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Electron spin resonance of single-walled carbon nanotubes and related structures

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We report new results on the electron spin resonance of single walled carbon nanotubes, peapods and double walled carbon nanotubes. A small ESR line is present in well purified samples and its temperature dependence reveals a striking ‘super-Curie’ paramagnetic rise. In addition, we identify a narrower line in peapod and DWNT samples, which displays similar behavior. The linewidth of both inner and outer species are metallic and the outer tube’s resonance broadens upon growth of the inner tubes. We observe a sudden decrease of relaxation rate below 20 K, in accordance with the opening of a spin-gap.

The quest to find the conduction electron spin resonance (CESR) of single walled carbon nanotubes (SWNT) has a long and tortuous history. SWNT, as an archetypical 1D system, is expected to have a very narrow CESR. In one of the first careful bulk studies of SWNT, and in follow up studies, Petit et al. reported a well defined CESR, in exceptionally high quality PLV produced SWNT with very low catalyst content, with a linewidth of 2.5 mT which showed Pauli-like T-dependence [1]. However, this signal was never reported again by others, perhaps because of the rapidly changing nature of SWNT production methods at the time. Bandow et al. [2] argued for the absence of CESR in SWNT based on an analogy with the well established g-anisotropy in graphite for planes parallel and perpendicular to magnetic field. His argument considered that each individual SWNT would contain both orientations locally, and a range in between, and thus any signal would broaden beyond detectability. In MWNT a well defined, metallic CESR was observed [3]. CESR was definitely established in SWNT, induced by K-doping [4]. These studies were invariably stymied by the presence of various, ill-characterised impurities and in particular by the presence of the strongly ferromagnetic catalyst particles. Some of us put forth a model that counter intuitively explains the striking absence of CESR in undoped SWNT and its appearance after K-doping. The model is based on the long spin diffusion length in SWNT and strong coupling to, and fast spin relaxation of, the conduction electrons in the ferromagnetic particles [4]. In a recent paper, it was demonstrated that a defect-induced resonance may be observed in SWNT that does not exhibit a narrow resonance before electron bombardment [5]. The resonance had anomalous temperature depend-

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ence, with a temperature dependent Curie-constant, i.e., the spin susceptibility dropped faster than $1/T$ without change in g-factor or linewidth. Several models were put forth to describe this T-dependence based on interactions of localized defects or shallow, localized states and conduction electrons, and on a possible exchange with the remains of ferromagnetic catalyst particles [5]. Here we refer to this sort of T-dependence as 'super-Curie' paramagnetism, when $M(T)$ falls much faster than $1/T$ with T, but emphasize that it is not related to the similarly named, well-known superparamagnetism of small ferromagnetic particles. Also, this 'super-Curie' paramagnetic behaviour is intrinsic to SWNT and is not due to the remaining ferromagnetic catalyst particles, except via a possible exchange mechanism as outlined in Ref. [5].

In this paper we describe a well defined, narrow resonance in SWNT, observed in materials coming from a large variety of sources that have undergone various purification and heat treatments. Thus we can be confident that the observed signal originates in SWNT, independent of impurity content and purification induced impurities. Our motivations for undertaking these studies were two-fold. Kim et al. developed an efficient purification scheme by which over 99% of the ferromagnetic catalyst particles were removed by filtration in a strong magnetic field gradient [6]. Therefore, these samples offered a chance of testing the model mentioned above and of looking for the elusive SWNT CESR. Meanwhile, both the Philadelphia and Vienna groups were producing high quality peapod and DWNT samples.

We studied a wide variety of SWNT, peapod and DWNT samples, partly to assure that the observed ESR signals do not originate in some impurity and inherently pertain to the nanotubes. In Philadelphia the purified SWNTs were prepared from PII-SWNTs (purchased from Carbon Solutions, Inc.) by air-oxidation, HCl treatment, and magnetic filtration as described in Ref. [6]. The SWNT control sample was produced by annealing the purified SWNTs at 650 °C for 10 hours. The peapod materials were produced by static-vacuum annealing at 650 °C for 9 hours in the presence of C_{60} vapor under conditions previously reported [7], and then further annealing at the same temperature for 1 hour under dynamic vacuum to remove excess C_{60}. Some of the peapod samples were vacuum-annealed at increasingly higher temperatures to react the encapsulated C_{60} to form inner nanotubes in the well-known DWNT structure [8]. The SWNT processing in Vienna had similar goals but the C_{60} used to fill the SWNT and form the inner tubes of the DWNT were ^{13}C enriched.

Figure 1a depicts the characteristic broad ESR spectrum of a typical SWNT material. The spectrum is dominated by the hundred mT broad and intense ferromagnetic resonance of the catalyst particles. However, in some samples, in particular in better purified ones, a weak line is also observed around $g = 2$. This signal was for a long time dismissed as belonging to the various impurities of SWNT on account of its small susceptibility and unexciting linewidth (0.4–0.5 mT), or not observed at all [5]. Our interest was perked in the narrow lines (Fig. 1c) because we observed the appearance of an even narrower line with increasing heat treatment temperature of the peapod → DWNT samples, as depicted in Figs. 1b and 2. Upon cooling we observed a strongly increasing susceptibility, for both the narrow DWNT resonance and the narrow resonance present in purified SWNT. In the case of DWNT samples we term the narrow line with typical width of approx. 0.2 mT inner tube resonance and the narrow line with typical width between 0.4–1 mT as the outer tube resonance (Fig. 1b).

The lineshape of both the inner and the outer tube resonance is well described by the typical derivative Lorentzian as demonstrated in Fig. 1. In highly conductive samples a distorted or Dysonian lineshape is often observed (as in Ref. [4]) and this effect is often sought as a hallmark of CESR. However, this is not necessarily the case as a Dysonian lineshape can be the simple consequence of a sample with a high microwave conductance, even if the resonance originates from an ordinary paramagnetic center embedded in the metallic matrix. Conversely, one can observe a CESR with perfect Lorentzian lineshape if the conductance is low (as in Ref. [4] at low K-doping levels in thin SWNT films) or if the sample is well dispersed into small, separated grains; as is done in our experiments.

We observe the following. The spin susceptibility, χ obtained by double integration of ESR spectra, at room temperature is estimated to be 1×10^{-8} emu/g, which compares well with that of the CESR of MWNT (1×10^{-8} emu/g), whereas in fully K-doped SWNT the CESR is 1×10^{-7} emu/g. The spin susceptibility of both the inner and the outer tube resonance increases faster than the characteristic $1/T$

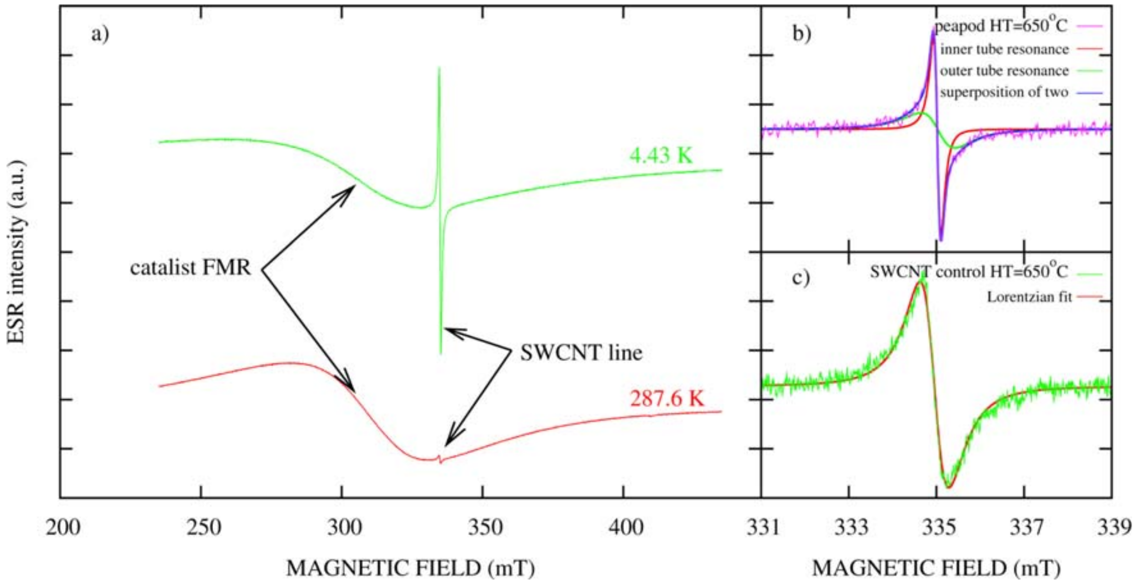

Fig. 1 (online colour at: www.pss-b.com) a) Typical room and low temperature spectrum of a purified SWNT sample showing the broad FMR of the catalyst particles and a small, narrow line at $g \sim 2$. The spectrum at low T exhibits a very strong line at $g \sim 2$. Panels b) and c) show the weak $g \sim 2$ line in the peapod and the control SWNT sample at room temperature, respectively. The solid lines are Lorentzian fits (see text).

dependence of a Curie-paramagnetism expected of localized defects or impurities. The data in Fig. 3 depicts the temperature dependence of $\chi \cdot T$. Curie-spins would give a constant, while Pauli-spins would give a linear behaviour. This rapid rise with decreasing T breaks down below approximately 15–20 K for both the inner and the outer tube lines. Both the inner and the outer tube resonances can be saturated easily with increasing microwave power, indicative of a long spin–lattice relaxation time expected in nanotubes. In addition, we find that the linewidth of the inner tube resonance is about 0.2 mT (temperature independent) for all samples independent of structure (peapods, or DWNT), contrary to the width of

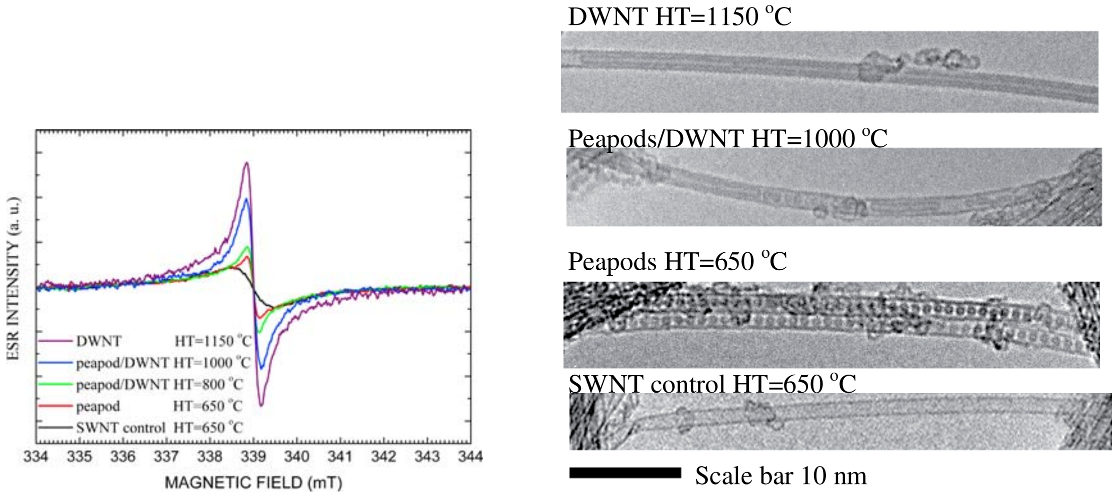

Fig. 2 (online colour at: www.pss-b.com) ESR spectra of a series with increasing heat treatment temperature after C_{60} encapsulation and of a control SWNT sample along with corresponding typical TEM images (scale bar corresponds to 10 nm).

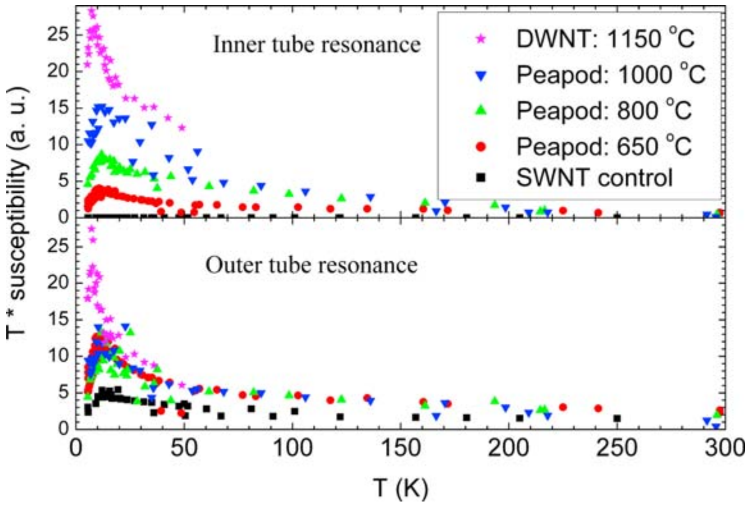

Fig. 3 (online colour at: www.pss-b.com) Temperature dependence of $\chi \cdot T$ (i.e. the ESR susceptibility multiplied by the temperature), for SWNT, peapod and peapod/DWNT and DWNT samples, for the inner and outer tube resonance.

the outer tube line which, while also *T*-independent, increases with increasing heat treatment temperature, as displayed in Fig. 4. Furthermore, we find the same 0.2 mT inner tube linewidth in the DWNT samples of the Vienna group where the inner tube was prepared from ordinary C_{60}, whereas the inner tube linewidth in DWNT samples made using ^{13}C enriched C_{60} increases to 0.35–0.4 mT. The linewidth of the outer tubes, of natural isotope carbon, is also insensitive to these changes of the inner tube. We propose that the narrow 0.4–0.8 mT line is the long sought CESR of SWNT. The main arguments in favour are that we find the same resonance in a wide variety of samples, its susceptibility is comparable to CESR of MWNT at room temperature, and that its linewidth is *T*-independent.

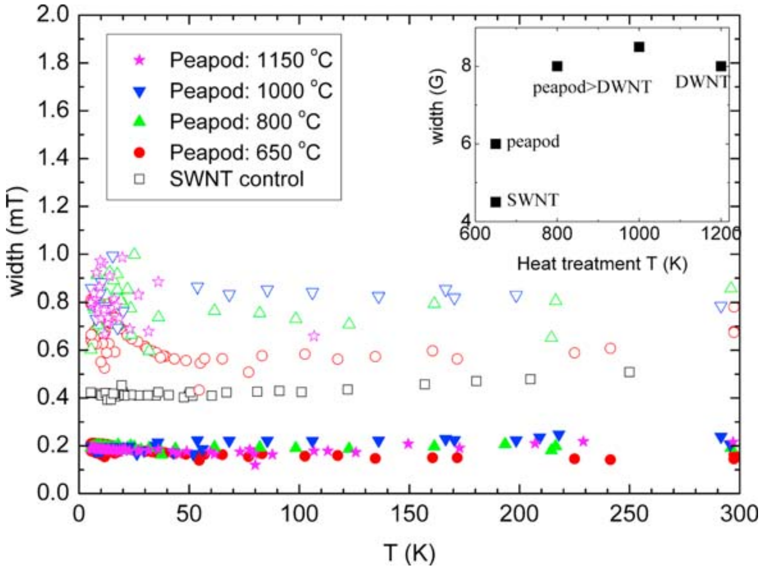

Fig. 4 (online colour at: www.pss-b.com) Temperature dependence of the Lorentzian linewidth of the inner and outer tube resonances (solid and open symbols respectively) for SWNT, peapod, peapod/DWNT and DWNT samples. Inset: outer tube resonance width vs. heat treatment temperature.

The striking 'super-Curie' paramagnetic temperature dependence of the susceptibility would at first suggest that the resonance cannot belong to the conduction electrons, as one would expect Pauli-paramagnetic behaviour. However, there is a growing consensus that SWNT is the first true manifestation of a Luttinger-liquid material [9] and, as it turns out, the temperature dependence of the spin susceptibility of a Luttinger-liquid is not well established theoretically [10]. Furthermore, while the resonance linewidth of interior structures (C_{60} or inner tubes) is independent of temperature or the length of the tubes (or heat treatment temperature) and is rather narrow, the width of the outer tube resonance increases with increasing degree of formation of inner tubes, as new relaxation pathways open up.

A key finding in favour of our hypothesis is that the linewidth of ^{13}C enriched inner tubes is larger than those of natural carbon. This increased spin relaxation is expected for CESR as the local moments of ^{13}C act as additional scatterers for conduction electrons. Such a broadening would not be expected for localized defect resonance even within the frameworks of Ref. [5]. A similar argument holds for the broadening of the outer tube resonance with the growing inner tube content (inset of Fig. 4).

The observed sudden change of the 'super-Curie' paramagnetic behaviour below 20 K is due to a sudden decrease of the spin relaxation rate. We explicitly studied this point by measuring the microwave power saturation dependence of the resonance (not shown), and found a sudden decrease in the saturation power below the same temperature. This could be due to the opening of a spin-gap in the electronic excitations which has been observed in NMR measurements [11].

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