Magnetic properties of multi-walled carbon nanotubes modified with cobalt

Magnetische Eigenschaften von mit Kobalt modifizierten mehrwandigen Kohlenstoffnanoröhren

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Magnetic properties of multi-walled carbon nanotubes (MWCNT) modified with cobalt were studied in detail in the temperature range (4.2–290) K. MWCNT which encapsulate Co nanoparticles were obtained using CVD methods. The low temperature SQUID magnetization measurements were supplemented by structural investigations with thermogravimetric analysis, HRTEM and SEM.

Keywords: MWCNT with cobalt / CVD / SQUID / magnetic susceptibility / hysteresis

Die magnetischen Eigenschaften von mit Kobalt-modifizierten mehrwandigen Kohlenstoffnanoröhren (MWCNT) wurden im Detail in einem Temperaturbereich von 4,2 bis 290 K untersucht. Die MWCNT mit Kobalteinschlüssen wurden durch CVD Methoden erhalten. Die bei niedrigen Temperaturen gemessenen SQUID Magnetisierungen konnten durch Strukturuntersuchungen mit thermogravimetrischen Analysen und Rasterelektronenmessungen ergänzt werden.

Schlüsselwörter: MWCNT mit Kobalt / CVD / SQUID / Magnetische Suszeptibilitat / Hysterese

1 Introduction

Carbon nanotubes (CNT) exhibit unique physical properties [1–2], in particular, they are chemically and thermally stable, characterized by high mechanical strength, thermal and electrical conductivity, large specific surface area. Now CNT are regarded as the most attractive building blocks for nanoelectronics: they are able to form a perfect spin-transport medium, since electron transport in them is one-dimensional and ballistic with a long spin relaxation time and weak spin-orbital effects. Also, even pure CNT, which are non-magnetic materials, are characterized by a giant magneto-resistance [3–4]. On the other hand, it is quite obvious that modification of CNT (intercalation and filling the internal cavities with different elements) would lead to significant differences in their electronic structure and properties [5–7]. Due to very large magnetic shape anisotropies, the encapsulation of magnetic phases in CNT could provide a feasible approach to achieve a magnetic order stabilization against a thermal fluctuations in systems having extremely reduced dimensions. Also, the ferromagnetic nanoclusters are expected to have much better magnetic properties than bulk metals due to their single domain nature [8].

Therefore, it is desirable to produce CNT with magnetic material inside of the tubes in a specific and controlled way. Beyond the geometrical advantage of a quasi one-dimensional CNT design, the carbon shells can provide an effective protection against oxidation. It is especially important, since applications of ferromagnetic nanoclusters are limited due to air oxidation. Finally, except for the interest related to practical applications, a study of these magnetic systems provides an avenue for the exploration of the magnetic order physics in close-to-one-dimensional structures. In particular, a number of fundamental questions can be addressed about the role of spin degrees of freedom in the quantum wires or Luttinger liquid, where specific effects associated with the spin-harge separation are expected.

Thus, the purpose of this work was to study magnetic characteristics of multi-walled CNT (MWCNT) modified with cobalt as a function of the magnetic field and temperature.

2 Experimental

Chemical vapour deposition (CVD) was used to produce CNT filled with cobalt. Basically, the growth process involved heating of a catalyst material to high temperatures in a tube furnace. It

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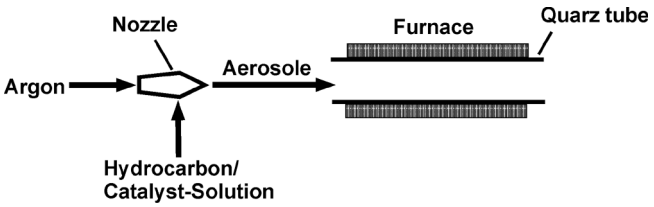

Fig. 1. Principle scheme of a spray pyrolysis reactor for the production of CNT

Bild 1. Schema eines Spraypyrolysereaktors zur Herstellung von CNT.

was followed by the injection of a hydrocarbon gas, being the carbon source, through the tube reactor for a chosen growth time. Then, under the flow of an inert gas to prevent oxidation of the carbon species, the system was cooled down to the room temperature. Finally, the carbonaceous materials grown over the catalyst have been collected.

In the course of CNT growth the key parameters were the chosen hydrocarbons, catalysts and the growth temperature. They were all together responsible for the properties of the obtained tubes. Our method was based on the catalytic decomposition of benzene (as the carbon source) and cobalt acetylacetonate (source of cobalt) in a tube furnace at different temperatures.MWCNT have been synthesized by simultaneous deposition of catalytic amounts of cobalt and carbon on the walls of a quartz tube reactor, *Fig. 1*. In the process the cobalt acetylacetonate decomposed and has provided the cobalt particles required for the nucleation of the CNT. After the reaction cobalt clusters were found inside of the CNT, whereas the aliened nanotubes have grown on the quartz glass reactor wall.The tube reactor has been placed in a furnace at 900 °C and connected to a gas inlet system. The synthetic route involved the spray pyrolysis of a cobalt acetylacetonate/benzene solution in an Ar atmosphere. To obtain short and well defined CNT the spraying time was held between 1 and 4 min. The control of the CNT length and diameter has been possible through the spraying time, the argon flow and the concentration of the catalyst solution. After slowly cooling down the furnace under argon (20 °C/min) the CNT formed well defined aligned layers on the tube walls, which can be mechanically removed from the tube.

The characterization of the products was performed by a scanning electron microscope (SEM, FEI XL30 LaB_6), *Fig. 2*. Samples have been glued to an alumina holder with silver paste and covered by 10 nm thick gold/palladium layers in an ion beam evaporator for contrast and stability reasons. Measurements have been mainly done with 30 kV acceleration voltage and variable electron spot size between 5 nm and 20 nm, depending on the magnification. High-resolution transmission electron microscopy (HRTEM) was done with a Philips TECNAI 20 S-TWIN apparatus with 200 kV, Fig. 2. Micrographs have been recorded with a 1024×1024 pixel CCD-Camera. For the CNT characterisation, the resolution (line resolution 0.14 nm, point resolution 0.24 nm) was suitable to resolve single carbon layers. Magnifications of up to 690,000 × s have been achieved. The thermogravimetric analysis (TG, Sartorius MC5) in air was used too for characterization of the samples. From SEM and TG we estimated that the content of MWCNT in the samples was higher

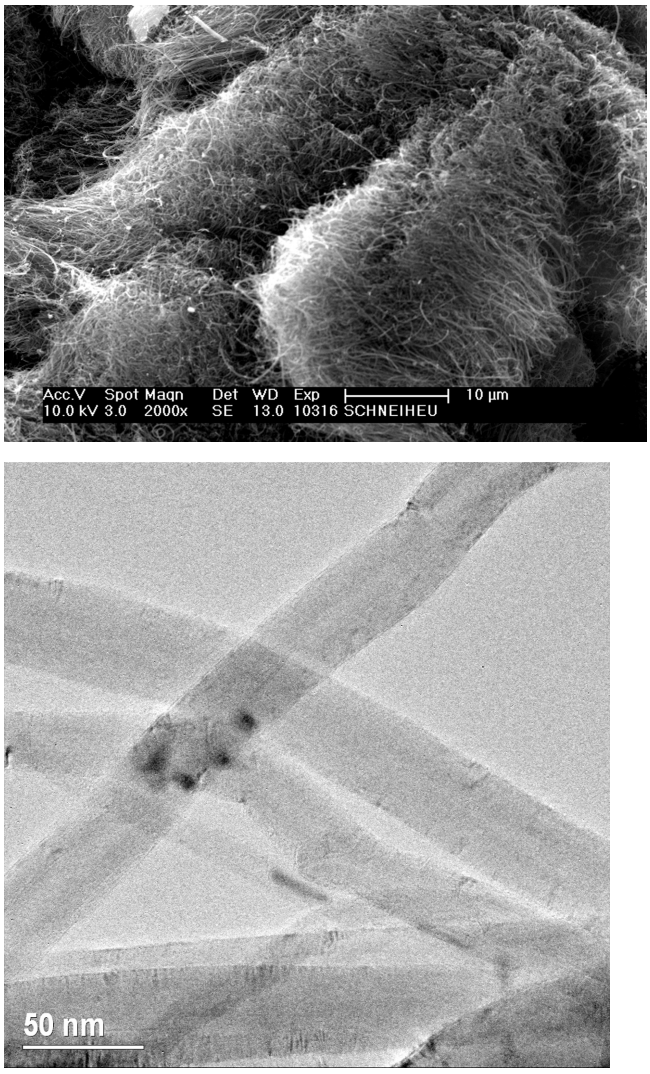

Fig. 2. SEM and HRTEM pictures of the MWCNT with Cobalt. Dark spots denote metal nanoparticles (Pictures taken with: SEM FEI XL30 LaB6; HRTEM Philips TECNAI 20 S-TWIN).

Bild 2. SEM und HRTEM-Bilder von MWCNT mit Kobalt. Dunkle Punkte sind Metallnanopartikel. (Bilder aufgenommen mit: SEM FEI XL30 LaB6; HRTEM Philips TECNAI 20 S-TWIN, 200kV)

than 90%. The diameter of the formed CNT was directly related to the cobalt cluster diameter. Therefore we could observe an increasing CNT diameter by increasing the cobalt acetylacetonate concentration.

In the low temperature range (4.2–290 K) the magnetic properties of the cobalt filled CNT were studied by an in-house SQUID (Superconducting Quantum Interference Device) magnetometer [9] in fields of up to 50 kOe with an absolute error not larger than about 10^{-6} emu for the measured magnetic moments. For the magnetization studies the samples were prepared by compacting the Co-encapsulated CNT powder (mass about 10 mg inside of an elongated aluminum foil cylinder with diameter of 1.5 mm and about 7 mm in length). For all measurements, the applied magnetic field was aligned along to the cylinder axis in order to minimize the effect of the demagnetization

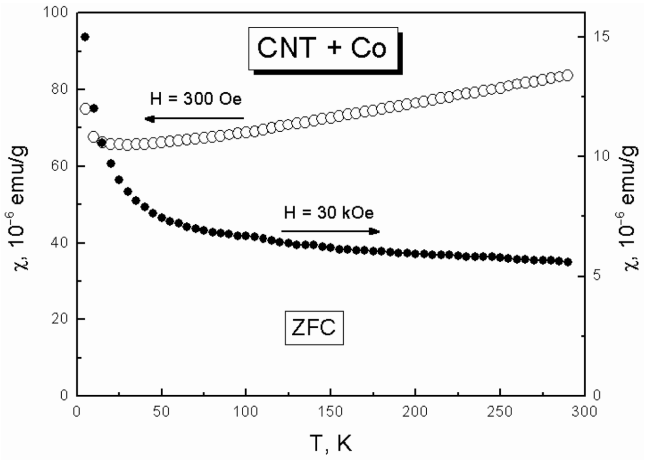

Fig. 3. Temperature dependences of magnetic susceptibility for fields *H*=300 Oe and 30 kOe.

Bild 3. Temperaturabhängigkeit der magnetischen Suszeptibilität für Felder *H*=300 Oe und 30 kOe.

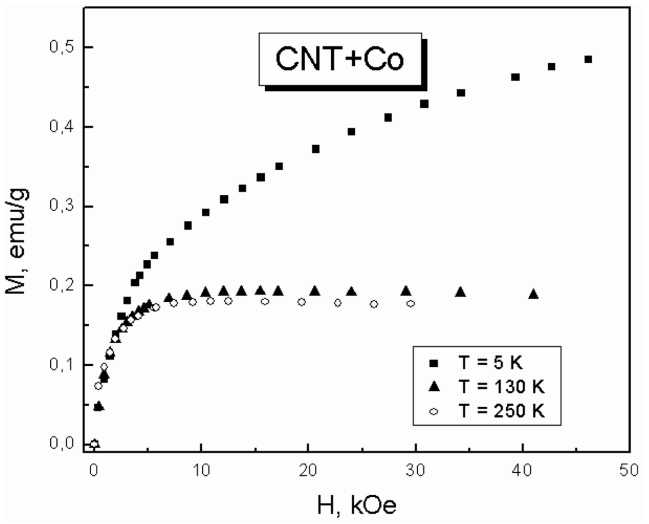

Fig. 4. Magnetization of MWCNT + Co at temperatures 5, 130, and 250 K.

Bild 4. Magnetisierung von MWCNT+Co bei 5, 130 und 250 K.

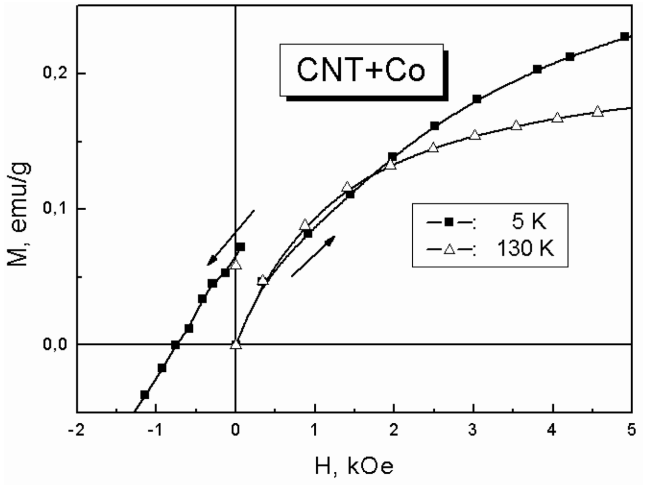

Fig. 5. Hysteresis effects in magnetization of MWCNT+Co at temperatures 5 and 130 K.

Bild 5. Hystereseeffekt in der Magnetisierung von MWCNT + Co 5 und 130 K.

in the magnetization data. The magnetization measurements were made after cooling the sample from room to helium temperature in a zero magnetic field (zero-field-cooled, ZFC). Then the temperature dependences of the magnetization *M(T)* were measured under a slow heating with the rate of about 1.5 K/min in the applied magnetic fields H = 300 Oe and 30 kOe. The field dependences of the magnetization were also measured for ZFC regime in magnetic fields up to 46 kOe at temperatures T = 5, 130 and 250 K.

3 Results and discussion

In *Fig. 3* we present the temperature dependences of the magnetic susceptibility $\chi(T)$, which were obtained for two values of the magnetic field: H = 300 Oe and 30 kOe. One can see, that substantially higher values of the magnetic susceptibility, rising with temperature, were observed in the lower field. Presumably, this points to the presence of comparatively large ferromagnetic clusters, since their contribution to the susceptibility decreases with the rising magnetic field due to the saturation effect. On the other hand, a very different behaviour of $\chi(T)$ was observed in the high magnetic field of 30 kOe, Fig. 3. The decreasing of χ with temperature and a conspicuous Curie-Weiss-like behaviour at low temperatures can be caused by the superparamagnetism of very small Co nanoparticles. The absence of a blocking temperature is noticeable in Fig. 3. The assumed superparamagnetism at low temperatures should give rise to a slow saturation of the magnetization at higher fields and, consequently, its increased relative contribution to the susceptibility.

Such expectations are actually in accord with the results of our magnetization measurements at different temperatures, presented in *Fig. 4*. In view of the lack of saturation at higher fields at low temperatures (5 K), there is a noticeable superparamagnetic behaviour of the studied sample. At the same time, at high temperatures this superparamagnetism appeared to be substantially less pronounced, and one can see a clear saturation achieved in the fields above 10 kOe for relatively large ferromagnetic clusters seen in the TEM picture, Fig. 2. From the listed *M(H)* data for T = 130 and 250 K, the saturation magnetic moment of about 0.17 emu/g was found, which appeared to be weakly dependent on temperature. Taking into account this value and the saturation moment of cobalt, we can roughly estimate the amount of Co in "large" magnetic clusters as about 0.1% of the sample mass. In fact, this estimation has provided only a rough lower limit of the cobalt content in the sample, due to unknown saturation of the superparamagnetic nanoparticles.

The existence of "large" magnetic clusters in the MWCNT + Co sample provides a hysteresis effect in the magnetization, presented in *Fig. 5* for temperatures 5 and 130 K. Basically, the sketched *M(H)* dependences correspond to ones given in Fig. 4.

The additional magnetization data in Fig. 5 were obtained when the imposed magnetic field has been turned off, and then driven back in the opposite direction (for T = 5 K only). As seen from Fig. 5, at temperatures 5 and 130 K the remanent magnetization values were 0.068 and 0.058 emu/g, respectively. Corresponding to the existence of a spontaneous magnetic moment there is a coercive field (about 750 Oe at T = 5 K), which appeared to be weakly dependent on temperature.

4 Conclusions

The synthesized MWCNT modified with cobalt were investigated with respect to their magnetic properties. Our magnetization studies have indicated that Co nanoclusters were formed with a substantial size distribution from few to tens nanometers. The larger particles are ferromagnetic up to 300 K with the coercive field of about 750 Oe. The smaller nanoparticles are responsible for a pronounced superparamagnetism observed at low temperatures. The existence of a spin glass state and the interactions between nanoparticles of various sizes could contribute to the observed magnetic behaviour.

Acknowledgments

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