Pressure-induced phase transitions in iron-filled carbon nanotubes: X-ray diffraction studies

Sukanta Karmakar,[1] Surinder M. Sharma,[1] P. V. Teredesai,[2] and A. K. Sood[2,3]
[1]*Synchrotron Radiation Section, Bhabha Atomic Research Centre, Mumbai 400085, India*
[2]*Department of Physics, Indian Institute of Science, Bangalore 560012, India*
[3]*Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research Centre, Jakkur Campus, Jakkur, Bangalore 560 064, India*
(Received 8 September 2003; revised manuscript received 12 January 2004; published 27 April 2004)

High-pressure x-ray-diffraction studies have been carried out upto 20 GPa on iron-filled multiwalled carbon nanotubes (MWNTs). The pressure dependence of the intertubular spacing d_0 of the filled MWNTs shows a sharp change at 9 GPa which is not observed in pristine MWNTs. The iron present as nanowires inside the MWNT is in the form of α-Fe and Fe_3C. Both of these phases show higher compressibility than their bulk form. Most interestingly, the structural modification of MWNTs at 9 GPa coincides with an iso-structural phase transition in the encapsulated Fe_3C, in sharp contrast to the absence of a transition in the bulk Fe_3C upto 70 GPa.

DOI: 10.1103/PhysRevB.69.165414 PACS number(s): 61.46.+w

INTRODUCTION

Carbon nanotubes are amongst the most exciting new materials being investigated because of their potential uses in new technologies and devices exploiting their unusual mechanical and electrical properties.[1,2] In particular, multiwall carbon nanotubes (MWNTs) are of interest to the growing microfluidic and nanofluidic industry.[3] These MWNTs are composed of several concentric cylindrical graphene tubules, with an intertube separation d_0 of $\sim$3.4 to 3.9 Å, which increases with decreasing radii.[4] Recently the synthesis of various metal filled carbon nanotubes has also been achieved successfully.[5–8] There have been a number of theoretical and experimental studies related to elasticity, strength, and toughness of MWNTs.[9–14] High-pressure x-ray-diffraction experiments on pristine MWNTs show that these nanotubes become partly amorphous when compressed above 8 GPa.[15] In addition, recent Raman scattering investigations on MWNTs show a small change in slope of the high-frequency tangential modes at $\sim$1 GPa, which has been attributed to the reversible flattening of the nanotubes.[16] While the metal filling does not significantly change shape and size of the nanotubes, it can affect the mechanical properties significantly. Molecular dynamics simulations[17] have shown that the buckling force of single-walled carbon nanotubes (SWNTs) is increased when filled with C_{60}, CH_4, and Ne. However, there is no high-pressure experimental study so far to understand the effect of filling on the elastic properties and stability of single-walled as well as multiwalled carbon nanotubes. In addition, such experiments will also help to understand the high pressure behavior of the nanocrystalline metallic wires or particles which are formed inside the nanotubes. With a view to understand the effect of metal filling on MWNTs, we have carried out high-pressure angle dispersive x-ray-diffraction experiments on pure and Fe-filled MWNT. A sharp change is seen in the intertubular distance d_0 in Fe-filled MWNTs at $\sim$9 GPa, in sharp difference to the pristine MWNTs. Encapsulated iron in the nanotubes is in the form of α-Fe and Fe_3C.[7,18] The pressure behavior of these nanocrystalline forms of α-Fe and Fe_3C are investigated and are shown to be very different from their bulk counter parts.

EXPERIMENTAL DETAILS

Fe-filled multiwall carbon nanotubes prepared by pyrolysis of ferocene along with acetylene using a two-stage furnace are same as described in Ref. 7. TEM studies show the presence of nanowires encapsulated inside carbon nanotubes.[7] High-resolution electron microscope image (Fig. 2 of Ref. 7) shows that there is no free space between the metal nanowire and the carbon nanotube. The nanowires show a distribution in their diameter and length, the diameter being in the range of 10–20 nm and the length in the 200–800 nm range. In addition to the nanowires, a small portion of iron nanoparticles, with 20–40 nm diameter, covered with graphite layer were also found.

For the purpose of high pressure experiments Fe-filled MWNTs (along with a few specs of gold) were loaded in a hole of $\sim$120 μm diameter drilled in a preindented ($\sim$70 micron) steel gasket of a Mao-Bell kind diamond-anvil cell (DAC). Methanol:ethanol:water(16:3:1) mixture was used as pressure transmitting medium which provides hydrostatic pressure environment until $\sim$15 GPa. The pressure was determined from the known equation of state of gold.[19] High-pressure angle dispersive x-ray-diffraction experiments, were carried out up to $\sim$20 GPa, at the 5.2 *R* beamline of Elettra Synchrotron source with monochromatized x rays ($\lambda = 1.0$ Å). The diffraction patterns were recorded using MAR345 imaging plate detector kept at a distance of $\sim$21 cm from the sample. Two-dimensional imaging plate records were transformed to one-dimensional diffraction profiles by the radial integration of diffraction rings using the FIT2D software.[20] Experiments on pure MWNTs were carried out using a laboratory x-ray-diffraction source (Mo K_α) along with an imaging plate and ruby pressure marker.

RESULTS AND DISCUSSION

Figure 1 shows the x-ray-diffraction profile of the iron filled multiwall carbon nanotubes at 0.3 GPa. The diffraction

