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Electron spin resonance from semiconductor–metal separated SWCNTs

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Electron spin resonance in the X band is reported for fully metal–semiconductor separated SWCNTs. For the experiments samples were immersed in ethanol or wrapped into a teflon foil. The response from the metallic tubes exhibits a strong asymmetry in the line shape whereas the asymmetry for the semiconducting (SC) tubes is comparatively small. In both cases the line widths are unusual small, of the order of 4 G. Particular attention is paid to SC nanotubes which exhibit a much stronger signal as compared to the metallic tubes. The signal intensity is nearly Curie like with a small enhancement beyond $1/T$ in the low temperature range. The $1/T$ behavior renders the ESR response unobservable at 300 K. The finite value for the asymmetry parameter in the SC tubes is assumed to originate from charges picked up during exposure to air or to ethanol.

1 Introduction The investigation of electron spin resonance (ESR) from single-walled carbon nanotubes (SWCNTs) has been a subject of extensive interest for more than a decade [1–4]. In the corresponding reports the ESR response is usually observed as a rather broad line which generally exhibits an asymmetric shape. This is not unexpected since experiments were carried out for mixtures of semiconducting (SC) and metallic (M) tubes. Typical line widths were in the range of 10–30 G. Particular attention has been paid to the detection of the ESR signal of free carriers in metallic tubes. The possibility for this has recently been questioned from theoretical arguments based on the Tomonaga–Luttinger liquid (TTL) character of the 1D electron gas in the tubes [5]. Also, standard catalysts such as Fe and Ni used for preparation of the tubes are magnetic and thus contribute disturbing background signals to the ESR experiments. The situation changed recently when SWCNT growth from non-magnetic catalysts became available [6] and large scale separation of SC and M tubes was demonstrated [7, 8]. In a fully metallic sample the 1D nature of the electronic system is relaxed if the bundle structure of the tubes is well expressed. Intercalation of electron donors did indeed reveal that a fully metallic system of bundled SWCNT does not any more exhibit TLL character [9]. Therefore the M–SC separated tube systems are a new challenge to study ESR in the SC as well as in the metallic system.

In this contribution we report on ESR experiments from purely or at least highly enriched SC SWCNTs in the temperature range between 300 and 1.5 K. The signal consist of a very narrow line of about 4 G width which is unobservable at room temperature but increases approximately as $1/T$ towards low temperatures. The line is assumed to originate from spin carrying impurities and exhibits decreasing line width with increasing temperature, indicative for increasing delocalization of the spins. A small asymmetry observed for the ESR response can be ascribed to weak p-doping of the sample.

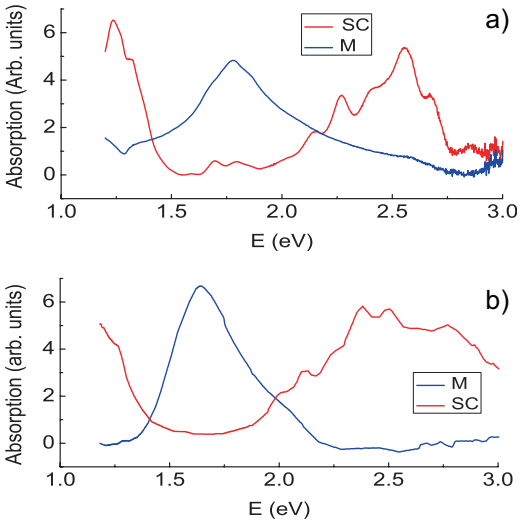

Figure 1 (online color at: www.pss-b.com) Optical absorption of SC–M separated SWCNTs for PtRhRe grown tubes (lower panel) and for FeNi catalyst grown tubes (upper panel), after background subtraction. Blue and red spectra represent metallic and SC tubes, respectively. The absorption peaks at 1.64 and 1.78 eV in the metallic samples correspond to the E_{11}^{M} transitions while the two peaks seen for the SC tubes represent E_{11}^{SC} and E_{22}^{SC}.

2 Experimental Single-walled carbon nanotube samples were grown by laser ablation using a PtRhRe catalyst as described elsewhere [10]. The high growth temperature requested for the Pt catalyst resulted in SWCNT with fairly large average diameter of 1.65 nm. These samples are called P40 in the following. For comparison similar tubes were prepared using a FeNi catalyst and are named MFe in the following. Both materials were purified by chemical and thermal treatment and eventually separated by density gradient high pressure liquid chromatography as described previously [8]. The efficiency of M–SC separation was checked by optical absorption in the energy range of the E_{11} and E_{22} transitions. Examples are depicted in Fig. 1. From an inspection of the absorption recorded for the P40 tubes a degree of separation of 98% can be estimated.

ESR experiments were performed using a Bruker Elexsys X-band spectrometer (9.45 GHz and 200 mW for dB = 0) with a rectangular TE_{102} cavity. Nanotubes were used in the form of bucky paper and accommodated in the spectrometer in a high purity quartz tube filled with ethanol. Alternatively, the bucky paper was wrapped into a teflon foil and mounted on a quartz rod which was inserted directly into the continuous He flow cryostat. Temperatures were measured with a Ge diode and a AuFe thermo couple. At low temperatures the relative accuracy of the temperature measurement was ±0.1 K.

3 Results Figure 2a depicts ESR signals recorded for selected M samples at two different temperatures. At room temperature the P40 tubes (red spectrum) did not show any signal indicating high purity of the material. In contrast, the

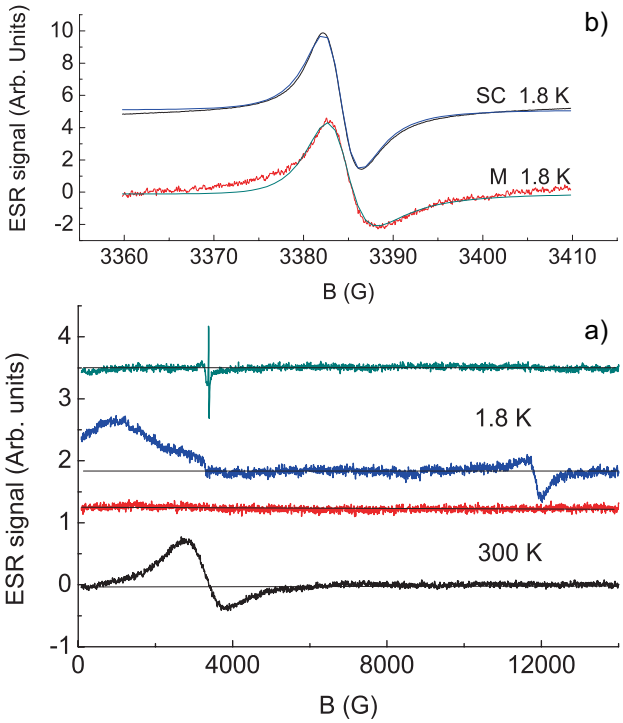

Figure 2 (online color at: www.pss-b.com) ESR spectra for two different metallic samples at room temperature (bottom) and at 1.8 K (top). Thin black lines represent zero signal (a). The spectra in (b) depict the response from metallic and SC tubes grown from the PtRhRe catalyst on an expanded field scale. The black smooth lines represent fits using Eq. (1).

MFe samples (black spectrum) exhibited a broad signal which obviously originates from the catalytic particles. At 1.8 K, a strong but very sharp signal appears for the P40 tubes with a similar signal but strongly covered by the response from the catalyst in the MFe samples. Figure 2b depicts the narrow ESR line for the P40 tubes on an expanded scale for M and SC species, respectively. While the response from the SC tubes is highly symmetric the metallic tubes exhibit a Dysonian line shape. Line widths are in both cases only about 4 G with slightly larger values for the M tubes.

As demonstrated in Fig. 2, both lines can be well described with a Dysonian profile of the form

$$\frac{d\chi}{dB} = A\left(\frac{-2(B-B_0)w\cos\phi}{[w^2+(B-B_0)^2]^2} + \frac{[w^2-(B-B_0)^2]\sin\phi}{[w^2+(B-B_0)^2]^2}\right), \quad (1)$$

where A, B_0, w, and ϕ are the signal amplitude, the resonance field, the line width, and the asymmetry parameter, respectively [1]. The latter relates to the positive (A) and negative (B) part of the ESR line derivative. Tan ϕ is the ratio between dispersion and absorption part of the magnetic susceptibility ($\chi = \chi''\cos\phi + \chi'\sin\phi$). Equation (1) is an approximation for non-diffusive spins to the more

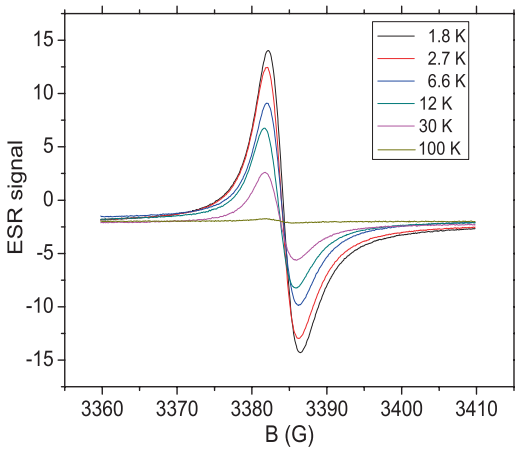

Figure 3 (online color at: www.pss-b.com) ESR spectra for PtRhRe grown SC SWCNTs recorded for a selection of temperatures as indicated.

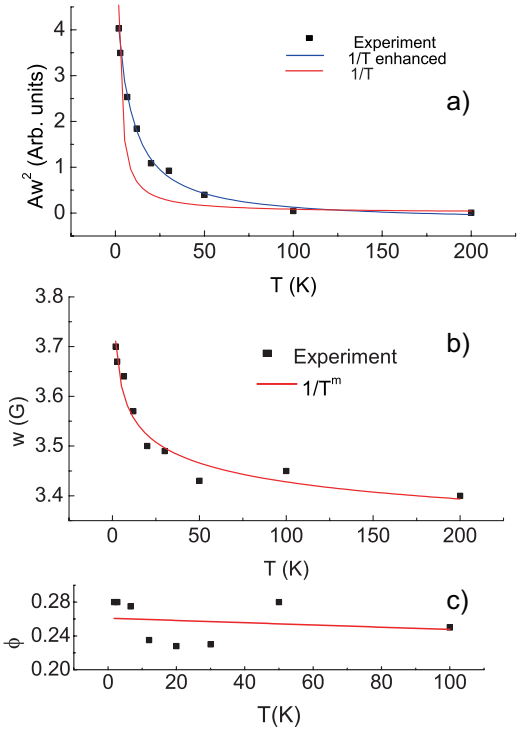

Figure 4 (online color at: www.pss-b.com) Temperature dependence of line parameters for the Dysonian profile of SC SWCNTs. From top to bottom: ESR susceptibility $\chi = Aw^2$, line width w, and phase factor ϕ. The full drawn lines depict fitted results using relations given in Table 1.

general original description of ESR lines in conducting material by Feher and Kip [11] and by Dyson [12].

For the M as well as for the SC samples the Dysonian profile represents the ESR response very well indicating a single species providing the spin. The parameters of the lines as obtained from the fit are, for the SC and M tubes, respectively: A (in arb. units) = (2.5, 0.19), w (in G) = (3.4, 4.35), and ϕ (in rad) = (0.22, 0.6). The rather large value of ϕ for the metallic tubes reflects their high conductivity.

In the following we concentrate on the response from the SC tubes which exhibit a much stronger signal. Figure 3 depicts a selected set of spectra recorded for the SC P40 tubes at various temperatures, all recorded for a power level of 35 dB. The strong temperature dependence of the signal is evident. The estimated concentration of the spins for the SC tubes is 40 spins per 1 μm tube length. The fit of such spectra with Eq. (1) allows to extract the temperature dependence of the three parameters A, w, and ϕ while B_0 is considered temperature independent. Results are depicted in Fig. 4.

The almost inverse temperature decay of the intensity is reminiscent of Curie spins. It fits well to the experiments except for some overshoot in the low temperature range where an exponential correction is needed. Functions and parameters for the fits are compiled in Table 1.

The line width w expected (not measured) at room temperature is only 3.35 G. It consists of a temperature independent and of a temperature dependent part and increases with decreasing temperature. At low temperature it is more than 20% smaller than the line width for the metallic tubes.

The finite value of the asymmetry factor is surprising. Based on the Dysonian model it indicates some conductivity even in the SC sample or a noticeable anisotropy or inhomogeneity of the g factor. Since the value for ϕ varies from sample to sample and as discussed later it can be as small as 0.1 the anisotropy or inhomogeneity, if any, is very small.

Measurements of the ESR signals did exhibit some dependence on the long time exposure of the tubes to ethanol. This was in particular observed for M tubes. To check on this effect for the SC tubes, test samples were also measured in a gaseous/liquid He bath after wrapping them in a teflon foil. Results of these experiments are depicted in Fig. 5. Even after short time exposure of the tubes to ethanol (ethanol 2 vs. ethanol 1) the ESR susceptibility increased, particularly at

Table 1 Fit functions for the Dysonian line parameters.

line parameter	function	fit function	parameter values
amplitude A	$1/T$	$(a/T) + a_0$	$a = 8.68$, $a_0 = 0$
	$1/T$ enhanced	$\{a[1 + b\exp(c/T)]/T\} + a_0$	$a = 6.37$, $b = 4.37$, $c = 5.58$ K, $a_0 = 0.2$
line width w	inverse power	$(a/T^m) + w_0$	$a = 0.7$ G, $m = 0.144$, $w_0 = 3.06$ G
asymmetry ϕ	linear	$aT + a_0$	$a = -0.00013$, $a_0 = 0.26$

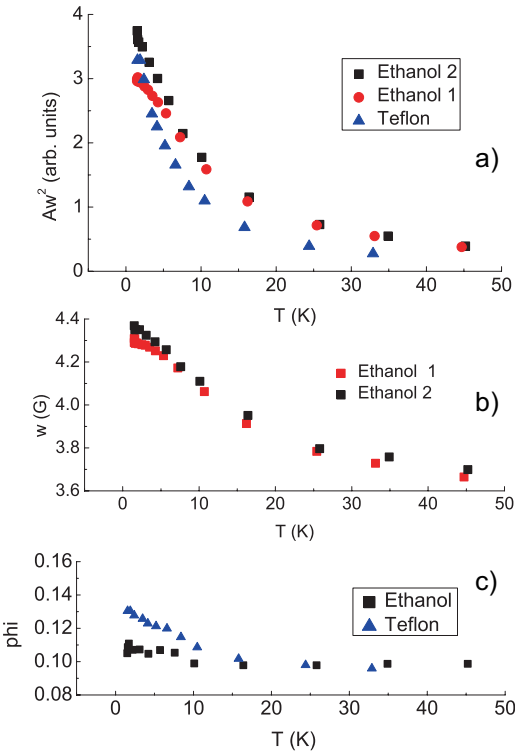

Figure 5 (online color at: www.pss-b.com) Influence of exposure of SC SWCNTs to ethanol as characterized by temperature dependence of Dysonian line parameters. From top to bottom: ESR susceptibility $\chi = Aw^2$, line width w, and phase factor ϕ. Blue triangles are for ESR measurements from teflon wrapped samples.

low temperatures but the increase was only 20%. The teflon wrapped samples exhibited full stability. The change in line width after ethanol exposure was within experimental error. Similarly, there was hardly any difference in the asymmetry factor between ethanol exposed and teflon wrapped tubes. The small value of ϕ for these samples (P40a) are remarkable and indicate very small anisotropy or inhomogeneity in the g factor.

4 Discussion Semiconductor–metal separation allowed for the first time to investigate the ESR response from SC and M samples separately. The lack of any ESR signal at room temperature is a clear indication of high quality of the samples and underlines the request of using tube material prepared with non-magnetic catalyst. The narrow width of the lines are an other proof for the sample quality. It is assumed to originate from inhomogeneous broadening. The larger width for the metallic tubes indicates spin relaxation by free carriers. The decrease of line width with increasing temperature is suggested to originate from some delocalization of the spins which leads to a motional narrowing process.

As deduced from the temperature dependence of the susceptibility the spins are Curie type. The enhancement of the susceptibility beyond a simple $1/T$ law can be interpreted as some spin generation with increasing temperature. The origin of the finite value for the asymmetry factor of the SC sample should not be traced back to an anisotropy of g, since it becomes very small in the teflon wrapped samples. It rather originates from either charge uptake due to exposure of the samples to air or ethanol or from small, of the order of 2%, contamination of the SC tubes with M tubes. No traces of catalytic particles could be observed. As for the teflon wrapped samples, if there is finite conductance the asymmetry parameter can still be small if the sample thickness is smaller than the skin depth.

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