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Spin-dependent magnetoresistance in multiwall carbon nanotubes

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PACS. 73.63.Fg – Electronic transport in nanoscale materials and structures: Nanotubes.
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Abstract. – The spin-dependent transport in multiwall carbon nanotubes, obtained by chemical vapour deposition in porous alumina membranes, has been investigated. The zero-bias anomaly is shown to follow the typical power law $GT^{-\alpha}(eV/kT)$. In the nanotubes contacted with Ni pads, the magnetoresistance due to the spin-polarised current (SD-MR) is destroyed. In the case of those contacted with Co pads, however, the SD-MR is observed. These measurements show that both the observation of a typical scaling law of the conductance (for nanotubes up to 1.5 μm) and a short spin diffusion length (less than 0.15 μm with nickel contacts and 0.7 μm with cobalt contacts) coexist through the nanotube. This observation may be interpreted in terms of a reminiscence of the Luttinger-liquid behaviour with spin-charge separation.

Carbon multiwall nanotubes (MWNT) and single-wall nanotubes (SWNT) are considered as the most promising building blocks for both nanoelectronics and molecular electronics. There are a wide variety of possible applications for carbon nanotubes, including spintronics [1], which has led to studies into spin-dependent transport in carbon nanotubes [2–5]. Aside from the possible industrial applications of spintronics, the study of such magnetic systems allows the investigation of fundamental questions, into the role of the spin degrees of freedom in quantum wires or Luttinger liquids (LL) [6, 7]. Here a specific behaviour is expected due to spin-charge separation [8–11].

In the present work, we measured samples consisting of one or a few nanotubes connected perpendicularly to Ni or Co ferromagnetic layers, where a tunnelling junction was present between the nanotubes and the metallic layer. The system is analogous to a metallic spin-valve junction, or a magnetic tunnelling junction (MTJ) where two ferromagnetic layers are separated by a spacer layer. In the present case, the spacer layer is a carbon nanotube (including tunnelling or diffusive junctions), instead of a metallic, or insulating layer. In the two former cases, a strong spin-dependent magnetoresistance (SD-MR) is observed providing that the spin diffusion length (spin-valve effect) is greater than the spacer layer.

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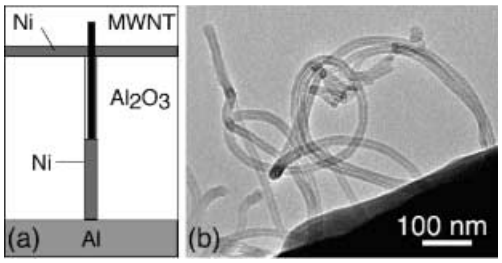

Fig. 1 – (a) Schematics of the Ni/MWNT heterostructure. (b) TEM micrograph of NTs emerging from the pores at the membrane surface.

A scaling law of the conductance, indicative of mesoscopic transport through the whole structure, is observed. Hence the spin polarisation of the current is expected to be conserved. A strong SD-MR is then expected over the length of the nanotubes. The results of the present study show that this is surprisingly not the case.

The samples are systematically characterised via the typical scaling law $G \propto V_{\mathrm{bias}}^{\alpha}$ at high-voltage bias V_{bias}, and $G \propto T^{\alpha}$ at low-voltage bias (G is the conductance, T the temperature and α is the scaling coefficient), as recently discussed in the literature for SWNT and MWNT [12–16], or short metallic wires [17]. This scaling law can be explained either from Luttinger liquid (LL) theory [8, 18, 19] in 1D quantum wires, or from intrinsic Coulomb blockade in MWNT [20], or via environmental Coulomb Blockade (ECB) theory applied to quantum wires [21, 22].

The spin-dependent magnetoresistance, related to the magnetic hysteresis of the contacts, was measured for each sample and correlated to the scaling coefficient α in order to try to observe an effect of the expected spin-charge separation. Our measurements confirm previous observations that the SD-MR is very small, whatever the length of the tube between the ferromagnetic contacts. A significant signal was however measured for some short nanotubes contacted exclusively with the Co layers. These measurements show that the observed scaling law (observed up to the maximum length between our ferromagnetic layers $1.5\,\mu$m) [12, 23, 24] exists in conjunction with a short spin diffusion length (below $0.15\,\mu$m with Ni contact and $0.7\,\mu$m with Co contacts).

The MWNT were grown by a CVD technique in nanoporous alumina membranes (see fig. 1(a)). The membranes were obtained through the anodization of Al [24] in a 0.3 mol/l oxalic acid solution. The anodization was carried out at 40 V over a period of 10 min. Under these conditions, the pore length in the membrane was $1.5\,\mu$m, with a pore diameter of 40 nm. Either Ni or Co wires of defined length were then electrodeposited in the pores [25, 26]. The area of electrodeposition was less than $1\,\mathrm{mm}^2$. The nanowires length was regulated via the electrodeposition time [25]. The membrane was then exposed to acetylene at 20 mbar and 650 °C in a tube furnace over a period of 5 min. This initiated the catalytic growth of the MWNTs from the top of the electrodeposited Ni or Co wires. The diameters of the MWNTs were highly consistent ranging to $23\,\mathrm{nm} \pm 2\,\mathrm{nm}$ (see fig. 1(b). After the growth phase, the nanotubes were kept in air for a few minutes before sputter deposition of a Ni or Co layer (100 nm thickness) to the membrane. The sample exposure before the sputtering of the second ferromagnetic contact led to a highly resistive contact, which was exploited for tunnelling spectroscopy. Since the density of the metallic wires grown in the pores was very low, very few MWNT were effectively grown. As such the samples prepared were similar to samples made

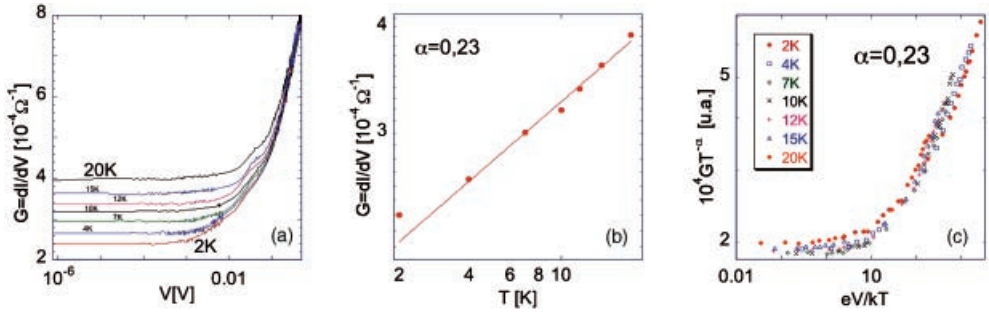

Fig. 2 – Sample A: (a) conductance G ($10^{-4}\,\Omega^{-1}$) as a function of $eV_{\rm bias}$ on a log scale at 2 K, 4 K, 7 K, 10 K, 12 K, 15 K and 20 K. (b) Log-Log plot of the temperature dependence of the zero-bias conductance as a function of the temperature. The line is a power law with $\alpha = 0.23$. (c) Scaling $GT^{-\alpha}$ as a function of the ratio $(eV_{\rm bias}/kT)$.

with bundles or ropes of nanotubes. Furthermore, this method allowed us to electrically bridge the nanotubes without the need for damaging chemical treatments to separate the MWNTs.

A statistical analysis of the samples (45 samples) has been undertaken. Each sample is defined by two sets of parameters, namely the intrinsic parameters (length, purity of the tube, presence of kinks) and the environmental conditions. The latters are described in terms of circuit theory by the impedance of tunnelling junctions, influence of other tubes contacted in parallel, and other sources of dissipation. The magnetic characteristics of the ferromagnetic contacts also vary from one sample to the other, but the magnetic configurations in such structures are well known from anisotropic magnetoresistance (AMR) [26] and domain wall scattering (DWS) [26] measurements.

For the 45 samples measured, the electrical resistances range from 1 kΩ to 100 kΩ. The scaling law is presented in fig. 2 for a typical MWNT with a length of ~ 600 nm (sample A, the resistance at 2 K was 5 kΩ). The differential conductance $G = {\rm d}I/{\rm d}V$ is first plotted as a function of the bias voltage $V_{\rm bias}$ for different temperatures, which shows the typical zero-bias anomaly (ZBA) demonstrated (fig. 2(a)). The values at zero bias $G(V_{\rm bias} = 0)$ follow the power law T^{α} with $\alpha = 0.23$ (fig. 2(b)) and in fig. 2(c), $GT^{-\alpha}$ is plotted as a function of $eV_{\rm bias}/kT$. All data collapses on a unique curve, indicative of a LL-like behaviour.

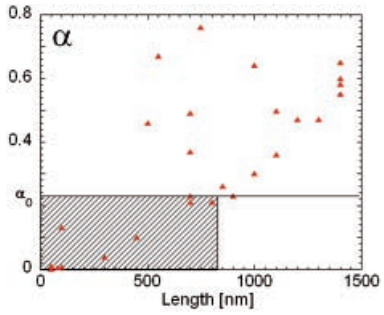

Fig. 3 – Scaling coefficient α as a function of the length of the MWNT. The grey zone corresponds to $\alpha \leq \alpha_0$, where α_0 is the theoretical value calculated for a Luttinger liquid.

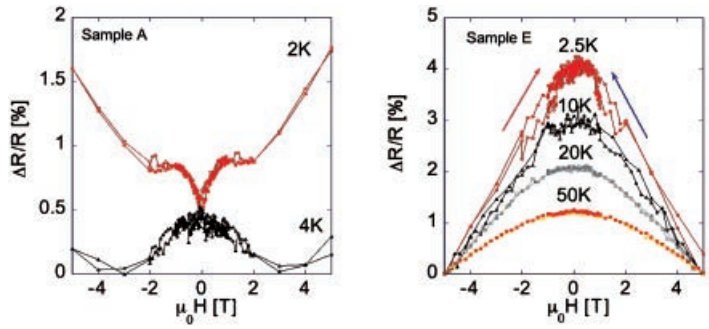

Fig. 4 – Magnetoresistance profile at large fields for samples A (the curve is shifted by 0.5% for clarity) and E. Sample A has a negative MR at low temperature and sample E has a positive MR.

Of the 45 samples, 27 follow the scaling law for the ZBA, which defines the coefficients α which are plotted in fig. 3 (*e.g.* sample A, C and D, fig. 5 below). Five samples show no significant ZBA (Ohmic behaviour: $\alpha = 0$), however 13 show a strong ZBA, but without scaling law (*e.g.*, sample B). The coefficient α is distributed within the interval $0 \leq \alpha < 1$ (fig. 3). Using the transmission line approach we have $\alpha = 2Re(Z)/R_0$, where $R_0 = h/e^2$ is the quantum resistance and Z is the impedance of the transmission line (*e.g.*, $Z = R \approx \sqrt{L/C}$ with the impedance L and the electrostatic capacitance C). The theoretical value for a LL is $\alpha_0 \approx 0.24$ [8, 18, 19, 21]. In a first approximation, as $\alpha \propto \sqrt{1/N}$ [21], if the number of transmission modes N is enhanced as a result of the large number of walls or impurities, the coefficient α is expected to lie below the ideal value α_0. On the other hand, α should be larger than the bulk value if structural defects, such as kinks or junctions, are present [14].

The correlation between α and the length l of the tube is plotted in fig. 3. Taking into account that the probability of the presence of a kink or defect in the tube is proportional to the length of the tube, we expect that for a small value of l $\alpha \leq \alpha_0*$, and for a large value of l $\alpha \geq \alpha_0*$. This is indeed observed in fig. 3, where there is neither sample verifying $\alpha \geq \alpha_0*$ below $l = 500\,\text{nm}$ (TEM pictures confirm that there is a vanishing probability of finding a kink or defect at this scale), nor sample verifying $\alpha \leq \alpha_0*$ above $l = 900\,\text{nm}$. The general tendency depicted in fig. 3 may be interpreted as the presence of defects, kinks or junctions in long CVD grown nanotubes. The small values of α seen for tubes shorter than 300 nm are due to the partial screening of the electron-electron interactions by the contacts.

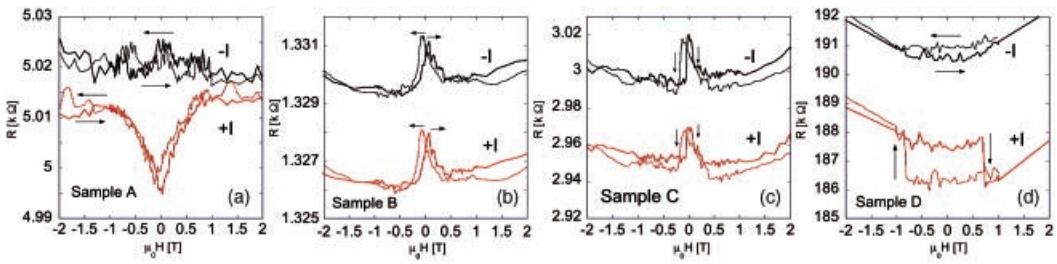

Fig. 5 – Spin-dependent magnetoresistance for four samples contacted with Ni. (a) Sample A, (b) sample B: AMR response $\alpha = 0.037$; (c) sample C: ZBA and no scaling property; (d) sample D, $\alpha = 0.6$.

If the transport properties at zero magnetic field can be described with a single parameter α, the MR properties are far more versatile and various kinds of signals have been reported in the literature [2–5, 12, 24]. Below, two different types of MR are discussed: the direct MR due to the direct action of the magnetic field on the charge, and the spin-dependent magnetoresistance due to the spin-polarised current. The MR has been measured for each sample with a field perpendicular to the tube axis between ± 5 T. At fields above 1.5 T, the magnetisation is saturated, and the profile gives the direct MR of the nanotube. As already reported in the literature, the observed MRs (fig. 4) are either positive (the resistance increases with increasing magnetic field) or negative, varying from one sample to the other. Except for the sign, both positive and negative MR are rather similar, with, in some cases, a transition from positive to negative MR at low temperature (fig. 4(a)). Statistically, magnetoresistance at 2.5 K is positive in 50% of the samples and negative in 25%, while 25% have no measurable trend (no MR at high field). We do not observe any correlation of the sign of the MR neither with the existence of the scaling law, nor with the value of the coefficient α, nor with the temperature profile of the conductance. Consequently, the origin of this behaviour must be ascribed to small numbers of dopants, which strongly modify the Fermi level from one sample to the other [27], but do not modify significantly the parameter α.

1) *Ni contacts.* At low magnetic field, the magnetisation of the wire (bottom electrode) is oriented at an angle of 90° with respect to the Ni layer (top electrode). The magnetisation of the Ni wire rotates uniformly when the applied field is increased (following the Stoner-Wohlfarth curve [26]), reaching the parallel configuration at about 0.6 to 1.5 tesla, depending on the length of the Ni wire. This leads to a 1% variation of the resistance of the nanowire. This effect is called the anisotropic magnetoresistance (AMR). The measurements as a function of weak external magnetic field give then access to the magnetoresistance as a function of the angle between the two ferromagnetic contacts, the so-called SD-MR (*i.e.* the effect of the spin polarisation of the current). Surprisingly, the present study has shown that the SD-MR value at moderate current value (*i.e.* 1 μA) was consistently low (below 1% of the total resistance), whatever the tube length from 150 nm to 1500 nm (see also ref. [4]). Three different kinds of SD-MR are observed, which have been illustrated in fig. 5 for samples A to D. Of the samples measured, 5 samples of type A, 7 samples of type B and 6 samples type of C were observed. Fifteen samples presenting the scaling of the conductance and no SD-MR signal were also obtained. In sample B (fig. 5(b)), for small tube lengths, the AMR [26] of the Ni wire was measured. In sample C (fig. 5(c)), a second type of SD-MR hysteretic response is also observed. In such cases, an important ZBA is present, but the conductivity cannot be scaled with the power law. The SD-MR is observed at low temperature only, and disappears between 4 K and 8 K. Sample A (presented in fig. 2) and sample D (for which $\alpha = 0.59$), display a third type of SD-MR *which depends on the direction of the current.* Such SD-MR is dramatically enhanced at very small or zero bias (see ref. [3]).

2) *Co contacts.* As shown in fig. 5, the nanotubes contacted with Co exhibit a rather important positive SD-MR at low temperature; $\sim 3.6\%$ (780 Ω for a tube length of about 700 nm) at 2.5 K in fig. 6. The sample shown has an α of 0.37 (inset of fig. 6). Neither the current density nor the sign of the current influence the signal directly. This magnetoresistance disappears rapidly at temperatures above 20 K.

The angular dependence is difficult to interpret as non-trivial magnetic configurations at intermediate angles of the applied external field are seen. In contrast to the Ni contacts, the magnetic configurations of the Co contacts assumed the antiparallel configuration. The electrodeposited Co is structured with large micrometric crystallites. The hcp crystallites are oriented preferentially perpendicular to the wire axis, leading to a magnetocristalline anisotropy perpendicular to the wire axis [28]. As a consequence, the antiparallel magnetic

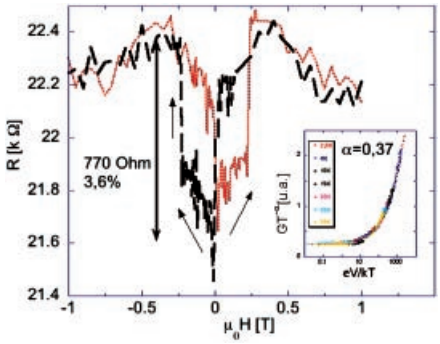

Fig. 6 – Spin-dependent magnetoresistance for one sample contacted with Co. The inset presents the scaling of the conductance of this sample, with $\alpha = 0.37$.

configuration can be reached through the magnetisation of the nanowire pinned perpendicular to the wire axis opposing the applied field (below 100 mT), with the magnetisation of the sputtered Co layer being magnetised in the direction of the applied field. This feature coincides with the prediction of Balents and Egger [10], concerning the spin-dependent transport in a Luttinger liquid, where a sharp peak is expected near the angle π between the two ferromagnetic contacts.

In conclusion, we have measured the spin-dependent transport properties of a series of MWNTs of varying lengths, contacted by ferromagnetic Ni and Co electrodes. Most of the samples exhibit a typical scaling law behaviour of the zero-bias anomaly as a function of temperature. Furthermore, it was observed that the magnetoresistance due to the spin-polarisation of the current is systematically destroyed in the nanotube, with the exception of some carbon nanotubes with Co contacts. *These measurements show that the observation of the typical scaling law for long nanotubes (up to* $1.5\,\mu$m*) coexists with a short spin diffusion length (less than* $0.15\,\mu$m *with* Ni *and* $0.7\,\mu$m *with* Co*).* We observed that the coefficient α is very sensitive to contact or tube defects (see strong scatters in fig. 3). However, we do not observe any correlation between α and the SD-MR (with both Ni and Co contacts). Accordingly, if SD-MR is destroyed by the presence of contact or tube defects, the scaling law is not destroyed by the same defects. Such characteristics are not possible in simple diffusive regimes (because spin-flip scattering occurs after many elastic scatterings) and are difficult to interpret in TMR structures. Thus, the role of spin-flip scattering on the electronic transport is by no means trivial in our nanotube devices. The possibility of a reminiscence of spin-charge separation is still a possible interpretation, which is corroborated by the fact that an antiparallel configuration of the Co contacts should be reached.

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REFERENCES

[1] Prinz G. A., *Science*, **282** (1998) 1660.
[2] Tsukagoshi K., Alphenaar B. W. and Ago H., *Nature*, **401** (1999) 57; Alphenaar B. W., Tsukagoshi K. and Wagner M., *J. Appl. Phys.*, **89** (2001) 6863.
[3] Zhao B., Moench I., Vinzelberg H., Muehl T. and Schneider M., *Appl. Phys. Lett.*, **80** (2002) 3144; Zhao B., Moench I., Vinzelberg H., Muehl T. and Schneider M., *J. Appl. Phys.*, **91** (2002) 7026.
[4] Orgasa D., Mankey G. J. and Fujiwara H., *Nanotechnology*, **12** (2001) 281.
[5] Kim J., Kim J.-R., Park J. W., Jim J.-J., Kang K., Kim N. and Woo B. C., *Physica E*, **18** (2003) 208; Kim J.-R., So H. M., Kim J. and Jim J.-J., *Physica E*, **18** (2003) 210.
[6] Voit J., *Rep. Prog. Phys.*, **58** (1995) 977.
[7] Lorenz T., Hofmann M., Grueninger M., Freimuth A., Uhrig G. S., Dumm M. and Dressel M., *Nature (London)*, **418** (2002) 614.
[8] Kane C. L. and Fischer M. P. A., *Phys. Rev. B*, **46** (1992) 15233.
[9] Si Q., *Phys. Rev. Lett.*, **81** (1998) 3191.
[10] Balents L. and Egger R., *Phys. Rev. Lett.*, **85** (2000) 3464; *Phys. Rev. B*, **64** (2001) 035310.
[11] Mehrez H., Taylor J., Guo H., Wang J. and Roland C., *Phys. Rev. Lett.*, **84** (2000) 2682.
[12] Schoenenberger C., Bachtold A., Strunk C., Salvetat J.-P. and Forro L., *Appl. Phys. Lett.*, **69** (1999) 283.
[13] Bockrath M. W., Cobden D. H., Lu J., Rinzler A. G., Smalley R. E., Balents L. and McEuen P. L., *Nature (London)*, **397** (1999) 598.
[14] Yao Z., Postma H. W. Ch., Balents L. and Dekker C., *Nature (London)*, **402** (1999) 273.
[15] Postma H. W. Ch., de-Jonge M. and Dekker C., *Phys. Rev. B*, **62** (2000) R10653.
[16] Bachtold M., de-Jonge M., Grove Rasmussen K., McEuen P. L., Buitelaar M. and Schoenenberger C., *Phys. Rev. Lett.*, **87** (2001) 166801.
[17] Weber H. B., Hussler R., Loehneysen H. v. and Kroha J., *Phys. Rev. B*, **63** (2001) 165426.
[18] Kane C. L., Balents L. and Fischer M. P. A., *Phys. Rev. Lett.*, **79** (1997) 5086.
[19] Egger R., *Phys. Rev. Lett.*, **83** (1999) 5547.
[20] Egger R. and Gogolin A. O., *Chem. Phys.*, **281** (2002) 447.
[21] Bockrath M. W., *Carbon Nanotubes Electrons in One dimension*, PhD Thesis, University of California, Berkeley (1999).
[22] Tarkiainen R., Ahlskog M., Penttila J., Roschier L., Hakonen P., Paalanen M. and Sonin E., *Phys. Rev. B*, **64** (2001) 195412.
[23] Avouris Ph., *Chem. Phys.*, **281** (2002) 429.
[24] Haruyama J., Takesue I. and Sato Y., *Appl. Phys. Lett.*, **77** (2000) 2891; Haruyama J., Takesue I. and Hasegawa T., *Appl. Phys. Lett.*, **81** (2002) 3031.
[25] Ohgai T., Hoffer X., Gravier L., Wegrowe J.-E. and Ansermet J.-Ph., *Nanotechnology*, **14** (2003) 978.
[26] Wegrowe J.-E., Comment A., Jaccard Y., Ansermet J.-Ph., Dempsey N. M. and Nozières J.-P., *Phys. Rev. B*, **61** (2000) 12216; Wegrowe J.-E., Sallin A., Fabian A., Comment A., Bonard J.-M. and Ansermet J.-Ph., *Phys. Rev. B*, **65** (2002) 012407; *J. Appl. Phys.*, **91** (2002) 6806.
[27] Roche S. and Saito R., *Phys. Rev. Lett.*, **87** (2001) 246803.
[28] Wegrowe J.-E., Kelly D., Franck A., Gilbert S. and Ansermet J.-Ph., *Phys. Rev. Lett.*, **82** (1999) 3681.