermal energy k_BT is smaller than the charging energy of the nanotube $E_C \equiv e^2/2C_{tube}$. In the quantum regime at lowest temperature, the single-particle level spacing ΔE can be resolved, i.e. $k_BT < \Delta E < E_C$, in contrast with the classical regime at higher temperature, where $\Delta E < k_BT < E_C$.[5] It has been shown that the value of ΔE is equal to the expected 'particle-in-a-box' energy level separation of electrons

*Published in Journal of Low Temperature Physics **118**, 495 (2000)

confined to the nanotube.[3] The magnetic field dependence of the molecular energy levels of carbon nanotubes is dominated by the spin degree of freedom. This Zeeman effect has been observed both in ropes[4](bundles of nanotubes) and in individual nanotubes.[6,3] The corresponding filling of single-particle levels however appears not to be straightforward. Both singlet-doublet[4] as well as spin-polarized filling[6] have been observed.

Coulomb blockade phenomena in small confined systems, where the two energy scales E_C and ΔE are both important, have been well studied.[7] The energy needed to add an electron to the nanotube is $e^2/C + \Delta E = 2E_C + \Delta E$.[5] When the thermal energy is lower than this, current through the system is blocked. The blockade can be lifted, however, by changing the electrostatic potential of the nanotube, e.g. by applying a voltage on a nearby gate electrode that is coupled capacitively to the nanotube. At that point, current is allowed to flow and a conductance peak is observed. As the gate voltage is changed further, a series of conductance peaks will become visible. In between these, the number of electrons is fixed. Whenever a peak is crossed, the number of electrons on the nanotube changes by one. The single-particle level spacing may be different for different numbers of electrons on the nanotube. This will lead to a variation in the distance between the conductance peaks $\Delta V_{gate} = (2E_C + \Delta E_n)/e\alpha$, where $\alpha \equiv C_{gate}/C_{tube}$ is the capacitive coupling of the nanotube to the gate and n is the number of electrons on the nanotube. We thus obtain the variation of addition energy with number of electrons and this is called the addition spectrum. It is related to the energy difference between consecutive ground states of the nanotube.

The blockade can also be lifted by raising the bias voltage. The two bias electrodes are coupled to the nanotube by tunneling contacts, but also capacitively. In a differential conductance measurement as a function of bias and gate voltage, the combination of both voltages leads to the well-known Coulomb blockade diamonds in the (V_{gate}, V_{bias}) plane, with corner points $(v_n \pm \Delta V_{gate}/2, 0)$ and $(v_n \pm \delta V_{gate}, \pm\Delta V_{bias})$.[7] Here v_n is a constant and $\delta V_{gate} < \Delta V_{gate}/2$ is an asymmetry parameter which depends on the exact values of all capacitances to the nanotube. Within this diamond, current is blocked and the number of electrons is fixed. The 'width' of this diamond is the distance ΔV_{gate} between the conductance peaks mentioned above. From the ratio of the 'height' ΔV_{bias} to the 'width' ΔV_{gate}, we can find $\alpha = \Delta V_{bias}/\Delta V_{gate}$.

The energy levels of the nanotube are also accessible in another way. At the point where the Coulomb blockade has been lifted by increasing the bias voltage, transport through the nanotube can take place because a molecular energy level is inside the window created by the applied bias

voltage. The occupation of the nanotube then oscillates between say n and $n+1$. When the bias voltage is increased further, a higher lying energy level can enter the bias window. Now, electron transport can also take place via this level. The increased probability in transferring electrons leads to a stepwise increase in the current and a peak in the differential conductance. Note, however, that the occupation of the nanotube still oscillates between n and $n+1$. Because the next energy level is higher in energy then the ground state which was already contributing to the transport, this level is called an excited state. If the capacitive coupling of this excited state to the bias and gate electrodes is equal to that of the ground state, these excited states are visible as lines running parallel to the sides of the diamond. The distance in gate voltage between this line and the side of the diamond is $\Delta E/e\alpha$. A collection of excited states in the nanotube will give rise to a collection of extra lines. Since we can now determine the energies of the excited states of the nanotube, this collection is called the excitation spectrum.

Within the constant interaction model,[8] the excited states of the nanotube are simply the energy levels of the next ground states, as visible in the addition spectrum. The addition and excitation spectra are thus simply related. Although the extension of this idea to correlated systems where electron-electron interactions are important is not trivial, support for its validity in quantum dots has been reported.[9]

In this paper, we present measurements of the addition and excitation spectra of a carbon nanotube and discuss the correlations between these. The magnetic field dependence of the states is reported as well.

2. SAMPLE DESCRIPTION

Single-wall carbon nanotubes were produced by the group of R.E. Smalley at Rice university, USA.[10] A small amount of this raw material is ultrasonically dispersed and spin coated on top of a SiO_2/Si-substrate containing a large array of predefined Pt electrodes. These electrodes are fabricated using a double layer (PMMA/MAA) resist, electron beam lithography, Pt evaporation and lift-off. The resulting electrodes are 20 nm high, 250 nm wide and 8 μm long and are separated from each other by 500 nm. The gate electrode is placed perpendicular to the other electrodes and separated from the ends by 2.5 μm. After deposition of the nanotubes, adjacent pairs of electrodes are checked for conduction due to the nanotubes, which corresponds to a typical resistance of 1 to 10 MΩ. The metallic nature of the nanotube is established by checking that the conductance cannot be modulated by a gate voltage.[11] Single nanotubes are selected by their apparent height of 1.4 nm or less in Atomic Force Microscopy.[12]

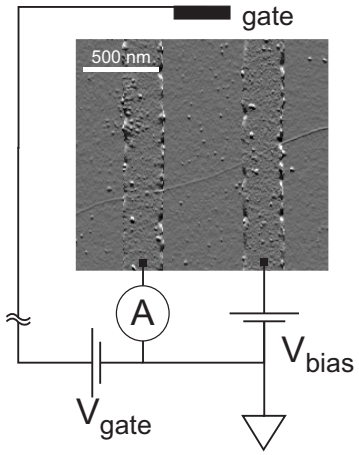

Fig. 1. *Tapping-mode AFM amplitude image of the nanotube, lying over two electrodes. The length of the nanotube segment in between electrodes is 540 nm while the total length is about 3 μm. The gate electrode is not visible in the AFM image and is indicated schematically. The bias voltage is applied asymmetrically.*

A tapping-mode AFM picture of the sample that is being studied in this paper is shown in figure 1, along with a schematic view of the electrical connections. The segment of this nanotube between electrodes is 540 nm, while its full length is about 3 μm. The room temperature resistance of this sample is 4 MΩ and increased upon decreasing the temperature. It was cooled down in a dilution refrigerator with a base temperature of 5 mK.

3. EXPERIMENTAL RESULTS AND DISCUSSION

We have measured the current through the nanotube as a function of V_{bias} and V_{gate}. Typical I – V_{bias} curves are shown in figure 2. Around zero bias voltage, the current is blocked by Coulomb blockade. At higher bias, the blockade can be overcome and a step in the current is observed. Increasing the bias voltage further, beyond a point that is set by the level spacing and the values of all capacitances, current through the nanotube can also flow through a next level and another step in the current is observed.

Additional features can be seen in the positive bias part of the curve obtained at $V_{gate} = -225$ mV. Here peak structures are observed in addition to the steps. This peak-like structure leads to negative differential conductance (NDC). Several mechanisms may lead to this NDC. For example, one possibility is residual carbon particles from the raw material, which may be lying between the nanotube and the contacts. Whenever one of the energy

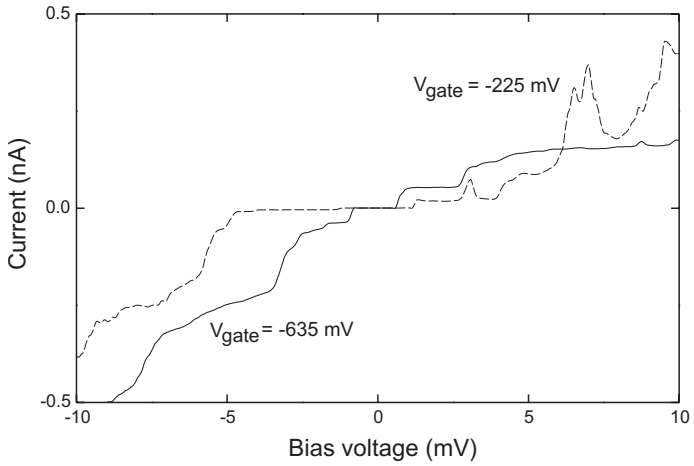

Fig. 2. *Bias voltage dependence of the current through the nanotube at two values of the gate voltage, i.e. -225 and -635 mV. Around $V_{bias} = 0$, current is blocked by Coulomb blockade. The plateaus in the current are due to resonant tunneling through molecular energy levels. Peaks are oberved as well (see discussion in text).*

levels of this particle crosses the bias window, a peak in current is observed. In a conductance spectrum, the positions of NDC will not shift in a similar manner as the excited states, because the capacitive coupling of this particle with the leads and gate electrode can be expected to be very different. We will not discuss these effects any further here.

Figure 3 shows the current through the nanotube as a function of gate voltage. A series of peaks is visible. In between these, the current is blocked by Coulomb blockade, and the number of electrons on the nanotube is fixed. The distance in gate voltage between peaks is $(2E_C + \Delta E_n)/e\alpha$.

One of the conductance peaks is examined in more detail as a function of temperature in figure 4. The solid lines are fits with $G = G_0(T)/\cosh^2(V_{gate}/2w(T))$,[5] where $w \equiv k_B T/e\alpha$ and $\alpha \equiv C_{gate}/C_{tube}$. The left and right insets show the obtained inverse maximum conductance, $1/G_0$, and width, w, versus temperature, respectively. Both are fit with a linear function. From the linear fit of the width versus temperature we obtain $1/\alpha = 35 \pm 5$. The fact that the maximum conductance is proportional to $1/T$ is evidence for resonant tunneling through single molecular levels.[5] A continuum of levels would lead to a constant maximum.[5]

We have measured current through the nanotube as a function of V_{gate} and V_{bias} and differentiated this numerically. The differential conductance spectrum we thus obtain is shown in figure 5a. The large light grey areas are the Coulomb diamonds mentioned earlier, the regions where current is

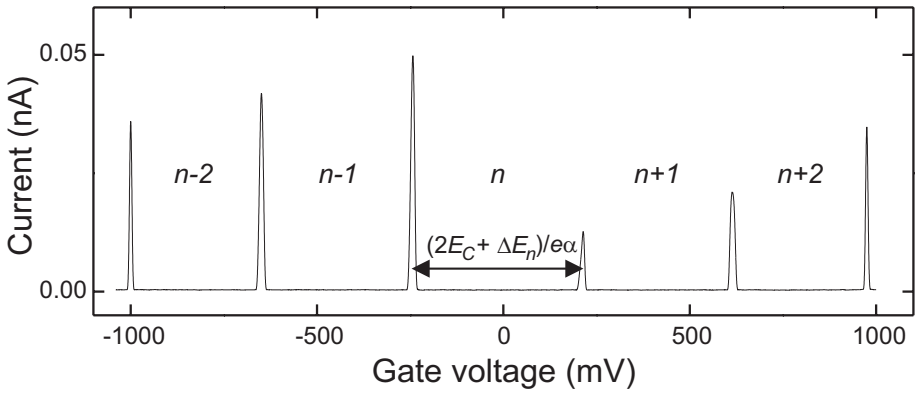

Fig. 3. *Current through the nanotube as a function of gate voltage at* V_{bias} *= 400* μV*. A series of conductance peaks is clearly visible.*

blocked. Lines with the same direction appear to be parallel. From the ratio of ΔV_{bias} to ΔV_{gate} we find $1/\alpha = 35 \pm 2$, in good agreement with the value found earlier. Several boundaries of the diamonds appear to have small kinks at $V_{bias} \approx$ - 5 mV (see in particular the $n+1$ diamond). Here the slope changes by 20 to 30 %. These kinks have been observed before and can be taken as a signature of ground-state to ground-state transitions due to electron-electron correlations.[6]

The lines running parallel to the boundaries of the diamonds can be associated with excited states. They are separated from the boundaries by $\Delta E/e\alpha$ in the gate voltage direction. Viewed from the ground state of occupation $n-1$ we identify an excited state running parallel to the border at positive bias voltage and at the high gate voltage side. This state is associated with transport through the first excited state and must thus be correlated with the width of the next coulomb diamond (occupation n) which in the simplest model is $(2E_C + \Delta E_n)/e\alpha$. At the lower gate voltage side another excited state can be seen. This is associated with depletion of the nanotube through the lower-lying level and thus must be correlated with the diamond with occupation $n-2$.

We have examined several excited states in a similar fashion, focussing on those positions in the diagram where these can be identified unambiguously. In figure 6 we have plotted the distance in gate voltage between ground state and excited state versus the corresponding diamond width. The addition and excitation spectra are clearly linearly related. Note that this is a remarkable effect in the case of carbon nanotubes where electron-electron interactions are important.[6,13,14] The slope of the linear fit, however, is 2.1, i.e. not equal to the value of 1 that is expected from the previous formulæ. It should be noted that this value is independent on any calibration errors

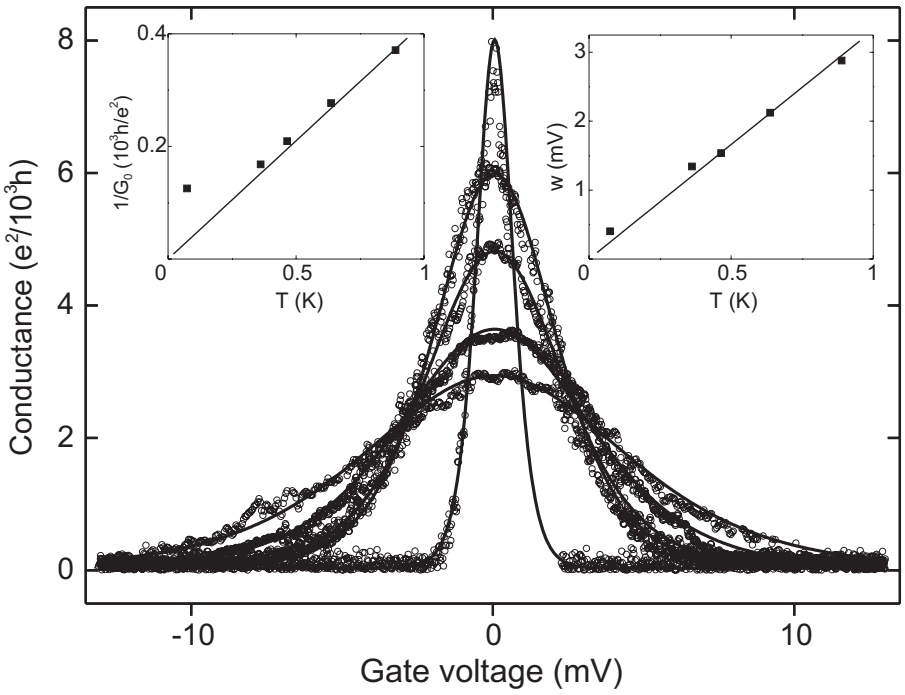

Fig. 4. *Linear conductance of the nanotube as a function of gate voltage and temperature at $V_{bias} = 10\ \mu V$. Shown is the transition from $n-2$ to $n-1$ at temperatures of 74 (sharpest), 362, 465, 637 and 889 mK (widest). The solid lines are fits with $G = G_0(T)/\cosh^2(V_{gate}/2w(T))$, where $w \equiv k_B T/e\alpha$. The insets show the obtained inverse maximum conductance $1/G_0$ and width w as a function of temperature. The deviation at the lowest temperature is probably due to the finite bias voltage (10 μV corresponds to 120 mK) and a higher effective electron temperature.*

in both V_{gate} and V_{bias} since we are comparing distances in V_{gate} only. This deviation is currently not understood, but may be a renormalization due to electron-electron interactions.

Independent of this, we can determine the charging energy from the intersection, $2E_C/e\alpha = 265$ mV, yielding $E_C = 3.8$ meV. The geometrical self-capacitance of the nanotube is $C = 2\pi\epsilon_0\epsilon_r L/\ln(2L/d)$,[15] where $d = 1.4$ nm and L are the diameter and length of the nanotube respectively and ϵ_r is the relative dielectric constant of the surroundings. We thus obtain $L = 3.2$ μm when taking $\epsilon_r = 1$, which is equal to the total nanotube length. This is comparable with earlier experiments in a similar geometry.[3,15]

From figure 6 we find that the average value of the separation in gate voltage between ground state and excited state in the excitation spectrum (horizontal axis) is 59 mV, which yields $\langle \Delta E \rangle_{exc} = 1.7$ meV. When measured

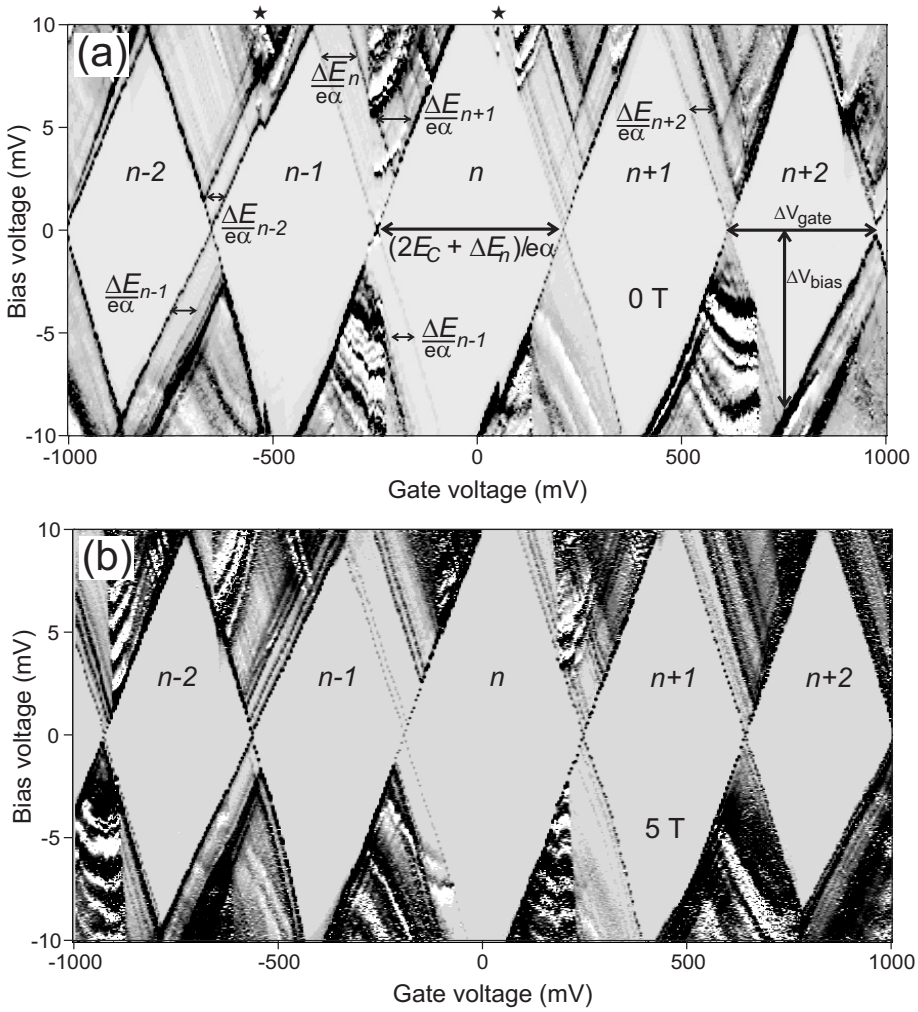

Fig. 5. *Differential conductance (dI/dV_{bias}) spectrum of the nanotube as a function of bias and gate voltage at 0 T (a) and 5 T (b). Light grey tones correspond to $dI/dV_{bias} = 0$. Darker shading corresponds to higher conductance. White regions are positions of NDC, $dI/dV_{bias} < 0$. (a) $B = 0$ T. The distances in gate voltage from the ground to the first excited state are labeled with $\Delta E_n/e\alpha$. The stars ($\star$) above the graph indicate positions where a sudden shift in the diagram occurs in the gate voltage direction. This is probably due to a switching offset charge that shifts the potential of the nanotube. We have corrected for this effect in determining the width of the diamond. (b) $B = 5$ T. At the sides used to construct figure 6, the levels split due to coupling of the magnetic field with spin. Exceptions to this are the sides labelled ΔE_{n-1} in (a).*

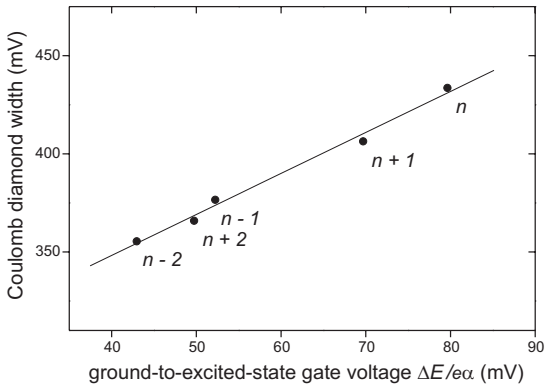

Fig. 6. *Coulomb diamond width, $\Delta V_{gate} = (2E_C + \Delta E_n)/e\alpha$, versus corresponding distance in gate voltage between ground state and excited state, $\Delta E_i/e\alpha$, for various numbers of electrons on the nanotube. The addition and excitation spectra are clearly linearly related. The slope of the linear fit is 2.1. The abscissa yields the value of $E_C = 3.8 \pm 0.2$ meV.*

in the addition spectrum, however, we find $\langle \Delta E \rangle_{add} = 3.5$ meV, which is different by a factor 2.1 as expected from the slope of the linear fit. The particle-in-a-box level spacing is given by $\Delta E = \hbar v_F/2L$.[3] We thus find a nanotube length of 1.0 μm or 0.50 μm from the excitation or addition spectrum respectively. The calculated length from the charging energy E_C and level spacing ΔE thus do not yield the same value. In order to force them to be equal, we need to set ϵ_r to 2.8 or 5.2 respectively. The relative dielectric constant of SiO_2 is 4.4, which is indeed in this range.

Up to this point, we have neglected spin degeneracy. In a finite carbon nanotube there are two sets of energy levels available, both of which can be filled with two electrons due to spin degeneracy. If these energy levels are degenerate, we expect the addition spectrum to be a series of $2E_C$, $2E_C$, $2E_C$, $2E_C+\Delta E$, etc. If this degeneracy is not present, we expect the addition spectrum to be $2E_C$, $2E_C + \Delta E$, etc. Neither the first, nor the second is observed in the addition spectra presented here. If two ground-state energy levels for the nanotube with, say, $n-1$ and n are degenerate, this leads to an addition energy of $2E_C$ for n electrons on the tube. In a series of 8 consecutive conductance peaks, the addition energy was always found to be larger than $2E_C$ by at least 2.3 meV. This implies that the spin degeneracy is not present.[16] We can now investigate this issue by applying a magnetic field.

Figure 5b shows the conductance spectrum in a perpendicular magnetic field of 5 T. Some of the lines which were identified as excited states as well as some of the ground states appear to have split. This splitting is due to

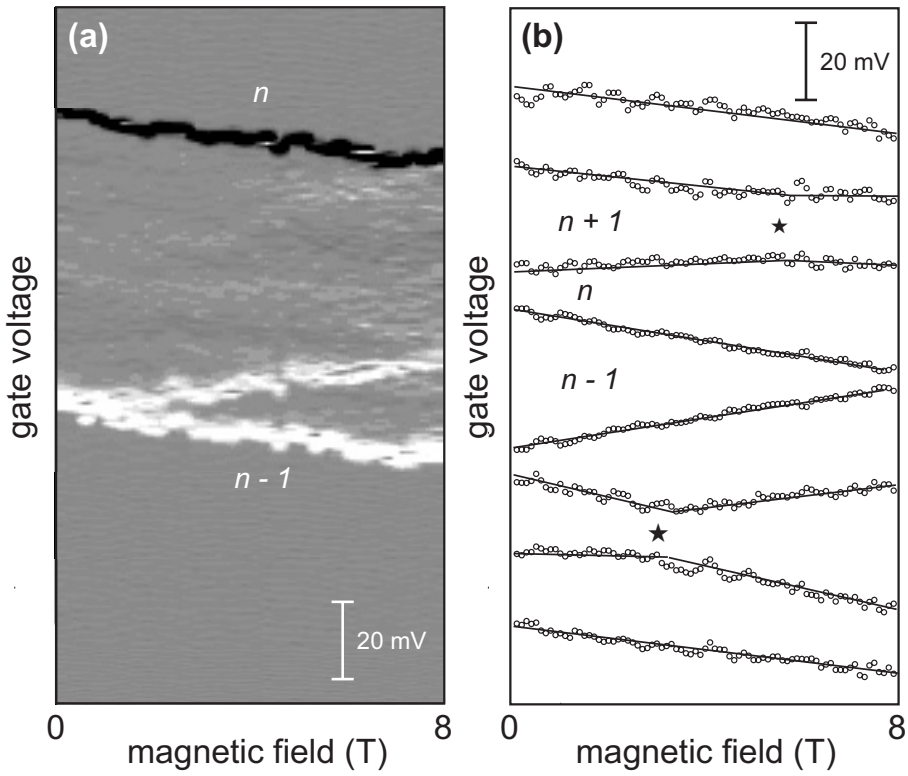

Fig. 7. *Magnetoconductance measurement on a nanotube. (a) Current through the nanotube at V_{bias} = 2.5 mV on the transition from $n-1$ to n as a function of gate voltage. Shown is dI/dV_{gate}, where white (black) corresponds to positive (negative) values. The low gate voltage ground state splits in two as the magnetic field is increased from 0 to 8 T. This splitting is linear and yields a Landé g_L-factor of* 1.9 ± 0.2. *(b) Zero-bias voltage conductance peak position as a function of magnetic field. The curves are shifted along the gate voltage axis for clarity. The solid lines are guides to the eye. The stars ($\star$) indicate kinks in adjacent lines.*

the Zeeman coupling of magnetic field with the spin of the electrons and is equal to $\Delta V_{gate}(B) = g_L \mu_B B/e\alpha$, where μ_B is the Bohr magneton. g_L is the Landé g_L-factor and has been reported to be 2 ± 0.5.[6] In a similar experiment on ropes,[4] a pattern of alternatingly splitting lines and non splitting lines was observed. This is not present in these data.

The evolution of this splitting with magnetic field is examined further in figure 7a. Shown is dI/dV_{gate} as a function of V_{gate} and B at a fixed bias voltage of 2.5 mV. This graph can be considered as a cross-section at constant V_{bias} of the conductance spectra in figure 5 where the white colour

corresponds to the low gate voltage boundary of the transition between $n-1$ and n. This side shows a linear splitting with magnetic field. From this splitting, we obtain $g_L = 1.9 \pm 0.2$. Measurements on other transitions yield values of g_L of 1.5 to 2.5.

The distance between the lower (white) and the upper (black) boundary of the current stripe in figure 7a does not change with magnetic field and is equal to 2.5 mV/α = 88 mV. This current stripe shifts with magnetic field. This shifting is related to the shifting of the zero-bias voltage conductance peak. In figure 7b we show the position of the zero-bias voltage conductance peak as a function of magnetic field for several consecutive peaks. The shifting of the current stripe of (b) is clearly due to the shifting of the conductance peak between $n-1$ and n. In the simplest model, this shifting is equal to $g_L \mu_B B/2e\alpha$. From this we find values for g_L ranging from 0.2 to 2.8. This is in direct contrast with the values found earlier and cannot be explained within a simple model. Furthermore, the first excited state in figure 7a is in the simplest model the next ground state, i.e. the transition from n to $n+1$. The shifting of this conductance peak in figure 7b, however, appears quite different. Measurements on other transitions yield similar discrepancies between excitation and addition spectrum regarding the spin-degree of freedom.

It appears that this spin degeneracy is visible in the excitation spectrum, but not in the addition spectrum in $B = 0$ T. Recently, it has been shown that the transport properties of nanotubes can be interpreted in terms of the Luttinger liquid model,[13,17] in which spin and charge are separated. This spin-charge separation turns the spin degree of freedom into a non-charged collective excitation. We hope that the present studies will encourage theoretical studies on the role of spin-charge separation on the addition and excitation spectra of carbon nanotubes. The first excitation spectra have been theoretically studied already for carbon nanotubes.[14] The predicted structure, however, is too simple to account for the structure in the present data.

In a nanotube, a pattern of either peaks going up, down, etc. or up, up, down, down, etc. is expected, depending on whether the two sets of energy levels are degenerate or not. This pattern is not present. In a previous experiment, it was found that all conductance peaks go down in gate voltage with increasing magnetic field.[6] This pattern is also not present.

Very recently the effect of a non-uniform gate potential profile on spin-flip scattering has been studied theoretically.[18] In this study, the particular potential profile gives rise to various internal spin flip processes, leading to a counter-intuitive shifting of the ground state with magnetic field. This may provide an interesting starting point to explain our data, but further

research is needed to experimentally address these issues in a controlled way.

Two positions in figure 7a, marked by stars ($\star$), show changes in the trend of the peak position versus magnetic field. In the simplest model, this can be explained as follows. When the ground state and the first excited state both split with magnetic field, this splitting is equal to $g_L\mu_B B/\alpha$. When this splitting becomes equal to the level-spacing ΔE, the energy-levels of the excited state with up spin (or down) and the ground state with down spin (or up) cross. This crossing then gives rise to kinks in the peak-position versus magnetic field.[6] From the condition $\Delta E_n = g_L\mu_B B/\alpha$, $g_L = 2$ and the values for ΔE_n from figure 6, we find magnetic fields larger than 10 T where these crossings may occur. This simple model of crossing can clearly not explain the present data. This may be due to e.g. electrostatic repulsion between the energy levels, i.e. exchange interaction.

Summing up, while some features in the spectra can be understood from available models, the general conclusion is that the excitation and addition spectra, and their relation, are very complex and not well understood.

4. CONCLUSIONS

We have observed resonant tunneling through single molecular levels in a carbon nanotube. The obtained addition and excitation spectra in zero magnetic field are linearly correlated. In a magnetoconductance measurement, Zeeman splitting of the molecular levels has been observed. The filling of single particle levels appears not to behave as expected from simple models. Internal spin-flip processes and interaction mechanisms may be important.

ACKNOWLEDGMENTS

The nanotube material is supplied by Richard Smalley and coworkers at Rice University, USA. We would like to thank Leo Kouwenhoven for stimulating discussions. This research was supported by the Dutch Foundation for Fundamental Research of Matter (FOM).

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