

Identifying the electron spin resonance of conduction electrons in alkali doped SWCNTs

M. Galambos¹, G. Fábrián¹, F. Simon^{*1,2}, L. Čirić³, L. Forró³, L. Korecz⁴, A. Rockenbauer⁴, J. Koltai⁵, V. Zólyomi^{6,7}, Á. Ruzsnyák⁵, J. Kürti⁵, N. M. Nemes⁸, B. Dóra⁹, H. Peterlik², R. Pfeiffer², H. Kuzmany², and T. Pichler²

¹Institute of Physics and Condensed Matter Research Group of the Hungarian Academy of Sciences, Budapest University of Technology and Economics, P.O. Box 91, 1521 Budapest, Hungary

²Faculty of Physics, University of Vienna, Strudlhofgasse 4, 1090 Vienna, Austria

³Institute of Physics of Complex Matter, FBS Swiss Federal Institute of Technology (EPFL), 1015 Lausanne, Switzerland

⁴Chemical Research Center, Institute of Chemistry, P.O. Box 17, 1525 Budapest, Hungary

⁵Department of Biological Physics, Eötvös University, Pázmány Péter sétány 1/A, 1117 Budapest, Hungary

⁶Department of Physics, Lancaster University, Lancaster LA1 4YB, United Kingdom

⁷Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences, P.O. Box 49, 1525 Budapest, Hungary

⁸GFMC, Departamento de Física Aplicada III, Universidad Complutense, 28040 Madrid, Spain

⁹Max-Planck-Institut für Physik Komplexer Systeme, Nöthnitzer Str. 38, 01187 Dresden, Germany

Received 15 May 2009, revised 1 July 2009, accepted 20 August 2009

Published online 30 October 2009

PACS 73.63.Fg, 72.80.Rj, 76.30.–v

* Corresponding author: e-mail ferenc.simon@univie.ac.at, Phone: +36 1 463 38 16, Fax: +36 1 463 38 19

We study the electron spin resonance (ESR) signal of pristine and potassium doped SWCNTs. We identify signals of a superparamagnetic background, a low intensity impurity, and of the conduction electron spin resonance (CESR). The latter only appears upon the alkali atom doping. To identify the CESR signal, we critically assess whether it could come from residual

graphitic carbon, which we clearly exclude. We give accurate values for the signal intensities and the corresponding concentration of spins and for the g -factors. The CESR signal intensity allows to determine the density of states on the SWCNT assembly.

© 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction Electron spin resonance (ESR) proved to be an efficient method to study different carbon phases such as graphite or intercalated graphite [1] and fullerenes [2]. The ESR observables are the signal intensity and line-width, which provide rich information about the electron–electron and electron–lattice interactions and about the immediate vicinity of the Fermi surface. In metals, the ESR signal intensity is proportional to the Pauli spin-susceptibility and the ESR line-width and g -factor are determined by the spin–orbit coupling strength.

Carbon being a light element, it is expected that ESR signal of its different phases should be narrow. It would thus give rise to a relatively sharp, i.e., easily observable ESR signal of the SWCNTs. This, together with the spectroscopic value of the ESR characterization motivated intensive

studies of the SWCNTs. However, the interpretation of the ESR results is still controversial.

Petit et al. [3] reported the observation of the ESR signal of itinerant electrons. Salvétat et al. [4] reported that the ESR signal occurring around $g \approx 2$ is caused by defects in the SWCNTs. Likodimos et al. [5] reported that a similar signal is related to the itinerant electrons whose low temperature behavior is accompanied with the opening of a spin-gap. Corzilius et al. [6] reported the observation of the itinerant electron ESR in SWCNT samples prepared by chemical vapor deposition. While we intend to make no judgement on this controversy, nor to clear the issue, we highlight some recent developments.

It is now generally accepted that the SWCNTs are ideal archetypes of a Luttinger-liquid (LL) [7, 8]. It was shown that

the LL phase prevents observation of the ESR signal in the pristine SWCNTs [9]. In turn upon doping with alkali atoms, an ESR signal develops [10]. This could be identified as originating from the conduction electrons and is therefore termed as a conduction electron spin resonance (CESR). It is also established that the doping induces a cross-over from the LL phase to the Fermi-liquid phase [8], whose ESR signal could be visible. However, the large heterogeneity of the SWCNT samples, the presence of impurities, catalysts, graphitic carbon, and the absence of a crystalline order calls for careful analysis of the ESR properties in both the pristine and the alkali doped samples.

Here, we report ESR measurements on SWCNTs doped with potassium. We find the emergence of the CESR signal of itinerant electrons upon doping with a signal intensity, that is, comparable to that expected from band structure calculations. We identify other signals of the ESR spectra such as that of the catalyst particles and an impurity phase. We show that the CESR intensity could not be explained by the presence of graphite, the CESR is therefore intrinsic to the SWCNT material.

2 Experimental We used commercial arc-discharge based SWCNTs prepared with Ni:Y catalyst and a mean diameter of 1.4 nm. The SWCNTs were purified with a tube weight content of 50%. Thoroughly ground fine powder samples of 3 mg were vacuum annealed at 500 °C for 1 h in an ESR quartz tube and inserted into an Ar glove-box without air exposure. K of about 1.6 mg was added to the samples. This is slightly higher than required for a KC_6 stoichiometry. The doping proceeds in liquid ammonia, it evaporates and its residue is removed with 200 °C vacuum annealing. The $\sim 12/\text{cm}$ upshift of the Raman G band [11] indicates a high level of doping, probably till saturation: KC_x , with $x \approx 7$ [8]. ESR was performed with a JEOL X-band spectrometer. We measured the g -factors with $\text{Mn}^{2+}:\text{MgO}$ (Mn^{2+} content is 1.5 ppm, $g = 2.0014$ [12]) by taking into account the second order hyperfine interaction of Mn^{2+} . The signal intensity was calibrated against $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The pristine sample in the form of a bucky-paper was studied by X-ray diffractometry with $\text{Cu K}\alpha$ ($\lambda = 0.1542 \text{ nm}$) radiation. Radial averages of the two-dimensional spectra were used to obtain the scattering intensity vs. the scattering vector, $q = 4\pi/\lambda \sin \theta$, with 2θ being the scattering angle. Towards small q -values, a power-law background was subtracted.

3 Results and discussion In Fig. 1, we show the ESR spectra of pristine and potassium doped SWCNTs. The broad background signal, which is observable on both spectra, has a g -factor of $g = 2.227$, and line-width of $\Delta B \approx 50 \text{ mT}$. The g -factor is compatible with Ni^{2+} spins, which has usually $g \approx 2.2 \dots 2.3$ [12]. We thus identify this signal as coming from the Ni^{2+} ions in the sample. We note that the Ni^{2+} ions occur in a high ($S = 1$) and a low spin state ($S = 0$) depending on the surrounding crystal-field [12]. The latter is ESR silent, thus the observed background signal

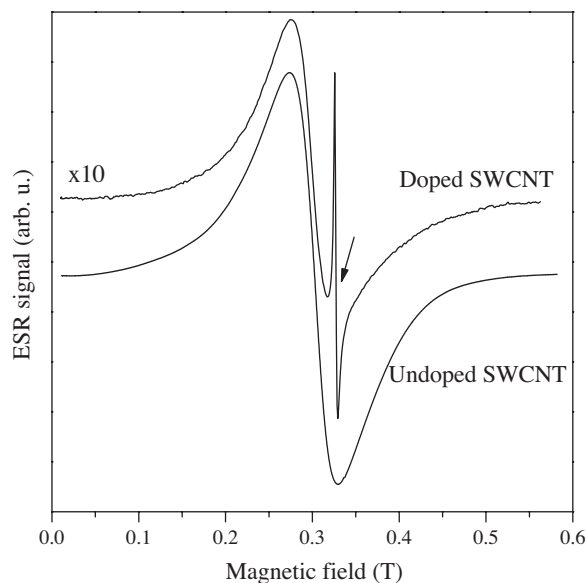


Figure 1 ESR spectra of pristine and K doped SWCNTs at $T = 300 \text{ K}$. The broad and intensive background comes from the magnetic Ni:Y catalyst particles. Arrow shows the narrow line emerging upon doping. Note that the ESR signal of the K doped sample is magnified to compensate for smaller signal intensity due to microwave losses.

comes from Ni^{2+} ions in the high spin state. We exclude the presence of metallic Ni as it would give a ferromagnetic resonance signal around 0.2 T.

The intensity calibration shows that the background signal intensity is equivalent to 2.8 mg Ni^{2+} ($S = 1$) spins. Since the mass of the whole sample is 3 mg, it cannot contain such an amount of Ni. The explanation for the observed large signal intensity could be the super-paramagnetic behavior of Ni clusters. Super-paramagnetism occurs when a few spins are strongly interacting and form small clusters of N ions with a super spin of $N \cdot S$. If the clusters are uncorrelated, their magnetism follows the Curie law at high temperatures. We confirmed from temperature dependent measurements (data not shown) that the background intensity indeed follows a Curie temperature dependence. The amount of Ni does not exceed 0.5 mg in our sample; thus the background signal is explicable if super-paramagnetic clusters are formed of eleven or more spins.

In addition to the background, a narrow $\Delta B \approx 0.6 \text{ mT}$ signal with $g = 2.0031$ is observed in the pristine sample, whose intensity follows a Curie temperature dependence. We identify this as coming from unpaired electrons, probably at defects in the SWCNTs. The intensity of this defect signal to the background is: $I_{\text{defect}}/I_{\text{bkg}} \approx 1 : 10^6$.

The ESR spectrum dramatically changes upon the alkali doping: a narrow signal with $\Delta B \approx 1 \text{ mT}$ line-width appears at $g = 2.0029$ (arrow in Fig. 1). As we shall show below, we identify this signal as coming from the conduction electrons. Upon doping, the signal intensity of the background decreases by a factor 10 because of microwave absorption

and de-tuning of the microwave cavity. However, the background can be used as an intensity reference, since the doping does not affect the Ni:Y catalyst. The proportion of the CESR signal intensity to the background signal is $I_{\text{CESR}}/I_{\text{bkg}} \approx 1 : 500$ for saturated doping. We note that this is about a factor 3 higher than that reported on the same samples using solid state vapor doping [13].

The intensity calibration gives that the CESR signal is equivalent to $2 \times 10^{-3} S = 1/2$ spins per C. To obtain this value, we used that 50 wt% of the sample consists of SWCNTs. This is equivalent to a spin-susceptibility of $\chi_0 = 2.5 \times 10^{-6}$ emu/(mol C) or $\chi_0 = 2.1 \times 10^{-7}$ emu/g. This is about a factor 4 larger than reported previously on electrochemically doped samples [10].

In the following, we critically assess the origin of the signal identified as the CESR. It is known that SWCNT samples may contain carbon in forms different from SWCNTs. The best known of these is graphite. Figure 2 shows an X-ray diffractogram on the pristine SWCNT samples, which indicates the presence of graphite. Although the graphite peak is pronounced with respect to the SWCNT bundle peaks, one cannot determine the relative amount of graphite as the X-ray is affected by the level of crystallinity of these carbon phases. Instead, we present spectroscopic arguments which strongly support the above identification.

We first focus on the pristine material and in Fig. 3 we show a comparison between undoped SWCNT and finely ground graphite samples. The pristine SWCNT ESR spectrum is identical to that shown in Fig. 1. For the graphite powder sample, a line-shape, which is characteristic for a randomly oriented powder with a g -factor anisotropy, is observed. This is the result of the in/out-of-plane anisotropy of the graphite g -factor, which is well known [1]. A solid curve shows a simulation for the graphite assuming a randomly oriented powder with a uniaxial

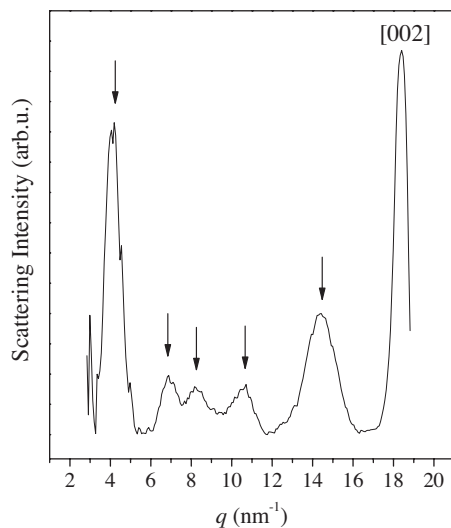


Figure 2 X-ray diffraction profile of pristine SWCNT. Arrows show the peaks due to the hexagonal SWCNT bundles. The graphite [002] reflection peak around $q = 18/\text{nm}$ is indicated.

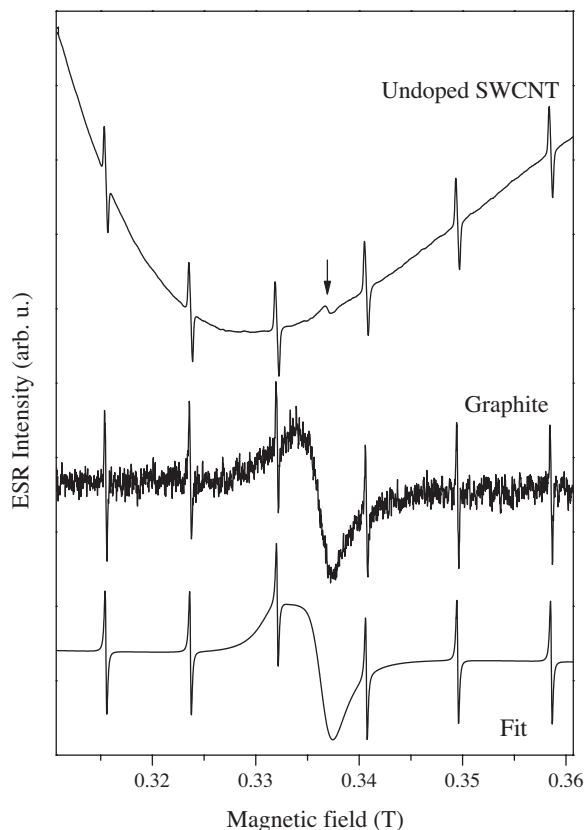


Figure 3 ESR spectra of pristine SWCNTs, finely ground graphite sample (both mixed with $\text{MnO}:\text{MgO}$ g -factor reference). Note the six narrow lines coming from the Mn^{2+} reference. Arrow indicates the small impurity line in the SWCNT sample. Solid curve is a fit for a powder with a uniaxial g -factor anisotropy.

g -factor anisotropy with $g_{\perp} = 2.0031$ and $g_{\parallel} = 2.0351$, in agreement with the literature data [1]. Clearly, the signal observable in the graphite does not resemble the impurity seen in the pristine SWCNT sample: it is broader and the center of the graphite ESR signal is at lower magnetic field than the one in the SWCNT sample. This supports that the narrow line in the pristine SWCNT sample comes from an impurity signal and is not related to graphite.

This also shows that there is no apparent graphite ESR signal in the pristine SWCNTs. However, one has to exclude that there is no unseen graphite ESR signal which could give rise to the observed intensive CESR signal upon doping. It is known about alkali intercalated graphite that its ESR signal increases significantly upon doping. In Table 1, we give χ_0 for pristine graphite and KC_8 , which shows a 40-fold increase in χ_0 . Clearly, one has to prove that no signal is observed with the 1/40th intensity of the CESR signal in Fig. 1 in *pristine* SWCNT sample.

In Fig. 4, we show the spectrum of undoped SWCNTs measured in a way, that is, optimized to enhance a broad, small amplitude ESR signal. We show a simulated powder graphite spectrum on the top of the broad SWCNT background signal with an intensity which corresponds to the 1/40th of that observed in the doped SWCNT sample.

Table 1 Density of states and spin-susceptibilities in carbonaceous materials.

	χ_0 (10^{-7} emu/g)	$D(E_F)$ (states/eV · C atom)
graphite [1]	0.16	0.0058, 0.0126
KC ₈ [1]	6.4	0.33
K ₃ C ₆₀ theory [2]		0.22–0.33
K ₃ C ₆₀ exp. [2]	8.4–13	0.33–0.53
pristine SWCNT [9]		0.0046
K doped SWCNT exp.	2.1	0.08
K doped SWCNT theory		0.12

Note that χ_0 is not available for pristine SWCNTs. The KC₇ stoichiometry was assumed to obtain the theoretical DOS for the K doped SWCNT.

The simulation shows that such a graphite signal would be visible beyond the experimental noise. This proves that no substantial graphitic carbon is present which could explain the observed intensive CESR signal in the doped samples. On the other hand, it proves that one does not observe an ESR signal from the undoped SWCNTs in agreement with the theoretical result [9].

We proceed to relate the experimental χ_0 of the doped SWCNTs with the band structure calculations of the density

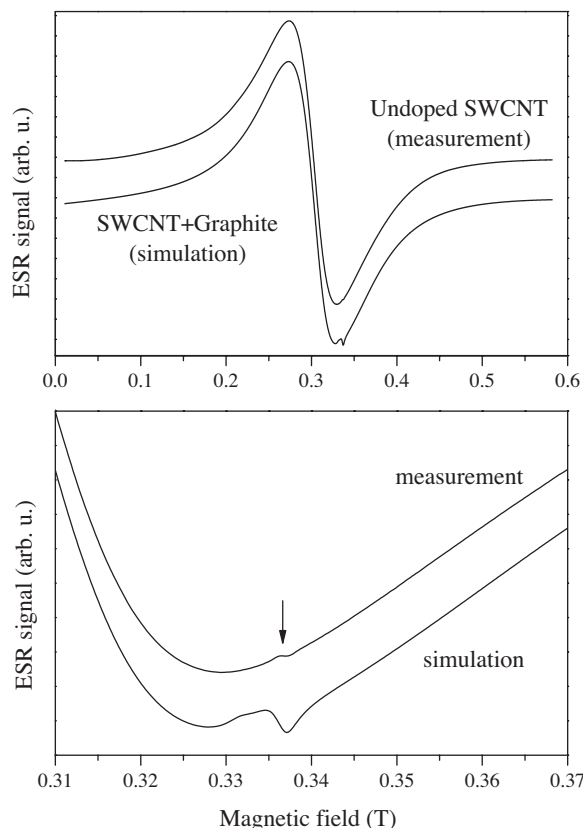


Figure 4 ESR spectra of pristine SWCNTs, and a simulated graphite signal on top of the broad background. The lower panel is an expanded scale. Arrow shows the narrow impurity in the pristine SWCNT. The broader graphite-like ESR signal is not observed in the measurement.

of states at the Fermi level, $D(E_F)$. The latter gives 0.12 (states/eV · C atom) and the details of the calculation are in Ref. [9]. The DOS is obtained from the Pauli susceptibility through: $\chi_{\text{Pauli}} = 1/4g^2\mu_B^2D(E_F)N_A$ in units of emu/mol, where $g \approx 2$, μ_B , k_B , and N_A are the Bohr magneton, the Boltzmann and Avogadro constants in cgs units. When this is related to the Curie susceptibility of $S = 1/2$ spins at room temperature, $\chi_{\text{Curie}} = 1.25 \times 10^{-3}$ emu/mol, gives $\chi_{\text{Pauli}}/\chi_{\text{Curie}} = k_BTD(E_F) = 2 \times 10^{-2}$ with the above value of χ_0 of the CESR signal. This gives the final result of $D(E_F) \approx 0.08$ (states/eV · C atom) which is in good agreement with the theoretical result, and shows that doped SWCNTs behave as a Fermi liquid.

4 Summary In summary, we identified the different ESR signals in pristine and potassium doped SWCNTs. We argue that the signal observed upon the potassium doping is related to the conduction electrons.

Acknowledgements Work was supported by the Austrian Science Funds (FWF) project No. I83-N20, by the Hungarian State Grants (OTKA) No. F61733, F68852, and K60576, by the Mecenatúra program of the National Office for Research and Technology (NKTH), and by the Marie Curie project PIEF-GA-2008-220094. V. Z. and F. S. acknowledge the Bolyai program of the Hungarian Academy of Sciences. Work in Lausanne was supported by the Swiss NSF and the IMPRESS Research Network.

References

- [1] M. S. Dresselhaus and G. Dresselhaus, *Adv. Phys.* **51**(1), 1–186 (2002).
- [2] O. Gunnarsson, *Rev. Mod. Phys.* **69**, 575–606 (1997).
- [3] P. Petit, E. Jouguelet, J. E. Fischer, A. G. Rinzler, and R. E. Smalley, *Phys. Rev. B* **56**, 9275–9278 (1997).
- [4] J. P. Salvetat, T. Fehér, C. L’Huillier, F. Beuneu, and L. Forró, *Phys. Rev. B* **72**, 075440-1-6 (2005).
- [5] V. Likodimos, S. Glenis, N. Guskos, and C. L. Lin, *Phys. Rev. B* **76**, 075420 (2007).
- [6] B. Corzilius, K. P. Dinse, J. van Slageren, K. Hata, M. Haluska, V. Skakalova, and S. Roth, *Phys. Status Solidi B* **245**, 2251–2254 (2008).
- [7] H. Ishii, H. Kataura, H. Shiozawa, H. Yoshioka, H. Otsubo, Y. Takayama, T. Miyahara, S. Suzuki, Y. Achiba, M. Nakatame, T. Narimura, M. Higashiguchi, K. Shimada, H. Namatame, and M. Taniguchi, *Nature* **426**, 540–544 (2003).
- [8] H. Rauf, T. Pichler, M. Knupfer, J. Fink, and H. Kataura, *Phys. Rev. Lett.* **93**, 096805 (2004).
- [9] B. Dóra, M. Gulácsi, J. Koltai, V. Zólyomi, J. Kürti, and F. Simon, *Phys. Rev. Lett.* **101**, 106408 (2008).
- [10] A. S. Claye, N. M. Nemes, A. Jánossy, and J. E. Fischer, *Phys. Rev. B* **62**, 4845–4848 (R) (2000).
- [11] H. Rauf, T. Pichler, R. Pfeiffer, F. Simon, H. Kuzmany, and V. N. Popov, *Phys. Rev. B* **74**, 235419 (2006).
- [12] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford University Press, Oxford, England, 1970).
- [13] F. Simon, M. Galambos, D. Quintavalle, B. Náfrádi, L. Forró, J. Koltai, V. Zólyomi, J. Kürti, N. M. Nemes, M. H. Rummeli, H. Kuzmany, and T. Pichler, *Phys. Status Solidi B* **245**, 1975 (2008).