Pressure dependence of Raman modes in double wall carbon nanotubes filled with α-Fe.

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The preparation of highly anisotropic one-dimensional (1D) structures confined into carbon nanotubes (CNTs) in general is a key objective in CNTs research. In this work, the capillary effect was used to fill double wall carbon nanotubes with iron. The samples are characterized by Mössbauer and Raman spectroscopy, transmission electron microscopy, scanning area electron diffraction, and magnetization. In order to investigate their structural stability and compare it with that of single wall carbon nanotubes (SWNTs), elucidating the differences induced by the inner-outer tube interaction, unpolarized Raman spectra of tangential modes of double wall carbon nanotubes (DWNTs) filled with 1D nanocrystallin α-Fe excited with 514 nm were studied at room temperature and elevated pressure. Up to 16 GPa we find a pressure coefficient for the internal tube of 4.3 cm^{-1} GPa^{-1} and for the external tube of 5.5 cm^{-1} GPa^{-1}. In addition, the tangential band of the external and internal tubes broadens and decreases in amplitude. All findings lead to the conclusion that the outer tube acts as a protection shield for the inner tubes (at least up 16 GPa). Structural phase transitions were not observed in this range of pressure.

Keywords: carbon nanotubes; Raman scattering; high pressure

1. Introduction

Aiming at using the carbon nanotubes (CNTs) as a nanohost to template the growth of one-dimensional objects, numerous authors have tried to fill CNTs, firstly multiwall carbon nanotubes (MWCNTs) [1–5], then single wall carbon nanotubes (SWCNTs) [6,7], with transition ferromagnetic metals, e.g. Fe, Co, Ni. In the case of iron filling, ferrocene was used as iron source, which was subsequently reduced at rather high temperatures, 850 °C–1050 °C. As a result, a mixture of cementite, γ-Fe and α-Fe was obtained [2–4]. Other groups have reported Fe filling, but without clearly specifying its nature [6,7]. More recently, clear evidence of the presence of α-Fe in MWCNTs of 20–25 nm, starting with ferrofluids (10 nm magnetite particles) was reported [5]. In this work, we have followed a novel approach [8] to the filling of double wall carbon nanotubes

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(DWCNTs), in which the external wall protects the internal one, which maintains its structure and chemical and physical properties. This fabrication process uses the capillary effect to achieve the filling of the nanotubes. In practice, the DWNT is placed in an aqueous solution of an iron precursor which is adsorbed in the hollow internal tube [7]. Our work may prove relevant in paving the road for the advanced use of Fe-filled DWCNTs as functional materials for sensing and electronic devices which could combine the advantages of charge and spin electrons for transport. In this work, we study the effect of high-pressure on DWNTs filled with Fe by means of Raman spectroscopy, in order to investigate their structural stability and compare it with that of SWNTs, elucidating the differences induced by the inner–outer tube interaction.

2. Experimental

DWCNTs were produced by catalytic chemical vapour deposition from a H_2-CH_4 mixture (18 mol % CH_4, heating and cooling rates 5 °C/min, maximum temperature 1000 °C, no dwell) using oxide (Mg, Co, Mo)O catalysts [9,10]. For the characterization of the Fe DWCNTs we adopted the following procedure:

(1) To identify the state of iron we used Mössbauer Spectroscopy (MS) at the 14.4 keV transition of ^{57}Fe, with a ^{57}Co in Rh source. The spectrometer was run in the triangular symmetric mode and calibrated with bulk α-Fe. The spectra were fitted with lorentzian shapes for the lines and a limited number of free parameters for each subspectrum, e.g. isomer shift (IS, relative to α-Fe), HWHM (GA), quadrupole splitting and the hyperfine field.
(2) The morphological and structural analysis of the sample was carried out using a combination of transmission electron microscopy (TEM) at different levels of resolution, TEM (JEOL JEM 1011), HRTEM (JEOL JEM 2100F), and scanning area electron diffraction (Phillips CM120).
(3) Raman spectra of the DWNTs were recorded in the back-scattering geometry using a micro-Raman, triple grating system (DILOR XY800) equipped with a cryogenic CCD detector. The spectral resolution of the system was about 1 cm^{-1}. High-pressure Raman measurements were carried out using a membrane cylindrical type diamond anvil cell. The 4:1 methanol–ethanol mixture was used as pressure transmitting medium and the ruby fluorescence technique was used for pressure calibration. For excitation, the 514 nm line of an Ar+ laser was focused on the sample by means of a 20× objective, while the laser power was kept below 5 mW, measured directly before the cell, in order to eliminate laser-heating effects on the probed material and the concomitant softening of the observed Raman peaks. The phonon frequencies were obtained by fitting Lorentzian functions to the experimental peaks.

3. Results

A TEM analysis of the sample gave us the first indications of the filling of the DWCNTs with iron. The experimental results indicate the presence of α-Fe nanowires inside the DWCNTs, with 1.5 nm average internal diameter and 2.2 nm average external diameter. The electronic state of iron was characterized using ^{57}Fe MS. In Figure 1(a) the room temperature spectrum indicates the predominant presence of the characteristic sextet of α-Fe (∼95%) and a small contribution of a doublet, attributable to a superparamagnetic oxide (∼5%). This is confirmed by observing the spectrum at 47 K in Figure 1(b), where in addition to the α-Fe spectrum, a slow relaxation magnetic spectrum due to the small superparamagnetic particles can be seen particularly by the presence of weak broad lines at high velocities (at app. +8, −8 cm/s). For a detailed analysis

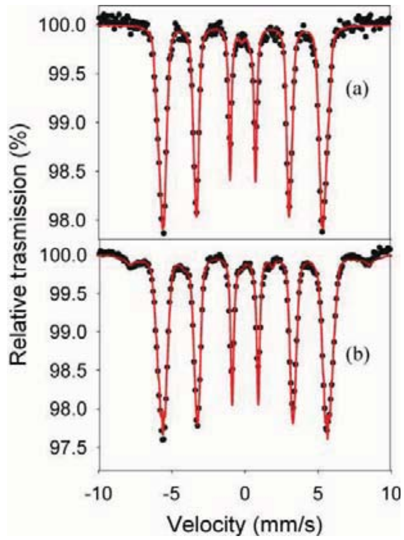

Figure 1. Mössbauer spectra of the Fe in DWCNTs (a) at 293 K and (b) 47 K temperatures.

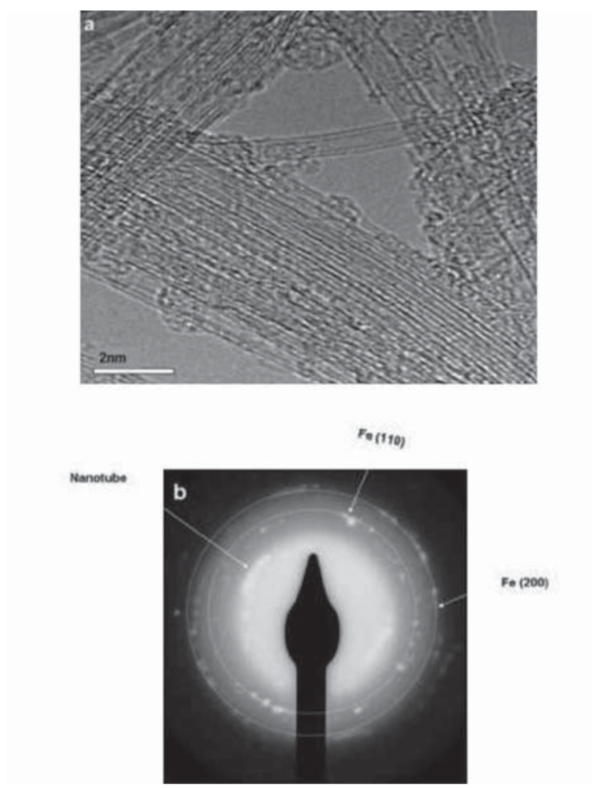

Figure 2. (a) HRTEM image, (b) selected area electron diffraction on bundles.

of Mössbauer results, see [10]. It is remarkable that in this work we obtained almost only α-Fe, whereas other authors obtained cementite (Fe_3C, 20%), γ-Fe (32%) and α-Fe (48%) in samples of Fe in MWCNTs prepared using other preparation techniques [2–4].

Figure 2(a) shows three bundles in three different directions and also a partial view of an isolated nanotube. In the lower part of the figure the bundle observed has a diameter $d_B = 12$ nm, which in the two-dimensional packing hexagonal model [11] could correspond to 40 DWCNTs. In Figure 2(b) there are two rings corresponding to α-Fe, the (110) and the (200). Those rings are non-continuous, indicating that there are preferential orientations of the Fe nanowires. We also indicate reflections (002) due to the DWCNTs ('nanotube' in the figure), corresponding to the inter-graphene distance $d = 3.37$ A of the two graphene layers of the double wall (here also the preferential orientations mentioned above are clear). Figure 3 shows at normal pressure the tangential modes and the D band which corresponds to the double resonance induced by the defects in the CNTs. The high value of the intensity ratio of the tangential external mode and the D band indicates that the crystalline quality of the nanotubes is rather good. Also, the larger intensity of the external mode with respect to the internal one indicates that in this sample the chiralities correspond predominantly to semiconductor nanotubes, with an important concentration of metallic ones, as confirmed by the presence of the band observed around 1508 cm^{-1}. Table 1 reports the frequency and width of the Raman peaks as extracted from spectra through Lorentzian fit. In the diamond anvil cell the low frequency radial breathing modes and the Raman confined modes of α-Fe nanowires were not observed (50–300 cm^{-1} range). The tangential optical phonon modes of the CNTs are sensitive to the in-plane stress and split into two contributions associated respectively with the external and internal tube. Figure 4 shows the Raman spectra as a function of applied pressure in the high frequency range obtained using the methanol–ethanol pressure medium. We

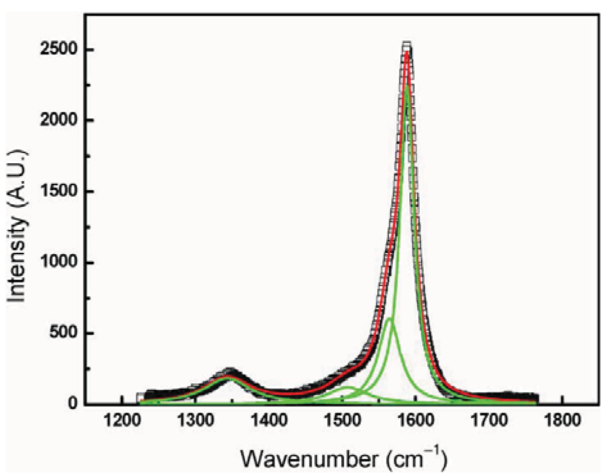

Figure 3. Raman spectra of tangential modes and D band region at normal pressure outside the diamond pressure cell.

Table 1. Fe in DWCNT frequencies and FWHM of phonons in the tangential modes region.

Wavenumber (cm^{-1})	Width
1343.6 ± 0.5 (D)	78 ± 2
1508 ± 1 (metallic)	68 ± 4
1564.4 ± 0.3 (internal)	37 ± 1
1588.45 ± 0.04 (external)	23.6 ± 0.1

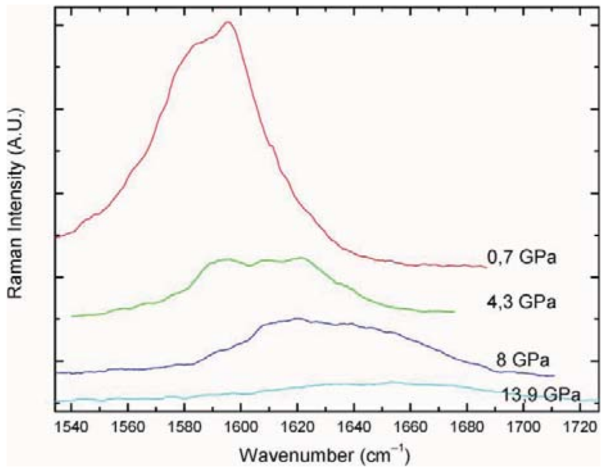

Figure 4. Raman Spectra of DWCNT in Fe at different pressures.

observe a splitting of the G band, the in-plane zone-center optical phonon mode of graphite. The splitting can be attributed to the internal and external tubes as will be shown below [12]. As observed with increasing pressure, the tangential modes shift towards higher wavenumbers and, in addition, the tangential band of the external and internal tubes broadens and decreases in amplitude. The band frequencies are shown as a function of applied pressure in Figure 5. The experimental points are fitted with a linear law up to 16 GPa and we find a pressure coefficient for the internal tube of 4.3 cm^{-1} GPa^{-1} and for the external tube of 5.5 cm^{-1} GPa^{-1}. The corresponding Raman features of the internal tubes appear to be less sensitive to pressure. All findings lead to the conclusion that the outer tubes act as a protection shield for the inner tubes (at least up 16 GPa). At 10 GPa the α-Fe nanowire does not undergo bcc-hcp phase transition. This has been confirmed with X-ray diffraction measurements under pressure in MWCNTs filled with α-Fe nanowires [13]. However, an increase in the transformation pressure in nanocrystalline materials compared to the bulk has also been observed in other materials.

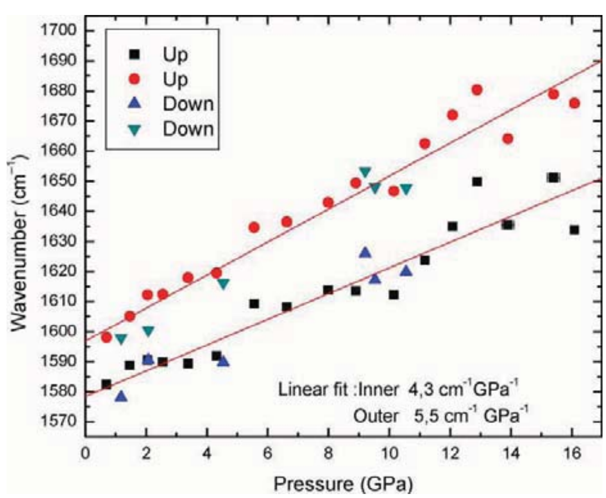

Figure 5. Pressure dependence of tangential modes of DWCNT in Fe for the inner and outer tubes.

4. Conclusions

In first instance the adopted chemical wetting method was successful, and iron entered almost all as α-Fe inside DWNTs and gives the opportunity to distinguish pressure induced spectral changes from internal and external walls in multiwall CNTs. The splitting of the G-band can be explained by considering a tangential discontinuity of the stress component as one goes from the external wall to the internal tube. The ratio of the pressure coefficient of internal and external walls remains the same, independent of the medium. All findings lead to the conclusion that the outer tubes act as a protection shield for the inner tubes (at least up to 16 GPa). For the applications, the fact that α-Fe is in the form of nanowires and also has striking ferromagnetic properties at room temperature, make this material promising for magnetic probes, atomic force microscopy (AFM) tips, and nanodevices for spin electronics.

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