Pressure Stimulated Electronic Transitions in Mats of Single-Walled Carbon Nanotubes

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Abstract. We report high pressure studies in mats of single-walled carbon nanotubes (SWNTs). Hydrostatic or quasi-hydrostatic pressure can probe many electronic features. Resistance - Temperature measurements in mats of SWNTs with different chemical cleaning treatment and under quasi-hydrostatic pressure, reveal some differences in the electronic characteristics: semiconducting-like behavior, Kondo-like features, due to magnetic impurities used to catalyse the nanotube formation, a metallic state and at high pressure a possible superconducting transition.

1. INTRODUCTION

Due to the quasi-one dimensional structure, carbon nanotubes which are formed with one or several wrapped graphene layers may behave in different electronic forms, depending on chirality and diameter. One wrapped graphene layer; called single-walled carbon nanotube (SWNT), is particularly interesting because its simplicity. The electronic characteristics will also depend on chirality and diameter [1-5]. At this respect, theoretical studies have revealed that the local density of electronic states (DOS) may be modified if the graphene sheet is wrapped in forms of zigzag, armchair or chiral configuration [4]. Armchair nanotubes are metallic, whilst zigzag ones can be metallic or semiconducting, depending on the chiral vector. From the experimental viewpoint recent studies have shown that in very narrow and isolated SWNTs exist superconductivity [6]. Signs of superconductivity have also been found in ropes of armchair SWNTs with critical superconducting transition temperatures below 0.55 K [7]. However, theoretical studies suggest that the superconductivity observed in ropes of nanotubes by Kociak *et al* [7] may be an intertube coupling effect between nanotubes [8], rather than an intrinsic electronic mechanism as was proposed by Tang *et al.* [6] for narrow nanotubes. More recently Falconi *et al*, [9] have reported signs of superconducting behavior in mats of SWNTs under high pressure conditions. The commercial samples studied by Falconi *et al* have magnetic impurities. Those materials were cleaned with diluted solutions of acids in order to decrease the metallic impurities founded inside and outside of the nanotubes. These metallic impurities, mainly Co, Fe or Ni, are used as a normal procedure

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to catalyze the formation of the nanotubes [9]. From the experimentalist point of view should be clear, that defects, metallic impurities, and also diameter and chirality, as was mentioned before in this introductory part, will change the electronic behavior [10].

In this report we addressed the study of mats of SWNTs with a very strict chemical treatment in order to decrease the amount of metallic impurities. Accordingly, we have subjected the SWNTs samples to a rigorous cleaning chemical process in order to investigate the role of metallic impurities and defects in their electronic behavior at atmospheric and high pressures. In this study we also paid attention to the role of defects in the samples. The reason, as is well known, acids treatments oxidize and attack parts of the nanotubes, creating defects, and in fact also opening ends caps of the tubes. The studies included here were mainly the determination of resistance versus temperature characteristics in mats of SWNTs under several high pressure values. The pressures were generated using a diamond anvil cell (DAC), and the maximum applied quasi-hydrostatic pressure was about 6 to 8 Gpa.

2. EXPERIMENTAL

SWNTs were obtained from MER Corporation, they have average diameters of 0.7 – 3 nm, and lengths from 2 – 20 μm. In order to prepare them for transport and high-pressure studies, they were initially purified as follows [11]; heated in air to 300 ˚C for 24 h and dispersed by ultrasound in hydrochloric acid (HCl) and refluxed for about 4 h at 100 ˚C. After that procedure, the samples were washed in distilled water and ethanol (spectrophotometric grade) and filtrated through a membrane filter of 0.20 μm pore size. This method produces a mat-like sample, which was dried for about 2 h at 100˚C. In order to remove the majority of the remaining metallic impurities, the previous samples were purified again by a strong acid solution. The procedure was the following chemical method; a mat of SWNTs of 50 mg, previously cleaned with HCl, was dispersed by ultrasound and refluxed in 150 ml concentrated nitric acid (70% Aldrich), for 5 h. The sample was washed in distilled water, suspended in ethanol and finally filtrated in a membrane filter. This procedure assures that metallic impurities will be removed to a great extent; spectrometric studies shown that impurities were reduced to a minimum values (90 %), in comparison to the commercial samples. However, one drawback is that the nanotubes surfaces may also be attacked as was verified by transmission electron microscopy (TEM) photographs. Fig. 1 shows one example of the SWNTs used for these studies. Fig. 1a shows cleaned nanotube with some metallic particles. Fig. 1b shows clean SWNTs. Traces of Co impurities still persist in spite of the concentrated acid cleaning treatment. We noted however, that in all our mat-samples studied, the carbonaceous material was almost completely eliminated with the chemical procedures indicated. For the quasi-hydrostatic measurements we used Cu-Be gaskets filled with fine powder of MgO < 2 μm size. The experimental set-up and procedure followed were described before in [12]. The experiments were performed from room temperature to about 1.6 K. Pb was used as a manometer to sense and calibrate the pressure [12].

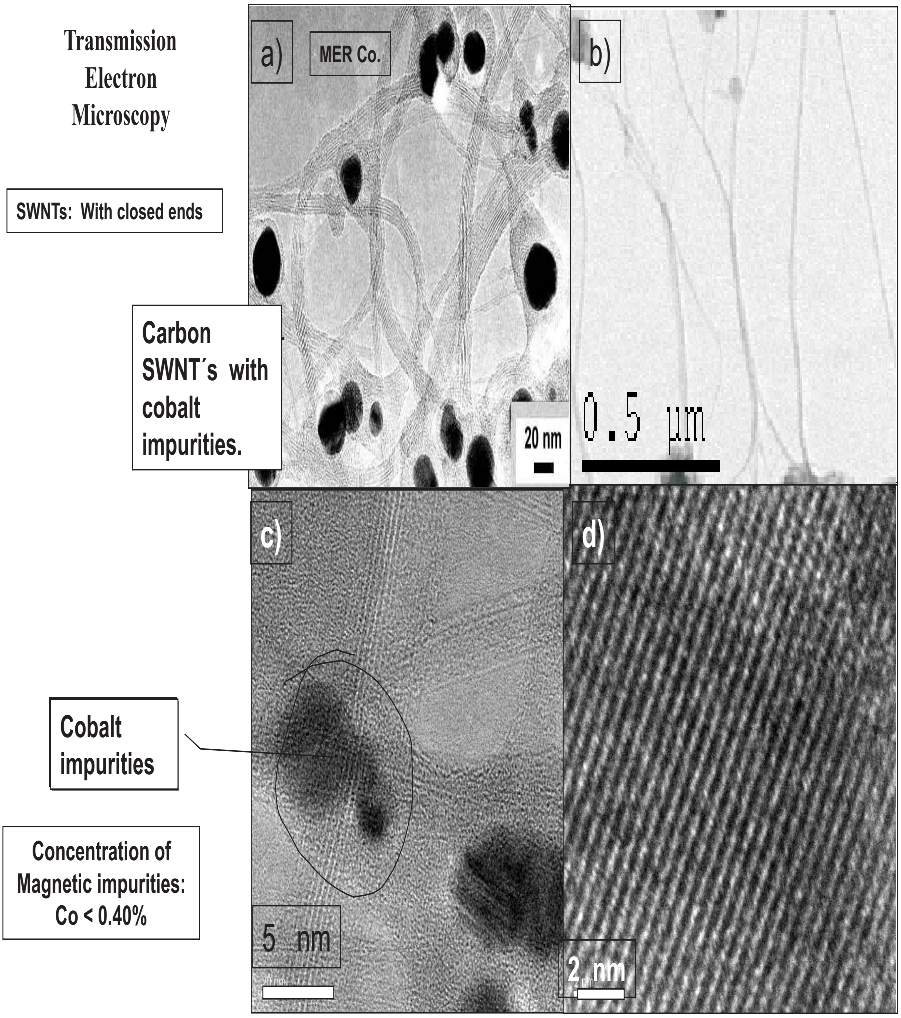
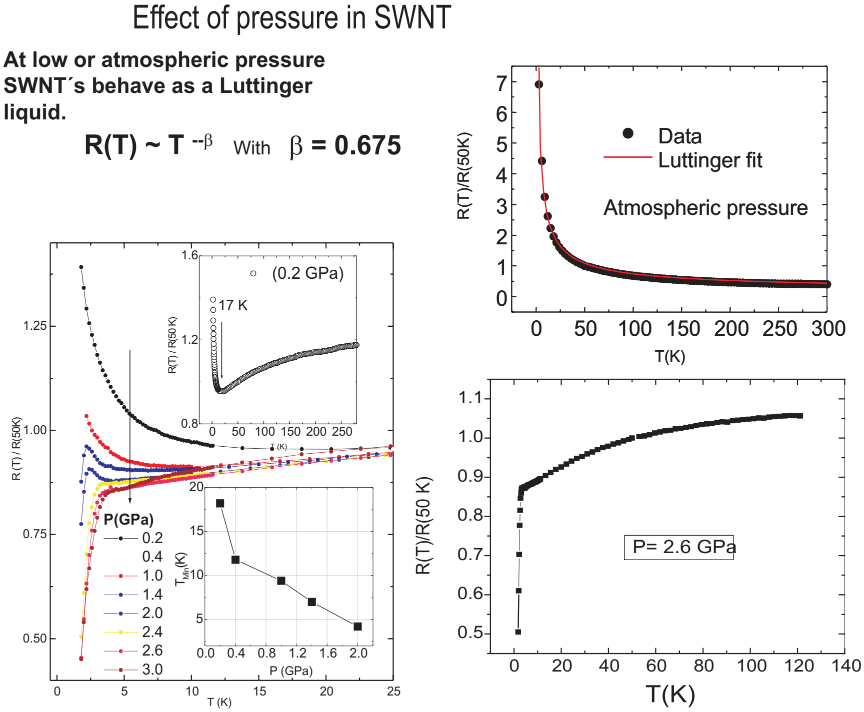


FIGURE 1. TEM images of purified SWNTs. Black spots are magnetic impurities of Co, Ni, or Fe. **a**). shows a picture of a nanotube with cobalt impurities. With the impurities probably inside and outside of the tubes. **b**). Shows a picture of single nanotubes **c**) shows images of bundles of nanotubes and magnetic impurities. **d**) shows an image of graphene structure.

3. RESULTS AND DISCUSSION

Resistance – Temperature, R(T), measurements, at different pressures, were performed with mat samples shaped to appropriate sizes and mounted in the diamond anvil cell. Measurements at atmospheric pressure were determined in a Quantum Design system from 300 - 2 K. WDX (Wavelength Dispersive X-ray Detectors)/EDX (Energy Dispersive Spectrometer) analysis was carried out in a JEOL transmission electron microscopy.

Those nanotubes from MER contain different amounts of Co, Ni or Fe. Once the SWNTs were cleaned with hydrochloric acid, we found atomic percentages of about 0.40, 0.12, and 0.03 for Co, Ni, and Fe respectively. The black spots in the photographs in Fig. 1 correspond to these impurities (mainly Co). Other TEM pictures show magnetic impurities inside and outside of the nanotubes. For the SWNTs cleaned with HNO_3, the metal atomic percentage diminished to very small values as was checked by WDX/EDX. However, as a collateral effect, the amount of defects in the nanotubes was increases because of the acid attack.



Effect of pressure in SWNT

At low or atmospheric pressure SWNT´s behave as a Luttinger liquid.

$R(T) \sim T^{--\beta}$ With $\beta = 0.675$

FIGURE 2. Normalized resistance vs temperature R(T) measurements at different quasi-hydrostatic pressures in mats of SWNTs cleaned with HCl acid. **a**) Normalized R(T) curve from high temperature to 1.6 K for the same sample showing the characteristic minimum of a Kondo type behavior. b) Shows the variation of the minimum with pressure. Such a minimum decreases as pressure is increased, until it disappears. In this particular set of measurements the minimum is reduced at a rate of -6.7 K/GPa. At high pressure, about 2.6 GPa, the behavior changes from non-metallic to metallic and presenting a dramatic reduction of R(T)/R(50 K) as observed in superconducting materials. Left panel (top) shows the Luttinger liquid behavior occurring at low pressures. The bottom panel (left) shows the superconducting transition when applied pressure was about 2.6 GPa.

Our determination of the R(T) data are shown in Fig. 2. The main panel of this figure shows the overall behavior of selected R(T) curves at different quasi-hydrostatic pressures for SWNTs cleaned with hydrochloric acid only. The presented data was normalized to the resistance value at 50 K. An analysis of the curves for this sample can be found in our previous work [9]. Measurements performed in various samples show that R(T) at atmospheric pressure, does not follow a Fermi liquid behavior, but a law, R $\sim$ T $^{-\beta}$and β with values from 0.65 to 0.7. These values are indicative of a Luttinger liquid behavior; there $\beta = (1-g)/2$, with the parameter $g \sim 0.2$, well below of the Fermi liquid value. These parameters were calculated using appropriate values for graphite; Fermi velocity $v_F = 8 \times 10^5$ m/s and screening length about 1000 Å (see Ref. [1]).

It is important to remark that the behavior observed in these mats is radically different to pyrolitic graphite or carbonaceous materials, our measurements in high purity pyrolitic graphite show a semiconducting-like behavior with a cusp at about 55 K. Fig. 3 shows R(T) characteristics of Pyrolitic graphite at normal pressure and 0.6 GPa.

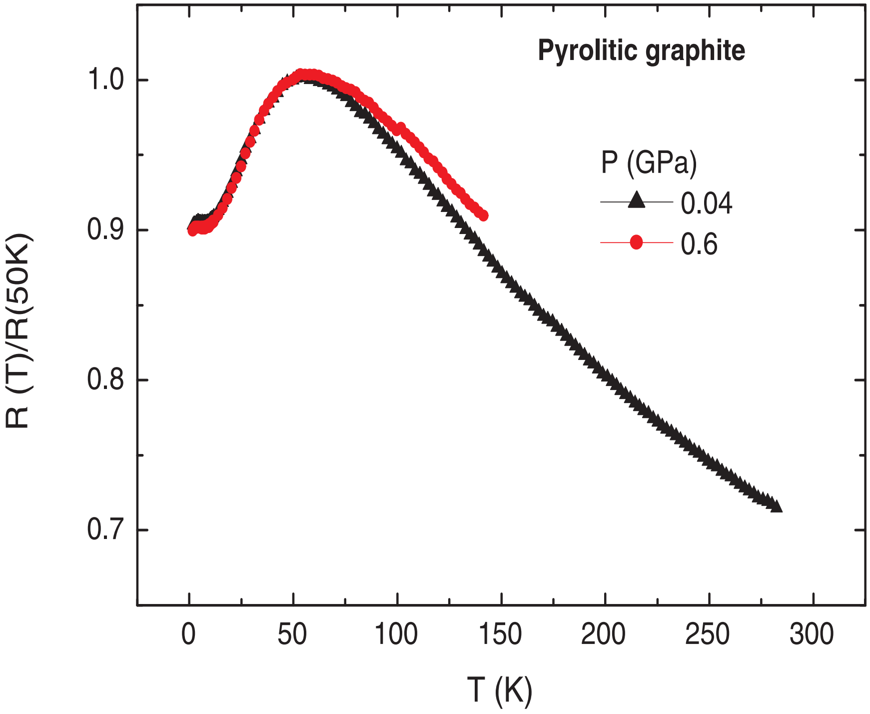


FIGURE 3. Resistance –Temperature characteristics of Pyrolitic graphite at low pressure close to atmospheric pressure and at 0.6 GPa. Note the cusp at about 55 K and the saturation value at 4 K.

Note the different behavior as the observed in SWNTs. The maximum in the cusp has only small changes with pressure. Lowering the temperature, R(T) decreases and reaches a saturation value at about 4 K, similar trend has been observed in other works [13,14].

Going back to Fig 2, in the left panel and inset a) we show a R(T) curve at low pressure of 0.2 GPa, in nanotubes cleaned only with diluted HCl. The behavior is clearly a Luttinger liquid. As the pressure was slightly increased we observed a radical electronic change; from Luttinger to a Kondo-like behavior stimulated by the increasing pressure. The minimum appears in R(T) localized at 18.2 K. Such a minimum follows a logarithmic increase at low temperatures, typical for Kondo effect. Once the sample was under additional increasing pressure, we observed that the minimum decreases in temperature with pressure, at a rate $dT_{min}/dP = -6.7$ K/GPa (see inset 2b left panel).

In the panel of Fig. 4 we show R(T) curves at several pressures for SWNTs cleaned with a strong solutions of two acids: HCl and HNO_3. The fit for the characteristic at room pressure (Fig. 4a) gives a value of β at around $\beta \sim 0.7$, which again is indicative of a Luttinger liquid behavior.

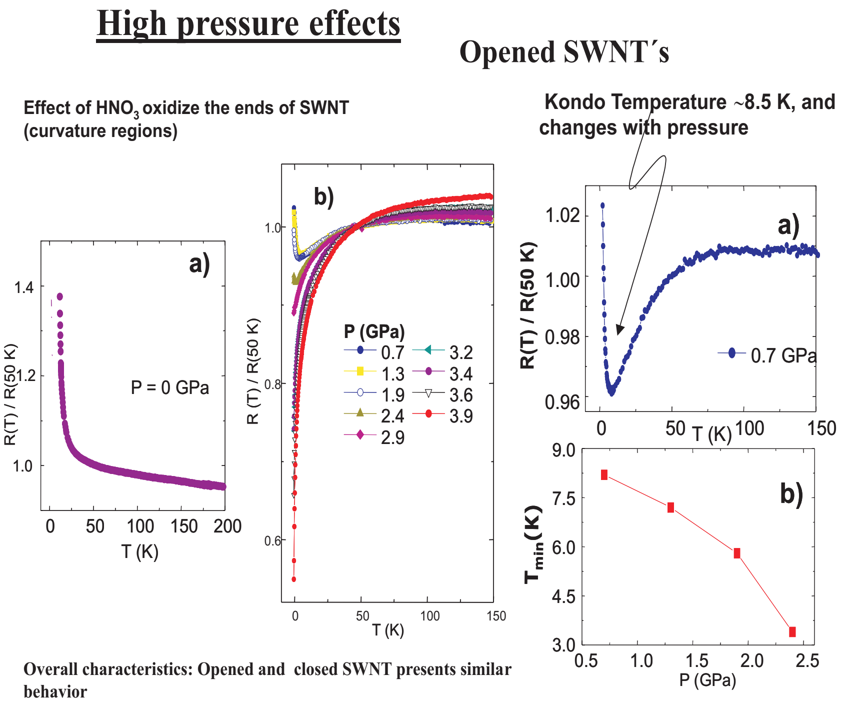


FIGURE 4. a) and b) Normalized resistance vs temperature measurements in mats of SWNTs cleaned with HCL and HNO_3 acids. The trend of behavior is qualitatively the same as for mats of SWNTs cleaned only with HCl. A minimum in the curve is clearly displayed at 0.7 GPa related to Kondo effect. The Resistance vs temperature at atmospheric pressure, fits a Luttinger liquid. Right insets: a) shows the Kondo minimum and inset b) the variation of the minimum with pressure. Note that the behavior is similar to other samples. At high pressure the minimum disappears and metallic characteristic appears. Higher pressures show a superconducting transition. But in this sample the transition is less abrupt [24].

In general in all the experiments presented in this work, the general trend of R(T) at room pressure seems to be similar from different samples, changing only a little, when the mat-like samples are cleaner. It is important to mention that in two recent reports [15,16] it has been found different electronic behavior to the found in our experiments. Bingbing *et al.,* [15] observed a two dimension variable range hopping, whereas Chen *et al*., [16] observe a Luttinger characteristic, this last behavior was found that persists with the applied pressure. In our experiments we found that the Luttinger liquid characteristic is rapidly suppressed by the applied pressure, and a Kondo-like feature appears at low temperatures, about 8.2 K under 0.7 GPa.

Independently of the chemical cleaning treatment, all the mats studied here show three main trends of behavior: i) from atmospheric to low pressures (about 0.2GPa) R(T) shows a semiconducting-like characteristic. ii) additional increase of the applied pressure to about 2.0 GPa changes the semiconducting-like to a Kondo-like feature. iii) with increasing pressure to above 2.4 GPa, R(T) curves suffer a dramatic change to a metallic behavior, and finally at about 3 K the resistance drops precipitously, as occurring in a superconducting transition.

We have found that when the pressure starts to be increased, the overall characteristics change dramatically in a similar way for all the SWNTs samples. We believe that the complex nature of the electronic changes with pressure are correlated to different phenomena such as: i) nanotube deformation, ii) stretching and squeezing by intertubular contact, iii) random orientation of nanotubes, and change of bonding from sp^2 to sp^3 due to change of curvature, iv) presence of metal impurities. SWNTs are squeezed in different degrees depending how compact and oriented is the mat, and depending in size and diameter.

One important factor in our samples could be the influences of magnetic impurities on the conduction electron spins, those will strongly affect the transport properties. The electrical transport of SWNTs, show an anomalous behavior which can be the result of such interaction. This anomalies are due to a spin-dependent scattering mechanism, as mentioned in other work [17,18], which leads to a narrow hybridization resonance peak in the electronic density of states near the Fermi energy (Kondo effect) [19]. The fact that the minimum decreases under pressure, may be explained considering the Fiete *et al*., model [20]. They found that ferromagnetic Co nanoclusters on metallic nanotubes tend to suppress the Kondo temperature; thus, for Co cluster the itinerant model leads to antiferromagnetic coupling between nanotubes and cluster spins. Experimentally the effect of pressure is to decrease the distance of Co antiferromagnetic nanoclusters. The resulting effect is that these become ferromagnetic, decreasing therefore the Kondo temperature [17,20]. The fact that the temperature related to the Kondo feature and the corresponding dT_{min}/dP rate are higher in the SWNTs mats cleaned with HCl, than those cleaned with HCl and HNO_3, we suspect that may be related to a diminution of the magnetic metallic impurities when the sample is cleaned with HNO_3.

If pressure is further increased the resistance minimum tends to disappear, and the R(T) characteristic at low temperature becomes metallic. As soon as this change occurs a reduction of R(T) is produced. Such resistance drop is produced at a pressure of about 2.4 GPa in mats cleaned with HCl and at about 2.9 GPa in the HNO_3 cleaned.

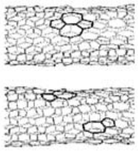
To finish with our description of the complex behavior of the transport properties on mats of SWNTs, a last feature observed was the change of R(T) at higher pressures (about 3-7 GPa). This is related to the dramatic and precipitously reduction of the resistance at high pressures. This extraordinary behavior can be definitely characterized as a superconducting transition. However in all our experiments the sample never reached zero resistance. It is worth mentioning that the minimum values of resistance reached (in terms of normalized resistance) for some of our SWNTs mats, when cleaned with HCl were 0.03 at about 3 GPa, in comparing with mats of SWNTs cleaned with concentrated HNO_3, (Fig. 4); the same trend occurs, but the minimum resistance only reaches values of about 0.5 - 0.9, which are much higher than those found in samples cleaned only with HCl. We suggest that this behavior is not fortuitous, and could be an indication of a reduction of the local density of electronic states due to the absence of ends caps in the tubes and to defects created by the oxidation process. We must stress that the experiments were repeated several times in order to check out that the data was reproducible.

Lastly, an interesting fact observed in all our measurements was concerning to the sample resistance. At high temperatures R(T) always increases as the pressure is increased, as shown in Fig. 5. In this figure we show for comparison, the general trend of R(P), taken at 115 K for all samples, as the percentage of change of ΔR/Ro versus pressure. It seems that the HCl cleaned nanotubes (samples b, and c) behave in different way to the HCl+HNO_3 cleaned (sample a) The trend indicates that resistance at high pressures always increases, but at different rate.

Pressure effects

SWNTs cleaned, closed ends, and opened with HCl + HNO_3

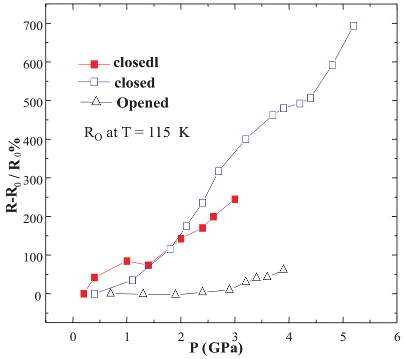
Pressure changes bonding → *sp*^{2} to *sp*^{3} resulting in localization.



Effect of oxidants (HCl +HNO $_3$) oxidation (mainly) at high curvature of SWNT´s: i.e. end caps.

Curvature in SWNT changes density of states. SWNT with closed caps increases density of states.

Overall behavior



General observed changes with closed and opened caps,

FIGURE 5. Percentage of change in resistance (ΔR/R_0) with pressure at 115 K for mats of SWNTs with different cleaning treatment. R_0 is the resistance at the lower pressure.

The percentage of change in HCl cleaned nanotubes is bigger than for samples cleaned with strong acids (HCl+HNO_3), We do not have a clear explanation for this different behavior, however a simple possibility is that the stressing of closed nanotubes is higher due to the influence of the end caps, in comparison to opened ones where the squeezing may be more easily produced with less pressure, of course here we are considering that a strong attack by HNO_3 destroys the end caps of the nanotubes. Maiti *et al.,* explain [21], that beyond a critical point several carbon atoms become sp^3 coordinated, in such a way that π delocalized electrons become σ localized [22,23]. Experimentally we found that the effect is reversible until a certain pressure, beyond that point, the resistance follows increasing as pressure is increased. If the pressure is released the resistance drops slightly but without coming back to the initial value. As one important last point related to the form of the superconducting transition, is that in general we observed that only in "closed" nanotubes mats, the transition to the superconducting state is more abrupt than in "opened" nanotubes. The explanation may be given in terms of the dimensionality of the system. Systems with low dimensional behavior present that kind of characteristic [24].

4. CONCLUSIONS

In summary we reported the electronic behavior observed in mats of single-walled carbon nanotubes. They present a complex electronic behavior. At low pressure the resistance R(T) behaves as 1-dimenstional system, thus a Luttinger liquid characteristic is observed. As the pressure is increased R(T) presents a minimum and a logarithmic growth at low temperature, typical of Kondo effect due to magnetic impurities used for the SWNT production process. The Kondo temperature evolves with pressure, and its rate of change is sample depending. At higher pressures, $\sim$ 4-5 GPa. the Kondo feature disappears, and a metallic characteristic develops. Further increase of pressure changes the metallic regime to a superconducting-like transition, which always was observed in all our mats of SWNTs. As this experiment indicates, the effect of pressure in the mats of nanotubes, is quite complex and may be characterized as a behavior of mats distributed in random directions. Of course the characteristics may be very different to what would be expected in single nanotubes. Thus, will be interesting in the future to study only one SWNT to quantify the many changes in the electronic properties that for sure must be observed when they are under high quasi-hydrostatic or hydrostatic pressures.

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