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Ferromagnetic decoration in metal-semiconductor separated and ferrocene functionalized single-walled carbon nanotubes

A. Chernov[1], M. Havlicek[2,†], W. Jantsch[2], M. H. Rümmeli[3], A. Bachmatiuk[3], K. Yanagi[4], H. Peterlik[1], H. Kataura[5], F. Sauerzopf[6], R. Resel[7], F. Simon[8], and H. Kuzmany[*,1]

[1] Fakultät für Physik, Universität Wien, Strudlhofgasse 4, 1090 Wien, Austria
[2] Institut f. Halbleiter- und Festkörperphysik, Johannes Kepler Universität, 4040 Linz, Austria
[3] Leibniz Institute für Festkörperphysik und Werkstoffforschung, Dresden, Germany
[4] Department of Physics, Tokyo Metropolitan University, Tokyo, Japan
[5] Nanotechnology Research Institute, AIST, 1-1-1 Higashi, Tsukuba 305-8562, Japan
[6] Technische Universität Wien, Atominstitut, Wien, Austria
[7] Institut für Festkörperphysik, Technische Universität Graz, Graz, Austria
[8] Budapest University of Technology and Economics, Budapest, Hungary

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[*] Corresponding author: e-mail hans.kuzmany@univie.ac.at, Phone: +43 1 4277 51306, Fax: +43 1 4277 51375
[†] Present address: Institut f. Physikalische Chemie, Johannes Kepler Universität, 4040 Linz, Austria

Spin resonance, magnetic measurements, and structural analysis are reported for metal-semiconductor separated SWCNTs after filling with ferrocene. Raman scattering performed after a heat treatment confirms partial transformation to double-walled CNTs but results from spin resonance (FMR), X-ray diffraction, and TEM evidence in addition the growth of ferromagnetic nanoparticles. For the metallic tubes the particles are identified as magnetite (Fe_3O_4) with full chemical stoichiometry. From the temperature dependence of the FMR response and from measurements of the magnetization by dc and ac SQUID the magnetite crystals are shown to undergo a Verwey transition. The transition temperature from the SQUID experiment is around 125 K as expected but considerably higher than observed from the FMR analysis. Results for semiconducting tubes are similar but magnetic particles are an order of magnitude smaller and exhibit different structures in addition to magnetite.

1 Introduction The investigation of ESR from single-walled carbon nanotubes (SWCNTs) has been a subject of extensive interest for more than a decade [1–4]. In recent work on SWCNT grown from the nonmagnetic catalyst PtReRh and metal–semiconductor (M-SC) separated by density gradient ultracentrifugation [5] it was shown that ESR response arises from defects partly generated during the M-SC separation process [6, 7]. No direct evidence from itinerant electrons could be observed for the M tubes. This behavior was explained by a theoretical work in which the ESR response from free carriers in a Tomonaga–Luttinger liquid (TLL) system was found to exhibit very broad lines which are very difficult to observe [8]. The TLL nature of the electrons in SWCNT has been proven from photo-emission experiments [9, 10]. In contrast to the observation for the pristine material, after strong doping the tubes with electron donors, such as potassium, a response from free electrons was observed [11]. In this case the Fermi level was strongly upshifted and the 1D character of the tubes was relaxed, albeit with the consequence that the structure of the bundles was strongly perturbed due to the intercalated alkali ions. In several other recent papers it was shown that filling SWCNTs with electron donors will also result in a doping of the tubes with a concomitant increase of the Fermi energy [12]. In this case the structure of the SWCNT bundles remains highly unperturbed and the tube system can be expected to transfer to a more 3D-like system with reduced electron–electron interaction, similar to the tubes doped with alkali metals. Therefore this type of tube doping could be another chance to see response from

free carriers in ESR. The transformation to a more 3D-like structure should be further enhanced for M-SC separated tubes where the bundles in the M tubes consist only of metallic species.

In this contribution we report on spin resonance and magnetization experiments from highly M-SC separated SWCNTs which were partly filled with ferrocene ($FeCp_2$). Successful filling was demonstrated from the observation of double-walled CNT after transformation of the filled tubes at 750 °C. After treating the tubes with ferrocene, spin resonance shows a very strong signal characteristic for ferromagnetic resonance (FMR) with a temperature dependence characteristic for the multiferroic crystal magnetite (Fe_3O_4). Proof for the growth of such crystals is derived from X-ray diffraction. Temperature dependent FMR and SQUID measurements confirm the presence of magnetite and showed an unusual Verwey transition.

2 Experimental Single-walled carbon nanotube samples were grown by laser ablation using a PtRhRe catalyst as described previously [13]. The high growth temperature required for the PtReRh catalyst resulted in SWCNT with fairly large average diameter of 1.65 nm. Subsequently the tubes were M-SC separated by density gradient ultracentrifugation [5]. The efficiency of M-SC separation was checked by optical absorption in the energy range of the E_{11} and E_{22} transitions. Separation better than 98% was achieved. The thus prepared tubes were tip opened by etching in air for 30 min at 430 °C. The opened tubes were exposed in a sealed quartz tube to vapor of $FeCp_2$ at 300 °C for 50 h to perform the tube filling. After 50 h the SWCNTs were removed from the quartz tubes and were ready for spin resonance, X-ray diffraction, and SQUID measurements. A small fraction of the tubes was again sealed into a quartz tube and transformed to double-walled CNTs by heating at 750 °C for 2 h.

Spin resonance experiments were performed using a Bruker Elexsys X-band spectrometer at 9.45 GHz and 30 dB power (0 dB = 200 mW) with a rectangular TE_{102} cavity. For the measurements the bucky paper samples were sealed into evacuated quartz tubes and measured between 1.5 and 300 K for magnetic fields between almost zero and 15 000 G. XRD measurements were carried out using a rotating anode X-ray generator equipped with a pinhole camera (Nanostar, Bruker-AXS), with an instrumental resolution of $q = 0.02\,nm^{-1}$ at Cu Kα with $\lambda = 0.1542$ nm. High resolution XRD was performed at the W1 beamline of the synchrotron HASYLAB in Hamburg for $\lambda = 0.11801$ nm. In order to obtain a diffraction pattern also for rather large d values grazing incidence diffraction was used with a coplanar scattering geometry in the detector scan mode. For the recording of magnetization curves ac and dc measurements were performed using a Quantum design MPMS SQUID magnetometer. Samples were accommodated in an especially designed quartz tube sample holder and measured in the temperature range between 10 and 150 K while protected by a He atmosphere.

3 Results Figure 1 depicts Raman spectra in the radial breathing mode region obtained for SC (left) and M (right) tubes. Red and black spectra were recorded after partial filling the separated tubes with $FeCp_2$ and after transformation of these tubes to DWCNTs, respectively. The new lines appearing after transformation clearly show the growth of inner tubes with RBM at 258.5 and 259 cm^{-1} for the SC and M tubes, respectively. However, as deduced from the relative intensity of these lines to the RBMs of the outer tubes, one can estimate that the concentration of inner tubes is at least a factor 20 smaller than for filling of unseparated laser ablation grown tubes. This is an indication that the substantial amount of $FeCp_2$ was either lost or reacted into an other species.

In Fig. 2 the FMR response from SC and M tubes is depicted after exposure to ferrocene (hereafter designated as SCf and Mf, respectively) for two selected temperatures. At room temperature the response for Mf tubes shows a very strong and broad but almost symmetric line, centered at B_0 around 2800 G. This is typical for a resonance from ferromagnetic systems. The linewidth is of the order of 900 G. In contrast, the response from the SCf tubes occurs at slightly higher fields and is highly asymmetric, indicating contributions from several ferromagnetic species or from very small, <5 nm, particles. The linewidth is more than 1500 G. At low temperatures the lineshape is quite unusual

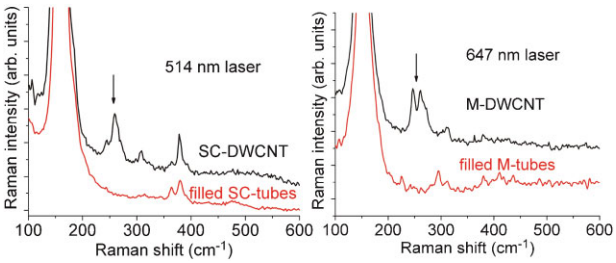

Figure 1 (online color at: www.pss-b.com) Raman spectra in the radial breathing mode (RBM) region for SC (left) and M (right) tubes after partial filling with $FeCp_2$ (red graphs) and after transformation to DWCNTs (black graphs). The arrows assign response from the inner tube RBMs. SC and M tubes were recorded with 514 and 647 nm lasers excitation, respectively, as indicated.

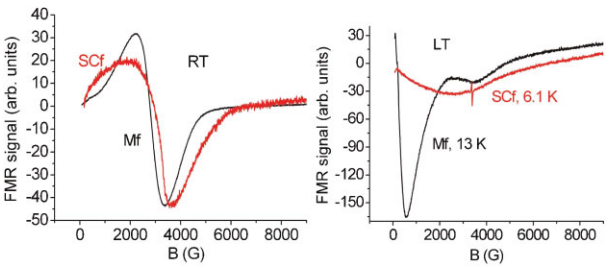

Figure 2 (online color at: www.pss-b.com) Ferromagnetic resonance (FMR) for SC and M SWCNTs after filling with ferrocene and recording at 300 K (left) and at low temperatures as indicated (right). Response for SCf and Mf tubes are scaled to show approximately the same signal height.

for both tube systems.The Mf tubes exhibit a deep and narrow dip at very low fields of the order of 400 G and a superimposed second resonance around 2900 G. The response from the filled SC tubes is similar but the dip is much broader and upshifted to around 2600 G. Also, the additional resonance at 2900 G is missing.

Since the lineshape for the M tubes is closer to the usual Lorentz type, at least at room temperature, more detailed studies were performed only for those species. The dramatic difference between the response at room temperature and at low temperature is a challenge to study the temperature dependence in detail. Results are depicted in Fig. 3 for a field range between zero and 7000 G. At room temperature and down to almost 100 K the response remains quasi-Lorentzian. This is still so at 100 K but the line broadened considerably. At 90 K a new feature appears as a dip at very low fields and the amplitude of the response becomes smaller concomitant with a broadening of the main line. At 85 K the dip has clearly developed and for only 5 K lower temperatures the low temperature type of response with the strong dip and the additional resonance is observed. Further reduction of the temperature does not introduce any more relevant changes to the spectra.

The dotted red lines in Fig. 3 are fits with Lorentz lines. Above 100 K two Lorentzians with independent but similar resonance fields B_1 and B_2 were used to fit the spectra. Typical values for B_1 and B_2 are 2891.2 and 2283.9 G, respectively, as found from the recording at 300 K. Corresponding linewidths are 840.9 and 1106.1 G. For the low temperature spectra three Lorentzians are required. For the low field component with B_0 of the order of 400 G positive and negative values of B_0 are used, since for such low resonance fields the right circular and the left circular component of the linearly polarized excitation field contribute. The second Lorentzian describes the additional resonance. Finally a broad line with low amplitude is used to take care of some background contribution. As an example the spectrum recorded at 50 K was fitted with the values $B_0 = \pm 283.6$ G and $w_0 = 530.4$ G for the low field resonance, $B_a = 2992.5$ G and $w_a = 732.6$ G for the additional resonance, and $B_b = 6876.4$ G and $w_b = 2223.2$ G for the background resonance.

The abrupt change of the FMR response between 90 and 80 K suggests a phase transition of the magnetic structure. One possibility for such transition is the Verwey transition of magnetite (Fe_3O_4) which has been repeatedly studied in transport experiments, XRD, and FMR [14–16]. It is usually observed at 125 K. Since the transition observed here occurs at considerably lower temperature its origin as a transition of magnetite can be questioned. Therefore extensive studies by X-ray diffraction were performed with a Cu Kα as well as with a synchrotron source. Figure 4 depicts some results as recorded with Cu Kα radiation. For the Mf tubes it shows a clear set of narrow lines. The identification of the recorded pattern as magnetite is straightforward as the lines correspond in all details to the reference pattern. This means the lattice planes and their distances can thus be identified. For the semiconducting tubes also magnetite lines can be identified in the noisy pattern but in this case lines are broader and several other structures contribute to the observed pattern. In order to obtain a reliable value for the lattice constant and a value for the particle size XRD using synchrotron radiation was performed for the M tubes. Fitting all reflexes with Lorentz lines reveals an averaged lattice constant of $a = 0.8398 \pm 0.0001$ nm for the fcc structure of magnetite. This value corresponds exactly to the value of $a = 0.8398 \pm 0.0003$ nm for magnetite as averaged from various sources, for example, Ref. [17] and demonstrates the high quality and perfect stoichiometry for the magnetite material observed here. From the averaged line width $\Delta q = 0.1375\ \mathrm{nm}^{-1}$ of the diffraction pattern a particle size $D = 46$ nm was deduced from the Scherrer formula

$$D = \frac{2\pi}{\Delta q}. \tag{1}$$

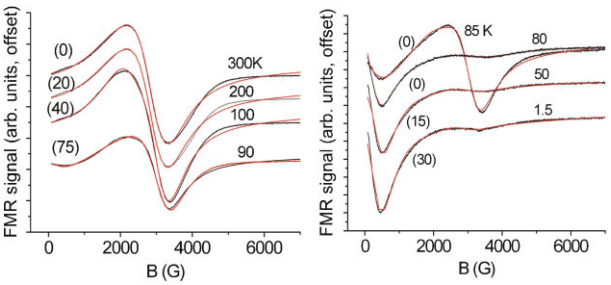

Figure 3 (online color at: www.pss-b.com) Ferromagnetic resonance for Mf tubes after reacting with ferrocene as recorded for selected temperatures. The latter are indicated on the right side of the corresponding spectra. Signals are unscaled but offset for better presentation. The value used for the offset is given in in parentheses for each spectrum. The numbers mean offset in % of the total signal amplitude for the measurement at 300 and 85 K, respectively. Dotted (red) lines are fits using Lorentzian lines as discussed in the text.

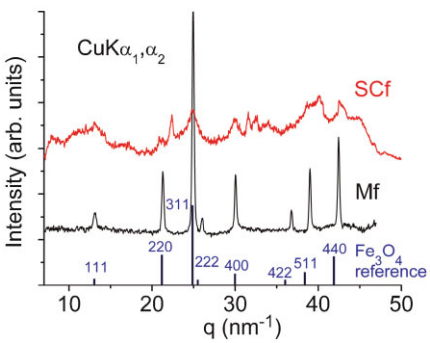

Figure 4 (online color at: www.pss-b.com) X-ray diffraction pattern recorded by Cu Kα radiation for SC (top) and M (center) nanotubes after the tubes were reacted with ferrocene. The bar pattern at the bottom represents line position and intensities for magnetite from international tables, together with the Miller indices of the scattering planes.

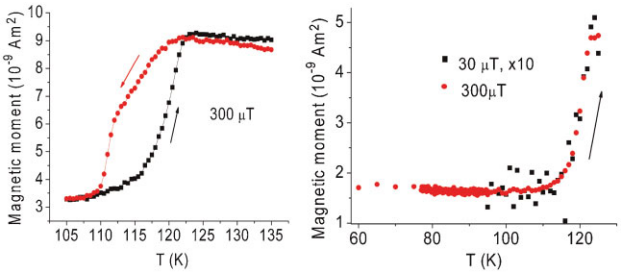

Figure 5 (online color at: www.pss-b.com) Ac magnetization of Mf tubes after treating with ferrocene as measured with an SQUID magnetometer. Left part of the figure shows the temperature hysteresis of the recording for excitation with 300 μT. The right part has the response for two different excitation fields as indicated and for a low temperature range extended down to 60 K.

For the SC tubes the particle size was at least an order of magnitude smaller.

Another check on the origin of the phase transition can be obtained from magnetization measurements. Figure 5 depicts ac results recorded from a SQUID. On cooling the tubes the magnetic moment is rather constant down to about 125 K but starts to decrease abruptly below this temperature. Eventually it reaches a three times smaller value at $T = 110$ K. This transition is fully reversible with a well expressed hysteresis along the transition. The critical temperature T_V where the transition starts, is only weakly depending on the direction of the temperature sweep. As depicted in the right part of the figure, extending the temperature to lower values does not reveal any new structures in $M(T)$, particularly not for values of T where the FMR results exhibit the phase transition. Also, at least for the low fields used here, no field dependence can be observed.

4 Discussion The Raman spectra obtained after annealing the ferrocene filled tubes give evidence for successful tube filling. The RBMs of the inner tubes have several components which originated from the same inner tube in different outer tubes [18]. However, most of the ferrocene available transforms to magnetite nanocrystals. Since all surfactants used in the separation process contain large amounts of oxygen it is suggestive to claim that some of these surfactants survive the purification process and serve as oxygen source for the growth of magnetite.

Magnetite is a well known multiferroic crystal with fcc crystal structure of spinel type [19]. It is a ferrimagnet as it consists of two sublattices A and B which are ferromagnetically ordered each, but antiferromagnetically ordered versus each other. As first observed by Verwey and Haayman [20] this crystal undergoes a charge ordering transition at $T_V = 125$ K in which a mobile negative charge in sublattice B eventually becomes localized, leading to an ordered structure. This charge ordering transition is accompanied by a dramatic reduction in conductance by several orders of magnitude and is now known as Verwey transition [21].

In detail, T_V depends on the stoichiometry of Fe_3O_4. It decreases with anion deficiency [22]. Also, any deviation from stoichiometry reflects in the lattice constant [23]. Since in our case the lattice constant has the correct value, we can be sure to have stoichiometrically correct crystals. Within some experimental uncertainty this is consistent with the observed phase transition around 125 K from the SQUID experiments.

The behavior of the FMR results above the Verwey transition is consistent with previous experiments [14, 15]. However, for the same sample the temperature dependence reveals a noticeably lower transition temperature as compared to the results from SQUID experiments. As the FMR experiments were carried out at much higher fields and high frequency this result indicates a dependence of T_V on field strength or frequency, or both. However a final interpretation for the discrepancy in transition temperature is not yet available.

The fact that two Lorentz lines are needed to provide a good fit to the FMR experiments is an indication for g-factor anisotropy as it is known from previous experiments [24]. The additional FMR response centered at 2992 G probably comes from an other ferromagnetic iron oxide compound. From experiments not discussed in this paper, it is suggested to originate from maghemite (γ-Fe_2O_3).

5 Conclusions In conclusion we demonstrated that PtRhRe grown and M-SC separated SWCNTs can be filled with ferrocene but most of the latter reacts with oxygen and especially for the metallic tubes magnetite (Fe_3O_4) nanocrystals are grown with full stoichiometry. The crystals exhibit a FMR with a dramatic transition to a low temperature response at 90 K. The latter is unique as it has a rather sharp resonance at very low fields. This transition has the signatures of a Verwey transition but occurs for temperatures 35 K lower than expected. On the other hand magnetization recorded for the same material in a SQUID magnetometer revealed a Verwey transition at 125 K as expected.

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