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Electron spin resonance (ESR) measurements on SWCNTs doped with alkali atoms (potassium) using a solid state reaction is reported. We find the emergence of the ESR signal of itinerant electrons upon doping with a signal intensity that is comparable to that expected from band structure calculations. The ESR line-width and microwave conductivity weakly depend on the temperature indicating that doped SWCNTs are bad metals. It is argued to result from the lack of crystalline order in the tubes and the large impurity concentration.

1 Introduction Electron spin resonance (ESR) is a well established and efficient method to characterize solids with itinerant electrons. It helped to resolve e.g. the singlet nature of superconductivity in elemental metals [1], the magnetically ordered ground state of the spin-density state in low dimensional organic metals [2] and in alkali doped fulleride polymers [3]. The ESR measurables, such as the signal intensity and line-width provide rich information about the electron-electron, electron-lattice interactions and about the immediate vicinity of the Fermi surface. In normal metals, the ESR signal intensity is proportional to the Pauli spin-susceptibility, the ESR line-width and g-factor are determined by the mixing of spin up and down states due to the spin-orbit (SO) coupling in the conduction band. In contrast, in correlated materials the Pauli susceptibility can be suppressed and the ESR spin lattice relaxation time, T_1, that is proportional to the inverse line-width, can be orders of magnitude shortened. Clearly, measurement of these parameters, i.e. the observation of ESR in SWCNTs is a compelling issue.

This motivated a more than a decade long search to find the electron spin resonance signal of itinerant electrons in pristine single-wall carbon nanotubes and to characterize its properties [4–6]. However, to our knowledge no conclusive evidence for this observation has been reported. An often cited argument, why the ESR of itinerant electrons has not been observed to date [4–6], is the large heterogeneity of such systems, the lack of any crystallinity, and the presence of magnetic catalyst particles [6]. It was also shown that the ground state of pristine SWCNTs is the Tomonaga-Luttinger liquid (TLL) [7,8] which crosses to a Fermi liquid (FL) upon alkali doping. However, ESR signal of conduction electrons has been observed in such electron doped carbon nanotubes [5]. This motivated us to revisit such doping experiments in order to learn insight into the electronic properties of the Fermi liquid state of SWCNTs.

Here, we report ESR measurements on SWCNTs doped with alkali atoms (potassium) using a solid state reaction. We find the emergence of the ESR signal of itin-

erant electrons upon doping with a signal intensity that is comparable to that expected from band structure calculations. The ESR line-width and microwave conductivity weakly depend on the temperature indicating that doped SWCNTs are bad metals. We argue that it is caused by the lack of crystalline order in the tubes and the large impurity concentration.

2 Experimental We used two types of SWCNTs for the doping with K. The commercial SWCNT made with the arc-discharge method and a Ni:Co catalyst had a mean diameter of 1.4 nm. A laboratory made laser ablation method based material was prepared using non-magnetic Pt:Rh:Re catalysts based on Ref. [9]. The commercial material was purified with repeated air oxidation and acid treatments and the laboratory based material was not purified. A thoroughly ground fine powder sample was prepared in order to enable penetration of microwaves. We used samples of typically 2 mg weight. The samples were annealed at 500 °C for 1 h in an ESR quartz tube and inserted into an Ar glove-box without exposing to air. A non-stoichiometric amount of alkali was inserted into the quartz tubes which were subsequently sealed under 20 mbar He. Alkali doping was performed by heating the quartz tube containing the SWCNT powder and the alkali. We found that a 1 h long heat treatment at 400 °C dopes the SWCNT to saturation. After this heat treatment, no change in the ESR signal or in the microwave absorption is observed. Compared to the previous electrochemical doping result [5], the solid state reaction has some advantages as it is not influenced by the presence of the electrolyte. However, it does not enable for reversible or well controlled doping. ESR experiments were performed on a Bruker Elexsys X-band spectrometer equipped with a cryostat. Microwave conductivity was measured with the cavity perturbation technique using a home-built apparatus operated in a locked frequency AC modulation mode [10]. Monitoring of the quality factor of the cavity and calibration of the ESR intensity with Mn:MgO ESR reference allowed to measure the absolute spin-susceptibility of the samples.

3 Results and discussion In Figs. 1. and 2 we show the ESR spectra of the pristine and K doped samples for the two kinds of SWCNT starting materials. Clearly, an additional signal around $g = 2$ develops with the doping in agreement with the previous studies [5]. This is assigned to the conduction electron spin resonance (CESR) of the SWCNTs. It is currently debated whether the CESR in pristine SWCNTs should be observable or some inherent reasons, e.g. the pristine SWCNTs being in a TLL correlated state should prohibit it. The Ni:Co catalyst based SWCNT sample shows the inevitable broad and intensive background signal which is unaffected by the doping and comes from the magnetic catalyst particles. Importantly, no such background is present for the Pt:Rh based sample in

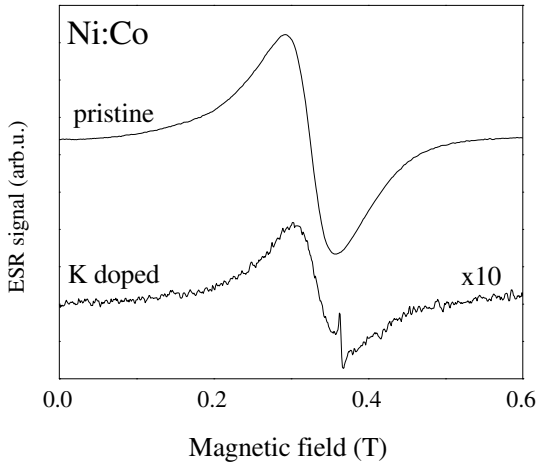

Figure 1 ESR spectra of pristine and K doped SWCNTs for the Ni:Co catalyst based SWCNT sample at $T = 300$ K. The broad and intensive background comes from the magnetic catalyst particles. The ESR signal of the K doped sample is magnified to compensate for smaller signal intensity due to microwave losses.

agreement with the original characterization of such samples [9]. We found that the ESR line-width is independent of the starting SWCNT sample and it is $\Delta H \approx 2$ mT in agreement with the previous result [5].

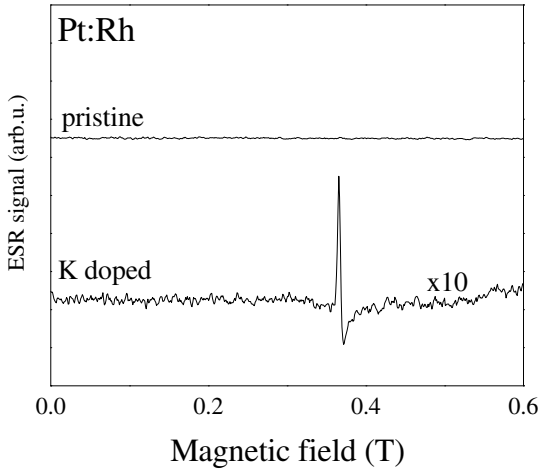

Figure 2 ESR spectra of pristine and K doped SWCNTs for Pt:Rh:Re based SWCNT sample at $T = 300$ K. Note the absence of a background signal for the starting material. The ESR signal of the K doped sample is magnified.

The alkali doping also affects the microwave conductivity of the sample. For the used fine powder samples, the cavity quality factor is proportional to the sample resistivity. Upon doping, the $Q = 4000$ for the pristine sample goes to $Q \approx 500$ indicating an about 10 fold increase in the

sample conductivity. In addition, the character of the temperature dependent Q factor changes: it is semiconducting like for the pristine material such as in other studies [11], which changes to a nearly temperature independent behavior. This latter temperature dependence is characteristic for a dirty or bad metal. The Q factor changes affect the observed signal intensity, which is taken into account by multiplying the ESR spectra for the doped samples. In principle, the ESR intensity should vary with $\sqrt{Q}$ [12], however for such a low Q as 500 no critical coupling can be achieved, which further lower the signal intensity. This can be easily calculated for the Ni:Rh sample, where the broad background serves as an intensity standard, however it is more complicated to determine this factor for the Pt:Rh based sample. For simplicity, we assume that the Q factor changes affect equally the two types of samples.

The increased conductivity has also a fingerprint on the spectral shape: we observe a typical asymmetric Lorentzian-like curve in Figs. 1 and 2, the so-called Dysonian line [13]. this kind of line-shape appears, when the microwave skin depth is comparable to the particle size. Observation of a Dysonian signal also means that the ESR intensity determination is less accurate due to the limited microwave penetration.

The ESR signal intensity provides a direct measure of the static spin susceptibility, χ_0 [14]. For metals, it is the Pauli susceptibility and

$$\chi_0 = \mu_0 \frac{g^2}{4} \mu_B^2 D(E_F) \qquad (1)$$

where g is the g-factor of the electrons, μ_0 is the permeability of the vacuum, and $D(\epsilon_F)$ is the density of states (DOS) at the Fermi energy.

To enable a comparison between the experiment and theory, we performed nearest-neighbor tight-binding calculations on a realistic SWCNT ensemble sample. In the calculation, we considered that semiconducting tubes do not contribute to the DOS and for metallic tubes, we took the corresponding DOS weighted by the tube abundance expected for a Gaussian distribution with a mean diameter of 1.4 nm and variance of 0.1 nm. The calculation yields the DOS as a function of the Fermi energy. The Fermi energy shifts upon doping, which can be calculated if the accurate stoichiometry of the alkali doped tubes is known. We obtain that the pristine SWCNTs has $D(\epsilon_F) = 5.3 \cdot 10^{-3}$ states/eV/atom and for a KC_8 stoichiometry this is increased to $D(\epsilon_F) = 0.095$ states/eV/atom. The 20 fold increase follows from the number of van Hove singularities in the DOS of the SWCNTs. The considered KC_8 stoichiometry is close to the saturated alkali doping. Unfortunately, the above described uncertainty related to the ESR signal intensity measurement does not allow an accurate comparison and we obtain the experimental DOS with a large absolute error bar: $D(\epsilon_F)_{exp} = 0.1 \pm 0.05$ states/eV/atom.

Nevertheless, taken the signal-to-noise ratio for the doped sample, we can state that a 20 times smaller signal could be firmly observed. Therefore, the CESR of the itinerant electrons should be observable if they had a signal intensity corresponding to the above DOS. Since we do not observe this signal, we are lead to conclude that the CESR in the pristine tubes is unobservable due to other reasons, e.g. due to the TLL nature of their ground state.

As mentioned above, the ESR line-width also carries important information about the metallic systems. In general, when an ESR line is relaxationally (i.e. homogeneously) broadened, which is the usual case for metals, the spin-lattice relaxation time is given by $T_1 = 1/\gamma\Delta H$, where $\gamma/2\pi = 28$ GHz/T is the gyromagnetic ratio of electrons. The knowledge of T_1 is vital for applications of SWCNTs in spintronics as this characterizes how fast a spin-polarized current loses its spin state [15]. To this end, we measured the temperature dependence of the ESR line-width in the 4-300 K range (data not shown) and we found that it does not show an appreciable temperature dependence. This is interesting in the view of the absence of temperature dependence of the microwave conductivity and points that the so-called Elliot-Yafet (EY) spin-relaxation mechanism is observed in the doped SWCNTs [16,17].

The EY theory states that the ESR line-width and the resistivity are proportional in metals. In other words, the T_1 and the momentum relaxation time, τ are proportional, the two being inversely proportional to the ESR line-width and the resistivity, respectively. The EY relation has been established for all elemental metals [16,18] and for a number of correlated metals where CESR has been observed [19]. The EY relation originates in the fact that conduction electron wave functions are not pure Zeeman states but are admixtures of the spin up and down states due to spin-orbit coupling. As a result, scattering on phonons or impurities can induce electron spin flip. The temperature independence of both the ESR line-width and the microwave resistivity suggest that τ is independent of the temperature. In usual metallic systems, this arises due to a large number of scattering centers, such as vacancies or impurities. In SWCNTs, the imperfectness naturally arises from the fact, that apart from the well defined chirality of the individual tubes, the ensemble SWCNT sample is not a crystal in any solid state physics sense. The situation would be very different for mono-chiral SWCNT samples or for individual tubes. However, such samples are not available in quantities required for ESR.

4 Summary In summary, we observed conduction electron spin resonance for SWCNTs doped with K using a solid state reaction. The development of the CESR line is particularly clear for SWCNTs based on non-magnetic catalysts. The Pauli susceptibility, deduced from the ESR signal intensity, agrees with band structure results. The temperature independence of the ESR line-width and the

microwave resistivity indicates that the doped tubes behave as bad metals due to the lack of any crystalline order. It also suggests that the Elliott-Yafet theory of electron spin-lattice relaxation is valid for this system.

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