Pressure-induced phase transformation and structural resilience of single-wall carbon nanotube bundles

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(Received 12 January 2001; published 2 May 2001)

We report here an *in situ* x-ray diffraction investigation of the structural changes in carbon single-wall nanotube bundles under quasihydrostatic pressures up to 13 GPa. In contrast with a recent study [Phys. Rev. Lett. **85**, 1887 (2000)] our results show that the triangular lattice of the carbon nanotube bundles continues to persist up to ~10 GPa. The lattice is seen to relax just before the phase transformation that is observed at ~10 GPa. Further, our results display the reversibility of the two-dimensional lattice symmetry even after compression up to 13 GPa well beyond the 5 GPa value observed recently. These experimental results explicitly validate the predicted remarkable mechanical resilience of the nanotubes.

DOI: 10.1103/PhysRevB.63.205417 PACS number(s): 61.48.+c, 61.10.Nz, 61.50.Ks, 81.40.Vw

I. INTRODUCTION

Due to the quasi-one-dimensional structure, single-wall carbon nanotubes (SWNTs) have been shown to have some unique and interesting physical properties.[1] These nanotubes have also been predicted to have extraordinary mechanical properties such as enormous flexibility in terms of complete structural reversibility on bending up to 110°.[2] In addition, molecular dynamics (MD) simulations predict that SWNTs may undergo fully reversible morphological changes under extreme deformations.[3,4] The synthesis of bundles of single-wall carbon nanotubes, with a narrow size distribution, has provided tremendous impetus to the experimental investigations.[5] Several high-pressure Raman investigations have been carried out recently.[6–9] In all of these studies, Raman intensity reduces dramatically beyond a few GPa and this has been suggested to be due to the loss of the electronic resonance in the Raman scattering cross-section because of the faceting of the neighboring tubes.[6] A slight change in the slope of pressure-induced Raman shifts at ~1.7 GPa has also been ascribed to a structural transformation from a triangular to a monoclinic lattice.[7] Recent Raman investigations by Teredesai *et al.*[9] indicate a structural phase transition near 10 GPa. This was conjectured to be due to faceting, as the frequency of the tangential mode approaches that of graphite. Also, all the Raman studies indicate reversibility of behavior upon unloading of the pressure. In particular, the data of Ref. 9 demonstrated the reversibility on pressure release from 25.9 GPa. However, due to the lack of information about the structural evolution of SWNTs under pressure, it was not possible to unambiguously relate these measurements to the microscopic changes in the SWNTs. A recent x-ray diffraction study[10] of SWNTs under pressure, suggests the vanishing of the triangular lattice at ~1.5 GPa and its regeneration if unloaded from less than 4 GPa. Beyond 5 GPa, these x-ray results indicate an irreversible change in total contrast to the results of Ref. 9. High-pressure behavior of SWNTs has also been investigated under nonhydrostatic stresses, using a piston-cylinder device without any pressure medium. This study, restricted to ~2.9 GPa, displays a reversible increase in the density of SWNTs to almost that of graphite.[11] This has been speculated to be due to the crushing or flattening of the cross section of the nanotubes from circular to elliptical shape under the nonhydrostatic stresses. So, to find a consistent interpretation of several experimental results mentioned above, it is necessary to investigate SWNTs using an intense x-ray radiation as the diffracted intensities are likely to be rather weak. In addition, it will be interesting to compare the behavior of SWNTs with that of other carbon polymorphs, e.g., C_{60} and C_{70} fullerenes that undergo irreversible and reversible pressure-induced amorphization.[12–14] We present here an *in situ* x-ray diffraction investigation of SWNT bundles and relate the results to other experimental and theoretical studies.

II. EXPERIMENTAL DETAILS

SWNT bundles were prepared by the standard arc discharge method. For this, a composite rod, made by filling powders of graphite, Y_2O_3 (1at. % Y) and Ni (4.2 at. % Ni) in a hole, was used as an anode and a simple graphite rod as a cathode. The material produced through a dc arc in He atmosphere was appropriately washed with several chemicals, decanted, filtered, dried, and characterized by transmission electron microscopy.[9,15] At ambient conditions, the x-ray diffraction peak corresponding to (1,0) plane of the two-dimensional triangular lattice shows that our SWNTs correspond to a lattice constant $\mathbf{a}_0$ of 17.97 Å. As the curvature of the nanotubes reduces the contact area on which the repulsive forces act on the tubes, the intertube gap is expected to be smaller than the (002) spacing of graphite. If the intertube gap is taken as 3.12 Å,[10] present SWNTs correspond to a tube diameter of 14.85 Å. Therefore, our sample consists of either (11,11) armchair tubes or (19,0) zigzag tubes or any other appropriate combination of integers *n* and *m*.[17] Thermogravimetric analysis of the sample showed graphite abundance to be ~8%. The sample, containing ran-

