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High frequency electron spin resonance study of peapods

A. Olariu[1], B. Náfrádi[1], L. Ćirić[1], N. M. Nemes[2], and L. Forró[1,*]

[1] Institute of Physics of Complex Matter, Laboratory of Nanostructures and Novel Electronic Materials, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
[2] Instituto de Ciencia de Materiales, CSIC, Cantoblanco, 28049 Madrid, Spain

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* Corresponding author: e-mail laszlo.forro@epfl.ch, Phone: +41-21-6934306, Fax: +41-21-6934470

We present high frequency Electron Spin Resonance (ESR) results on a peapod sample. In a previous low frequency ESR study on peapods and double-walled nanotubes the observation of a non-Lorentzian line shape was reported. This effect was tentatively attributed to the presence of two distinct Lorentzian signals, coming from the outer tube and from the inner tube or from fullerenes. Here we report ESR measurements in a broad frequency (and magnetic field) range, which help to resolve this uncertainty. Since, with increasing magnetic field, no splitting of the line is observed, just a linear increase with frequency, we attribute the non-Lorentzian shape to g-factor distribution. The extracted line width weakly increases with temperature.

1 Introduction Carbon nanotubes have been the object of intense research ever since their discovery in 1991 [1]. Electronic proporties of these systems are determined by the folding of graphene, that can induce either a metallic or a semiconductor behaviour, as predicted by tight binding calculations. It has been shown that in bulk samples about one third of the tubes are metallic and two thirds are semiconductors. To date single-walled nanotubes (SWNT), double-walled nanotubes (DWNT), peapods (SWNT filled with C_{60} structures) and multi-walled nanotubes (MWNT), have been studied by various techniques, including ESR.

Electron Spin Resonance (ESR) is a valuable tool for the investigation of the spin behaviour in these systems, especially those which have metallic properties. In metals, the study of conduction-electron spin resonance (CESR) allows the determination of three physical quantities: i) the g-factor value, given by the position of the resonance in magnetic field; ii) the static spin susceptibility, proportional to the density of states at the Fermi level, obtained by double integration of the spectrum; iii) the spin relaxation rate, which is given by the line width. According to the model of Elliott based on band calculations [2], the relaxation rates for spin and momentum are proportional, hence the temperature dependences of the resistivity and the line width are similar.

In one dimensional systems the spin relaxation rate is very long, and therefore one expects a very narrow line. In the case of interaction between nanotubes, e.g. in 'buckypaper', the relaxation mechanism is dominated by interchain coupling. As an example, a previous ESR study on quasi-1D organic conductors [3] indeed showed that relaxation times are about 3 orders of magnitude larger than in 3D metals [4] with comparable spin-orbit interaction.

2 Single-walled carbon nanotubes SWNT are excellent candidates for the study of 1D electronic systems. Due to dimensionality, conduction electrons in these systems no longer have a Fermi-liquid behaviour. The Coulomb repulsion instead induces a Luttinger-liquid behaviour, implying the absence of Landau quasiparticles, spin-charge separation and the suppression of the density of states next to the Fermi level. Evidence of a Luttinger liquid behaviour has been found in SWNT through transport measurements [5] and also in photoemission studies [6,7]. The magnetic ground state of a Luttinger-liquid is nevertheless not thoroughly understood to date. In perfect 1D systems one expects that fluctuations result in a paramagnetic ground state. In Ref. [8] calculations on coupled nanotubes predict SDW correlations that decay exponentially with temperature and the presence of ferromagnetic interaction.

The ESR spectrum for SWNT has been theoretically calculated in Ref. [9] and is expected to have a very different shape from that observed for MWNT, which is Lorentzian [10]. In SWNT a double-peak spectrum should be observed, related to the spin-charge separation. However, from the experimental point of view, the signal is very difficult to put into evidence. The double peak structure has never been observed experimentally, perhaps because nanotubes form bundles and therefore are not perfect 1D systems. The predicted low density of states at the Fermi level implies a weak ESR signal. Also, the presence of catalyst particles, typically ferromagnetic, induces a dramatic broadening of the line. Another reason for broadening is the presence of defects that considerably shorten the relaxation time of the electronic spin. The finite length of the tube might also be responsible for broadening, as the extremities can relax the spin lifetime. In bulk samples, tubes with different chirality have different electronic properties. The ESR line is therefore the superposition of lines corresponding to different tubes chiralities, which can result in further broadening of the spectrum.

There were only few claims in the literature for the observation of CESR in SWNT. In Ref. [11], a narrow Dysonian (non symmetric derivative of a Lorentzian) line with a Landé factor $g = 2.001 \pm 0.001$ was observed at 10 GHz. In order to observe this signal, ferromagnetic catalyst particles were removed by vacuum-annealing the sample.

An intrinsic ESR signal was reported in bulk SWNT with 'armchair' wrapping [12], for which band theory predicts a metallic character. A very narrow signal of weak intensity was observed in samples of exceptional quality, in addition to a very broad line that was attributed to the presence of catalyst particles. The narrow line was of Lorentzian type and, by integrating, the authors obtained a susceptibility which was constant over a wide range of temperatures, suggesting a Pauli metallic character. Nevertheless, further attempts to measure CESR in SWNT have failed [13], or have been inconclusive [14].

The observation of a narrow ESR line was reported in our previous work in Ref. [15]. A weak signal of similar intensity was observed on SWNT-batches of variable purities. Surprisingly, in this work, the spin susceptibility falls very rapidly with temperature. For this so-called 'super-Curie' behaviour, the susceptibility decreases faster than $1/T$. The extracted line width slightly increases with temperature for $T > 50$ K, suggesting an Elliott behaviour of the conducting nanotubes.

CESR has been clearly observed in K-doped SWNT [16] where a Dysonian line shape was recorded. The signal intensity appeared to grow with K-doping, while no signal was observed in the pure sample. The mechanism proposed was that the spin life time for the electron is very long, and therefore its relaxation is dominated by the ferromagnetic catalyst particles. By K-doping, the relaxation time becomes shorter, because of the disorder introduced by the dopant atoms, and hence most spins relax before meeting a catalyst particle. Therefore, this allows observation of an intrinsic narrow line.

Note that CESR has been clearly evidenced in multi-walled nanotubes [10, 17]. A symmetric Lorentzian line with g varying with temperature, $g = 2.012$ at $T \sim 296$ K was observed. At high temperature the extracted susceptibility was Pauli like, i.e. temperature independent. Similar behaviour was also observed for graphite, and is expected for a Fermi-liquid system.

3 Peapods Further insight in to the electronic properties of nanotubes can be obtained by studying peapods or double-walled nanotubes. Figure 1 presents typical TEM images of peapods and SWNT. Peapods were synthesised for the first time in 1998 [18] by filling SWNT with fullerenes. By a high temperature reaction, the fullerenes unfold and the peapod transforms into a DWNT [19]. The advantage is that the inner wall in these materials is perfectly free of catalyst particles. In this case one might however have to take into account a possible coupling between the two nanotube walls.

In the case of peapods, one should take into account the one-dimensional row of C_{60} molecules. This will also be a conductive entity, especially if they acquire an electron from the nanotube. Quasi-1D chains of fullerenes have been intensively studied in the past. As an example, the alkali fullerene RbC_{60}, in which C_{60} molecules form 1D polymers, has been shown to be a quasi 1D-metal at hight temperatures [20]. It is likely that the electronic properties would be similar for the C_{60} in peapods and for the inner tube in DWNT. ESR measurements at low frequency on DWNT and peapods that are presented in the next section support this suggestion.

In this paper, we present detailed ESR measurements at high field on a peapod sample that was previously studied in Ref. [15]. This sample had been synthesised following the standard procedure mentioned in the previous paragraph. The outer wall nanotube of this system was synthesised from PII-SWNT purchased from "Carbon Solutions" by air-oxidation, HCl treatment and magnetic filtration as described in Ref. [21]. The peapod was then produced by static vacuum annealing at 650 °C for 9 hours in the presence of C_{60} vapor, as described in Ref. [22]. The sample was then further annealed at the same temperature for 1 hour under dynamic vacuum to remove excess C_{60}.

3.1 X-band measurements In Ref. [15], ESR measurements on SWNT, DWNT and peapods from a variety of sources were reported. The measurements were taken at 9.39 GHz on a standard X-band Bruker ESR spectrometer ELEXYS E500. The spectra obtained for both DWNT (not shown) and peapods had similar line shapes that were symmetric, but non-Lorentzian. Note that, as

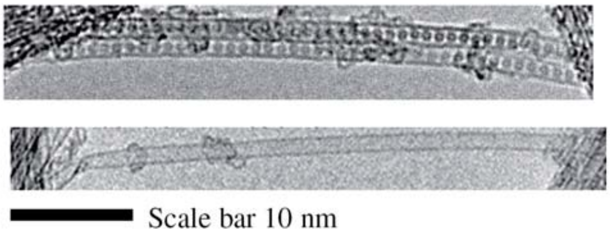

Figure 1 Typical TEM images for peapods and SWNT.

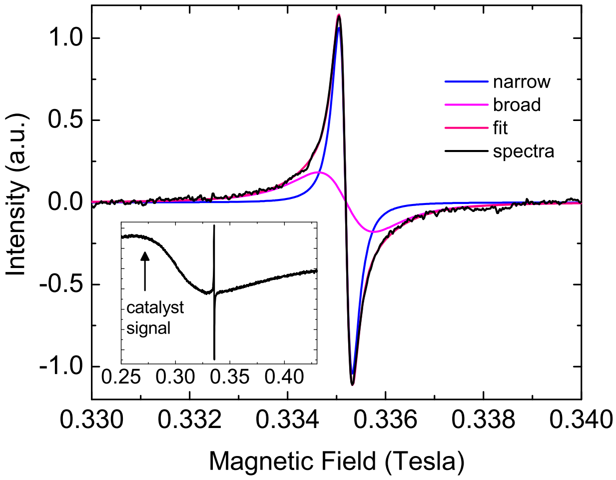

Figure 2 (color online) ESR signal at 9.39 GHz, intrinsic to the peapod. The shape is not Lorentzian, as one would expect for the CESR signal. The fit is the superposition of two Lorentzian lines, a broad and a narrow one, as explained in the text. Inset: full spectrum showing the intrinsic narrow line and the very broad signal which is due to catalyst particles.

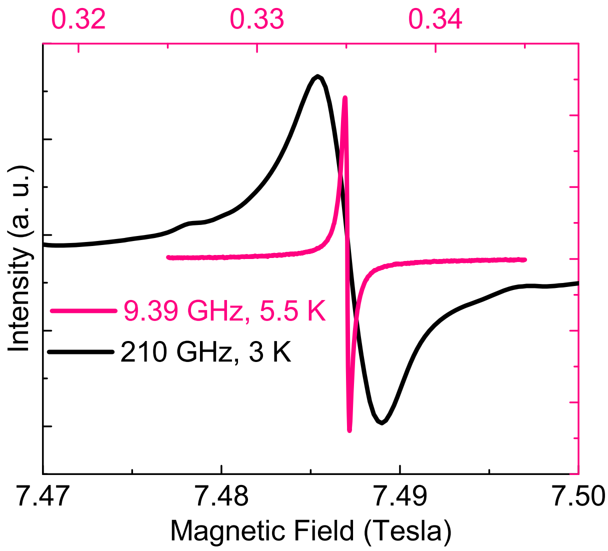

Figure 3 Spectra obtained at 210 and 9.39 GHz on the peapod. The two lines are superposed so that the field window shown is the same, 30 mT.

stated above, either a Lorentzian or an asymmetric Dysonian line shape has been evidenced in SWNT. In Ref. [15], the non-Lorentzian line shape was attributed to the superposition of two signals, a narrow and a relatively broad one, both Lorentzian, that would be due to the outer and inner tube/fullerenes. The obtained spectrum is presented in Fig. 2. The very broad signal (inset of Fig. 2), extended over more than 0.2 Tesla, is due to the catalyst particles, while the narrow signal is considered to be intrinsic to the peapod. This figure also shows the fit (in red) obtained by the superposition of the two Lorentzian lines. These lines are also shown in blue and magenta. The narrower line, of about 0.2 mT width, was attributed to the inner fullerene chain, while the broader line, of width 0.4-1 mT, was attributed to the outer tube. Note that the fit by the superposition of two Lorentzian lines supposes that the coupling between the outer tube and the inner fullerene chain is very weak.

The T-evolution of the susceptibility, as extracted by double integration of the signal, as well as of the line width, were tracked for both signals on a wide temperature range, from 4.4 K to 300 K. The susceptibility of both the inner and outer electrons had a "super-Curie" behaviour, in analogy with the SWNT. Note that the same kind of behaviour was found for all the samples, peapods and DWNTs studied in Ref. [15]. As for the line width, it had only a weak, metallic-like, temperature dependance. However, the numerical values obtained for the susceptibility and the line width were dependent on the sample studied, via the temperature of annealing. Also, in view of the 'super-Curie' behaviour of the susceptibility, one cannot completely rule out the possibility that the observed signal was due to paramagnetic impurities. ESR study of samples with paramagnetic impurities doped in-situ might provide an answer to this question.

3.2 High field measurements An alternative explanation to the non-Lorentzian line shape obtained for the peapod in X-band measurements is to consider a distribution of g-values. The superposition of two distinct lines as suggested in Ref. [15] is basically expected for peapods with one orientation with respect to the applied magnetic field. For powder samples, as is the case here, the spectrum is instead a superposition of lines coming from peapods with all possible orientations with respect to the field. We therefore expect a complex signal, since both the g-factor and the line width might depend on the field orientation. In

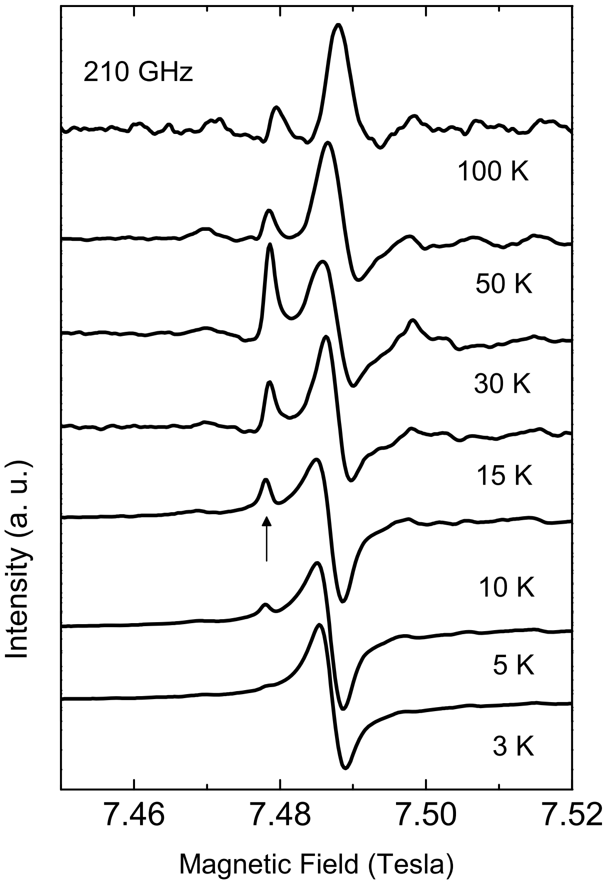

Figure 4 Sequence of spectra measured at 210 GHz on peapod between 3 and 100 K. The arrow indicates a spurious signal.

order to obtain more information about the line shape, we performed ESR measurements at high frequencies.

Our home-made ESR spectrometer allows sweep of the magnetic field in the range 0-16 Tesla and work at the fixed frequencies 210, 315 and 420 GHz [23]. For the current study, most measurements were done at the fixed frequency of 210 GHz and, by sweeping the magnetic field, in the range 7.44-7.52 Tesla. We have taken scans in the temperature range from 3 to 100 K. The signal intensity decreased with temperature, and above $T \sim 100$ K, the signal to noise ratio was too low to allow accurate measurement. The signal intensity also decreases when increasing the working frequency, and therefore 315 and 420 GHz measurements were performed only at low temperature.

The spectrum obtained at $T = 3$ K on peapods at 210 GHz is presented in Fig. 3, with comparison to the one obtained at 9.39 GHz. The high frequency line shape could not be fitted by a Lorentzian or Dysonian line, in agreement with results obtained in X-band measurements. In order to allow direct comparison between the two spectra, the lines have been superposed on a double-axis plot with the same field window (30 mT). The line width broadens from about 8 G at 9.4 GHz to 30 G at 210 GHz. Note that if two different lines were present, as suggested in the first section, the difference between the positions of the two lines should scale with the applied field. We should therefore expect a splitting of the spectrum into two different lines at high frequencies. In the case of the second scenario, of a distribution of g-factors, one instead expects broadening of the line. The comparison of the spectra presented in Fig. 3 therefore supports the second scenario. More evidence for this is given by measurements at 315 and 420 GHz at $T = 3$ K, for which further broadening of the line is observed, as shown in the inset of Fig. 5.

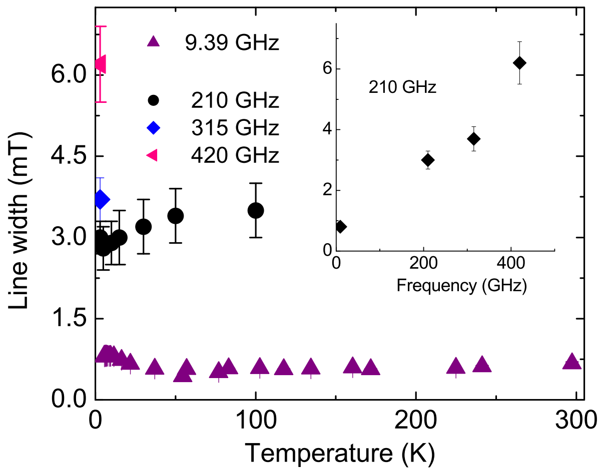

Figure 5 Temperature dependence of the ESR line width measured at various frequencies on the peapod.

The evolution of spectra taken at 210 GHz with temperature is shown in Fig. 4. Above 10 K, a spurious signal, with different phase, appears somewhat downshifted (~ 7.4785 T) with respect to the main component. A careful analysis of the spectrum indicates the presence of additional lines of lower intensity. A very high statistics spectrum would be necessary in order to characterise them.

Figure 4 shows only little temperature-dependance of the line width. The line width, obtained by fitting with a single Lorentzian line, is presented in Fig. 5, in comparison with results obtained at all the working frequencies. Note that, at 9.39 GHz, the line width is that of the broader line obtained from the 2-Lorentzian fit. The line width at high frequencies appears to have a weak temperature dependence. This is in agreement with the results obtained at 9.39 GHz.

4 Conclusion We presented a new ESR study on a broad frequency range at high field on a peapod sample. We addressed the issue of the non-Lorentzian line shape that has been reported in a previous work at low frequency. Here we suggest that since with increasing magnetic field only broadening of the line occurs, without splitting, the non-Lorentzian line shape is due to a distribution of g-factors. This is induced by the bulk nature of the sample implying different orientations of the peapods with respect to the applied magnetic field. In agreement with low-frequency data, the line width extracted at high frequency has only weak temperature dependance.

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