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Magnetic order and superconductivity observed in bundles of double-wall carbon nanotubes

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ABSTRACT

The magnetotransport properties were studied in hundreds of micrometer length double-wall carbon nanotubes (DWCNT) bundles. Above 15 K the resistance shows an ohmic behavior and its temperature dependence is well described using the variable-range hopping for one-dimensional system. The magnetoresistance is negative and can be explained using an empirical model based on spin-scattering processes indicating the existence of magnetic order up to room temperature. At temperatures between 2 and 15 K the resistance is non-ohmic and the current–voltage characteristics reveal the appearance of a potential, which can be well described by a fluctuation-induced tunneling conduction model. In this low temperature range and at low enough input current, a positive magnetoresistance appears – in addition to the negative one – with an extraordinary hysteresis in field and vanishes at $T \sim 15$ K, suggesting the existence of a superconducting state. Magnetization results partially support the existence of both phenomena in the DWCNT bundles.

1. Introduction

The search for superconductivity and magnetic order in carbon-based materials triggered a large number of studies in recent years. Experimental as well as theoretical works indicate that magnetic order at high temperatures in graphite is possible through the influence of vacancies and/or hydrogen (for recent reviews see [1,2] and refs. therein). In contrast to graphite and in spite of theoretical predictions on the possibility to have magnetic order due to hydrogen or vacancies in carbon nanotubes (CNT) [3–5], the observation of this phenomenon in these carbon structures appears to be more difficult. Apparently, only the hydrogenated CNT prepared in [6,7] showed the existence of magnetic order at room temperature. However, and in clear contrast, several studies reported the existence of superconductivity through measurements in single nanotubes as well as bundles of them (single- and multi-wall) [8–15]. Apparently, the critical temperature obtained for the CNT depends on the sample and the experimental method used; it ranges between ~0.5 and ~15 K.

The origin of the observed superconductivity in CNT is still under debate. Maxima in the electronic density of states,

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called van Hove singularities, have been used as possible origin for the superconducting-like signals measured after application of a gate voltage [15], purely electronic mechanism in certain geometries of ultra-small diameter ($\lesssim 2$ nm) [16], an overwhelming attractive electron–phonon interaction in double-wall CNT (DWCNT) specially when the outer tube is metallic [17], are some of the theoretical concepts one finds nowadays in recent studies predicting superconductivity in CNT.

In this experimental work, we studied the electrical transport properties of bundles of, mostly, DWCNT as a function of temperature and magnetic field. The observed negative magnetoresistance of the CNT-bundle in the whole temperature range indicates the existence of spin dependent scattering processes up to room temperature, similar to that found in materials with defect-induced magnetism (DIM), see e.g., [18]. We found that an extra contribution to the magnetoresistance appears at $T < 15$ K and at low enough input currents. This fact and the observed positive magnetoresistance with its hysteretic behavior suggest the existence of superconductivity in a similar temperature range as the one found recently in DWCNT [11] as well as in pyrolytic graphite flakes under an electric field [19]. The temperature dependence of the magnetization, its hysteresis and other features support also the existence of magnetic order and to some extent of superconductivity.

2. Experimental details

2.1. Carbon nanotubes synthesis

The used procedure to synthesize the CNT was the following: The wafers for the growth substrates were prepared by e-beam evaporation (base pressure between 7×10^{-7} and 2×10^{-6} Torr) where 1.2 nm Fe and 10 nm Al_2O_3 films were deposited on 4 inches diameter silicon wafers. The gases used for the carbon nanotubes (CNT) growth were Ar (99.9995%, Maxima), C_2H_4 (99.5%, Maxima), H_2 (99.999%, Maxima), and a mixture of 99% Ar with 1% oxygen, which we will denote as Ar/O_2 (Maxima). The flows were maintained using electronic mass flow controllers (MKS, model 1179A). The experiment was performed on 0.5 cm^2 catalyst substrates and with the same gas preheating and fast heating techniques previously described [20,21]. The synthesis were performed using a fused-silica tube (internal diameter of 22 mm) placed in two atmospheric-pressure tube furnaces (Lindberg Blue) with controlled flows of the source gases – Ar, H_2, C_2H_4, and Ar/O_2. The first furnace (set at 770 °C) preheated the gases. The growth substrate was positioned in the second furnace (at 755 °C) for the annealing and growth steps. The substrate were inserted into the furnace for a 15 min anneal with 100 sccm of Ar and 400 sccm of H_2, followed by a 30 min growth cycle with 100 sccm of Ar, 100 sccm of Ar/O_2, 400 sccm of H_2 and 200 sccm of C_2H_4. At the end of CNT growth, the H_2 and C_2H_4 were turned off and the substrate was post-annealed in the remaining Ar and Ar/O_2 for 2 min. Then the Ar/O_2 gas was turned off, and H_2 gas was turned on for an additional minute of anneal. Then the H_2 gas was turned off, and the sample was removed from the heated zone and positioned above a cooling fan (with Ar still flowing within the tube) until it was cool enough to be removed for characterization.

2.2. Characterization methods

The morphology of the CNT was examined using scanning electron microscopy (SEM, Quanta FEG 250), high-resolution transmission electron microscopy (HRTEM, JEOL 2010) and a dual beam microscope NovaLab XT200 from FEI. Fig. 1 shows two TEM pictures where we can recognize the double-wall and the diameter of the CNT. Fig. 2 shows scanning electron microscope (SEM) pictures of the measured bundles with the voltage–current electrodes at the edges (a). In Fig. 2(b) we can recognize that most of the CNT are connected. Although we could not measure directly the transport response of a single interconnection, we speculate that these may have some contribution on the observed behavior we describe below. Information about the elemental composition of the bundles was obtained from energy dispersive X-ray (EDX) analysis. Any traces of magnetic elements like Fe, Ni, etc., were below the experimental resolution of 50 ppm. However, from recently published studies [22] we know that EDX analysis is not really appropriate to find and characterize traces of magnetic impurities embedded in carbon-based materials. Therefore a further characterization of the magnetic impurities has been made using particle induced X-ray emission (PIXE), a method that provides better resolution and other advantages in comparison to EDX [22]. The PIXE results indicate the existence of Fe dispersed within the bundle of DWCNT with a concentration $\lesssim 250 \pm 50$ μg Fe per gram of carbon, a concentration equivalent to $\lesssim 60 \pm 15$ ppm Fe. This concentration is not relevant for electrical transport measurements, because the small amount of Fe-based grains are dispersed and likely attached either at some of the edges and/or at the surface of the DWCNT. However, if this Fe concentration shows magnetic order, it might provide a clear contribution to the total magnetization of the bundles and will be taken into account in the discussion. The concentration of other magnetic impurities is more than one order of magnitude below that of Fe and therefore not relevant for the interpretation of the results.

Micro-Raman spectrum was obtained at room temperature and ambient pressure with a Dilor XY 800 spectrometer at 514.53 nm wavelength and a 2 μm spot

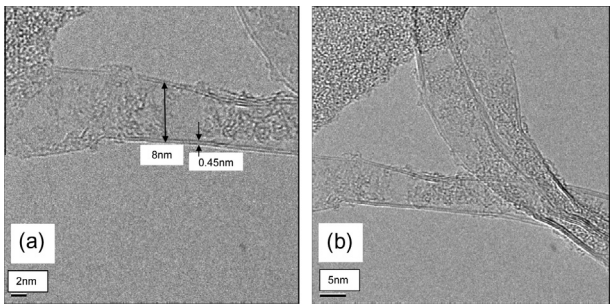

Fig. 1 – Transmission electron pictures of the measured DWCNT.